SOLID STATE AND AQUEOUS BEHAVIOR OF URANYL PEROXIDE CAGE CLUSTERS

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Abstract

by

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Uranyl peroxide cage clusters include a large family of more than 50 published clusters of a variety of sizes, which can incorporate various ligands including pyrophosphate and oxalate. Previous studies have reported that uranyl clusters can be used as a method to separate uranium from a solid matrix, with potential applications in reprocessing of irradiated nuclear fuel. Because of the potential applications of these novel structures in an advanced nuclear fuel cycle and their likely presence in areas of contamination, it is important to understand their behavior in both solid state and aqueous systems, including complex environments where other ions are present.

In this thesis, I examine the aqueous behavior of U$_{2d}$P$_{12}$, as well as aqueous cluster systems with added mono-, di-, and trivalent cations. The resulting solutions were analyzed using dynamic light scattering and ultra-small angle X-ray scattering to evaluate the species in solution. Precipitates of these systems were analyzed using powder X-ray diffraction, X-ray fluorescence spectrometry, and Raman spectroscopy. The results of these analyses demonstrate the importance of cation size, charge, and concentration of
added cations on the aqueous behavior of uranium macroions. Specifically, aggregates of various sizes and shapes form rapidly upon addition of cations, and in some cases these aggregates appear to precipitate into an X-ray amorphous material that still contains $\text{U}_{24}\text{Pp}_{12}$ clusters.

In addition, I probe aggregation of $\text{U}_{24}\text{Pp}_{12}$ and $\text{U}_{60}$, another uranyl peroxide cage cluster, in mixed solvent water-alcohol systems. The aggregation of uranyl clusters in water-alcohol systems is a result of hydrogen bonding with polar organic molecules and the reduction of the dielectric constant of the system. Studies of aggregation of uranyl clusters also allow for comparison between the newer uranyl polyoxometalate family and century-old transition metal polyoxometalates.

To complement the solution studies of uranyl cage clusters, solid state analyses of $\text{U}_{24}\text{Pp}_{12}$ are presented, including single crystal X-ray diffraction and preliminary single crystal neutron diffraction. Solid state analyses are used to probe the complicated bonding environments between $\text{U}_{24}\text{Pp}_{12}$ and crystallized counterions, giving further insight into the importance of cluster protonation and counterions in uranyl cluster systems. The combination of solid state and solution techniques provides information about the complicated nature of uranyl peroxide nanoclusters, and insight towards future applications of clusters in the advanced nuclear fuel cycle and the environment.
Dedicated in Loving Memory of Joseph E. Murphy
CONTENTS

Figures.................................................................................................................. xi

Tables.................................................................................................................... xxx

Acknowledgments................................................................................................. xxxiii

Chapter 1: Introduction ............................................................................................ 1
  1.1 Actinides ........................................................................................................... 1
  1.2 Nuclear Energy ................................................................................................. 2
  1.3 Uranium in the Environment ........................................................................... 8
  1.4 Uranium Minerals ........................................................................................... 9
  1.5 Transition Metal Polyoxometalates ............................................................... 13
  1.6 Uranyl Polyoxometalates .............................................................................. 19
  1.7 Neutron Diffraction of Uranyl Compounds .................................................. 23
  1.8 Dissertation Overview ................................................................................... 25

Chapter 2: Materials and Methods ........................................................................ 27
  2.1 Synthesis of Uranyl Peroxide Pyrophosphate Nanoclusters ......................... 27
  2.2 Small Angle X-ray Scattering ......................................................................... 28
  2.3 Ultra Small Angle X-ray Scattering ............................................................... 32
  2.4 Dynamic Light Scattering ............................................................................. 35
  2.5 Static Light Scattering ................................................................................... 39
  2.6 Single Crystal X-ray Diffraction ................................................................... 42
  2.7 Single Crystal Neutron Scattering .................................................................. 44
  2.8 Powder X-ray Diffraction .............................................................................. 46
  2.9 Electrospray Ionization Mass Spectrometry .................................................. 47
  2.10 Raman Spectroscopy .................................................................................... 49
  2.11 X-ray Fluorescence Spectrometry ................................................................. 50
  2.12 Inductively Coupled Plasma Optical Emission Spectroscopy ..................... 50

Chapter 3: Solubility of U$_{24}$P$_{12}$ ........................................................................... 52
  3.1 Introduction ..................................................................................................... 52
  3.2 Experimental Procedure ................................................................................ 53
    3.2.1 Synthesis of U$_{24}$P$_{12}$ ......................................................................... 53
    3.2.2 Inductively Coupled Plasma- Optical Emission Spectroscopy ............... 54
    3.2.3 Ultrafiltration ......................................................................................... 55
  3.3 Uranium Concentration in Solution Over Time for U$_{24}$P$_{12}$ .................... 55
Chapter 7: Concentration and Time Dependence of Aggregation of $U_{24}P_{12}$ with Trivalent Cations

7.1 Introduction ........................................................................................................ 166
7.2 Experimental Procedure .................................................................................. 166
  7.2.1 Dynamic Light Scattering ........................................................................... 168
  7.2.2 Ultra-Small and Small Angle X-ray Scattering ........................................ 168
  7.2.3 Powder Diffraction of Precipitates ............................................................. 169
  7.2.4 X-ray Fluorescence of Precipitates ............................................................ 169
  7.2.5 Raman Spectroscopy of Precipitates ......................................................... 169
7.3 Dynamic Light Scattering of Solutions of $U_{24}P_{12}$ with Added Trivalent Cations
  7.3.1 Concentration Dependence of Aggregation for $U_{24}P_{12}$ with Added Trivalent Cations ............................................................................................................. 170
  7.3.2 Time Dependence on Aggregation for $U_{24}P_{12}$ with Added Trivalent Cations ............................................................................................................. 170
7.4 Ultra-Small Angle X-ray Scattering of Solutions of $U_{24}P_{12}$ with Added Trivalent Cations ............................................................................................................. 175
  7.4.1 Modeling of USAXS Data for $U_{24}P_{12}$ with Added Trivalent Cations 175

Chapter 6: Concentration and Time Dependence of Aggregation of $U_{24}P_{12}$ with Divalent Cations

6.1 Introduction ........................................................................................................ 136
6.2 Experimental Procedure .................................................................................. 137
  6.2.1 Dynamic Light Scattering ........................................................................... 138
  6.2.2 Ultra-Small and Small Angle X-ray Scattering ........................................ 138
  6.2.3 Powder Diffraction of Precipitates ............................................................. 139
  6.2.4 X-ray Fluorescence of Precipitates ............................................................ 139
  6.2.5 Raman Spectroscopy of Precipitates ......................................................... 140
6.3 Dynamic Light Scattering of Solutions of $U_{24}P_{12}$ with Added Divalent Cations ............................................................................................................. 140
  6.3.1 Concentration Dependence of Aggregation for $U_{24}P_{12}$ with Added Divalent Cations ............................................................................................................. 140
  6.3.2 Time Dependence on Aggregation for $U_{24}P_{12}$ with Added Divalent Cations ............................................................................................................. 143
6.4 Ultra-Small Angle X-ray Scattering of Solutions of $U_{24}P_{12}$ with Added Divalent Cations ............................................................................................................. 145
  6.4.1 Modeling of USAXS Data for $U_{24}P_{12}$ with Added Divalent Cations 145
  6.4.2 Guinier Approximation for $U_{24}P_{12}$ with Added Divalent Cations 152
  6.4.3 Pair Distance Functions for $U_{24}P_{12}$ with Added Divalent Cations 155
6.5 Powder Diffraction of Precipitates of $U_{24}P_{12}$ with Added Divalent Cations 158
6.6 X-ray Fluorescence of Precipitates of $U_{24}P_{12}$ with Added Divalent Cations 161
6.7 Raman Spectroscopy of Precipitates of $U_{24}P_{12}$ with Added Divalent Cations 161
6.8 Discussion ......................................................................................................... 163
Chapter 10: Aggregation of Uranyl Clusters in Mixed-Solvent Systems ............................................. 234
  10.1 Introduction .......................................................................................................................... 234
  10.2 Experimental Methods ........................................................................................................ 234
    10.2.1 Sample Preparation ....................................................................................................... 234
    10.2.2 Dynamic Light Scattering of Mixed-Solvent Cluster Solutions .................................. 236
  10.3 Solutions of U$_{24}$P$_{12}$ in Mixed-Solvent Systems .................................................................. 238
    10.3.1 Water-Methanol Solutions Containing U$_{24}$P$_{12}$ .................................................. 238
    10.3.2 Water-Ethanol Solutions Containing U$_{24}$P$_{12}$ ..................................................... 240
  10.4 Solutions of U$_{24}$P$_{12}$ in Mixed-Solvent Systems ................................................................. 242
    10.4.1 Water-Methanol Solutions Containing U$_{60}$ ............................................................. 242
    10.4.2 Water-Ethanol Solutions Containing U$_{60}$ ............................................................... 244
  10.5 Discussion ............................................................................................................................ 246

Chapter 11: Preliminary Neutron Diffraction Studies of U$_{24}$P$_{12}$ ..................................................... 249
  11.1 Introduction .......................................................................................................................... 249
  11.2 Experimental Procedures ...................................................................................................... 250
    11.2.1 Synthesis of Millimeter-Sized Crystals of U$_{24}$P$_{12}$ .................................................. 250
    11.2.2 Mounting of Crystals of U$_{24}$P$_{12}$ .......................................................................... 250
    11.2.3 Preparation for Neutron Diffraction of U$_{24}$P$_{12}$ .................................................... 251
    11.2.4 Structure Solution of U$_{24}$P$_{12}$ ................................................................................ 255
  11.3 X-ray Diffraction of U$_{24}$P$_{12}$ .......................................................................................... 256
  11.4 Preliminary Neutron Diffraction of U$_{24}$P$_{12}$ .................................................................... 257
  11.5 Discussion ............................................................................................................................ 260

Chapter 12: Conclusions .................................................................................................................. 262
  12.1 Importance of Conducted Research ....................................................................................... 262
  12.2 Solubility and Characterization of U$_{24}$P$_{12}$ ....................................................................... 262
  12.3 Cation Mediated Aggregation of U$_{24}$P$_{12}$ ........................................................................ 264
  12.4 Aggregation of Uranyl Peroxide Nanocluster in Mixed Solvent Systems ......................... 266
  12.5 Neutron Diffraction of U$_{24}$P$_{12}$ ....................................................................................... 266

Appendix A: Publications and Conference Presentations ............................................................... 268
  A.1 Publications .......................................................................................................................... 268
  A.2 Publications in Preparation .................................................................................................... 268
  A.3 Conference Presentations ....................................................................................................... 268

Appendix B: Modeled Ultra Small Angle X-ray Scattering Patterns ............................................. 270
  B.1 U$_{24}$P$_{12}$ with added Lithium ............................................................................................... 270
  B.2 U$_{24}$P$_{12}$ with added Sodium ............................................................................................. 271
  B.3 U$_{24}$P$_{12}$ with added Potassium .......................................................................................... 272
  B.4 U$_{24}$P$_{12}$ with added Rubidium ........................................................................................... 273
  B.5 U$_{24}$P$_{12}$ with added Cesium ............................................................................................... 274
  B.6 U$_{24}$P$_{12}$ with added Silver .................................................................................................. 275
  B.7 U$_{24}$P$_{12}$ with added Magnesium ......................................................................................... 276
  B.8 U$_{24}$P$_{12}$ with added Calcium ............................................................................................. 277
  B.9 U$_{24}$P$_{12}$ with added Strontium ............................................................................................ 278
Appendix C: Peak Fitting for the Pair Distance Distribution Functions from Ultra Small Angle X-ray Scattering Data ........................................ 283
C.1 PDDF Peak Fitting for Aqueous Solutions of 10 g/L U$_{24}$Pp$_{12}$ .................. 284
C.2 PDDF Peak fitting for Aqueous Solutions of 20 g/L U$_{24}$Pp$_{12}$ .................. 285
C.3 PDDF Peak Fitting for Aqueous Solutions of 20 g/L U$_{24}$Pp$_{12}$ .................. 286
C.4 PDDF Peak Fitting for Aqueous Solutions of 40 g/L U$_{24}$Pp$_{12}$ .................. 287
C.5 PDDF Peak Fitting for Aqueous Solutions of 50 g/L U$_{24}$Pp$_{12}$ .................. 288
C.6 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Lithium .............................................................. 289
C.7 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Sodium .............................................................. 290
C.8 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Potassium ......................................................... 291
C.9 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Rubidium ......................................................... 292
C.10 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Cesium ......................................................... 293
C.11 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Silver ......................................................... 294
C.12 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Calcium ......................................................... 295
C.13 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Magnesium ......................................................... 296
C.14 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ withAdded Strontium ......................................................... 297
C.15 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Lanthanum ......................................................... 298
C.16 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Europium ......................................................... 299
C.17 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Holmium ......................................................... 300
C.18 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Aluminum ......................................................... 301

Appendix D: Multi-Angle Dynamic Light Scattering for Dilute Solutions of U$_{24}$Pp$_{12}$ with Added Cations ................................................................. 302
D.1 Multi-angle Dynamic Light Scattering Data for 0.5 g/L solutions of U$_{24}$Pp$_{12}$ with added Potassium ................................................................. 302
D.1.1 U$_{24}$Pp$_{12}$ with added Potassium at source-sample-detector-distance of 30° ................................................................. 302
Appendix E: Single Angle Dynamic Light Scattering Data of Uranyl Cage Clusters in Mixed Solvent Systems

E.1 DLS Studies of Clusters of U$_{24}$P$_{12}$ in Water-Methanol Solutions ..................................... 317
   E.1.1 U$_{24}$P$_{12}$ in 2:1 Water-Methanol Solutions ......................................................... 318
   E.1.2 U$_{24}$P$_{12}$ in 1:1 Water-Methanol Solutions ......................................................... 319
   E.1.3 U$_{24}$P$_{12}$ in 1:2 Water-Methanol Solutions ......................................................... 320

E.2 DLS Studies of Clusters of U$_{24}$P$_{12}$ in Ethanol-Water Solutions ...................................... 321
   E.2.1 U$_{24}$P$_{12}$ in 2:1 Water-Ethanol Solutions ......................................................... 322
   E.2.2 U$_{24}$P$_{12}$ in 1:1 Water-Ethanol Solutions ......................................................... 323
   E.2.3 U$_{24}$P$_{12}$ in 1:2 Water-Ethanol Solutions ......................................................... 324

E.3 DLS Studies of Clusters of U$_{60}$ in Methanol-Water Solutions ............................................. 325
   E.3.1 U$_{60}$ in 2:1 Water-Methanol Solutions ............................................................. 326
   E.3.2 U$_{60}$ in 1:1 Water-Methanol Solutions ............................................................. 327
E.3.3 $\text{U}_6\text{O}_6$ in 1:2 Water-Methanol Solutions .................................................. 328
E.4 DLS Studies of Clusters of $\text{U}_6\text{O}_6$ in Ethanol-Water Solutions ................. 329
  E.4.1 $\text{U}_6\text{O}_6$ in 2:1 Water-Methanol Solutions ........................................... 330
  E.4.2 $\text{U}_6\text{O}_6$ in 1:1 Water-Methanol Solutions .......................................... 331
E.5 $\text{U}_6\text{O}_6$ in 1:2 Water-Methanol Solutions ............................................... 332

Appendix F: Concentrations of Uranium from ICP-OES Analysis .......................... 333
  F.1 Bulk Experiment of Dissolution of Crystals of $\text{U}_{24}\text{Pp}_{12}$ ....................... 333
  F.2 Maximum Concentrations from Small Batch Dissolution of $\text{U}_{24}\text{Pp}_{12}$ .... 334

Bibliography .............................................................................................................. 335
FIGURES

Figure 1.1 The Open Fuel Cycle, where the front end of the cycle is shown in blue, irradiation is shown in purple, and the back end is shown in orange. The green arrows indicate natural or depleted uranium (\(^{235}\text{U}\) content is less than 0.7%), while the black arrows indicate enriched uranium (\(^{235}\text{U}\) content is greater than 0.7%). Currently, the United States has no permanent geologic repository, so the open fuel cycle ends at interim, on-site storage.

Figure 1.2 Fission Yield for \(^{235}\text{U}\), where the curve indicates the percent yield at a particular mass number. Maxima of these distributions occur at mass number 95 (molybdenum) and 137 (barium). A local minimum between these two maxima occurs at mass number 118 (tin). This represents the percent yield of mass that occurs when \(^{235}\text{U}\) undergoes fission and the nucleus fragments.

Figure 1.3 The Closed Fuel Cycle, where the front end is shown in blue, irradiation is shown in purple, and the back end is shown in orange. The light green arrows indicate natural or depleted uranium (\(^{235}\text{U}\) content is less than 0.7%), while the black arrow indicates enriched uranium (\(^{235}\text{U}\) content is greater than 0.7%). The dark green arrow indicates a secondary waste stream, from which the uranium has been separate. In a closed cycle, irradiated fuel is reprocessed to recover uranium and plutonium, which can go back to the conversion step and used again.

Figure 1.4 Relative Solubilities of Uranyl Minerals where the thick box borders are the mineral phases that form upon introduction of the dissolved uranyl ion to the conditions described by the boxes with dotted line borders. Minerals located at the top of the diagram are more soluble, and minerals located at the bottom of the diagram are more soluble (adapted from *Reviews in Mineralogy*, 1999).

Figure 1.5 Construction of a POM extended Structure where (a) represents a pentameric unit which then combine to form bowls or dodecahedron, as shown in (b) and (c) respectively. The dodecahedron can also form an extended polyhedron (d) by separating the edge sharing. The separated tetramers form the large spherical system (e) by the individual pentagonal units being interconnected by linker units (indicated by the small spheres in (e)) (adapted from Muller, et al. 2001).

Figure 1.6 Polyhedral representations of common POM topologies where the blue octahedra are the metal oxide core, where the blue polyhedra represent metal oxide core. POM (a) is the Lindqvist ion, POM (b) is the Anderson ion, POM (c)
is the Keggin ion, POM (d) is the Wells-Dawson ion, and POM (e) is a Preyssler polyoxoanion. Heteropolyions are shown in yellow (Lopez, Carbo, Bo, & Poblet, 2012).

Figure 1.7: POMs serving as building blocks for larger structures, starting with the metal oxide unit, which self assemble into nanometer scale POMs. These POMs can then self-assemble into particles, dots, micelles, wires, tubes, or films to form zero-, one- and two-dimensional micrometer scale objects with applications in catalysis, molecular electronics, and energy (Long et al., 2010).

Figure 1.8 The crystal structure of studtite (Burns & Hughes, 2003), where the uranium atoms are shown in yellow, uranyl oxygen atoms in light red, equatorial oxygen atoms in red, and hydrogen atoms in white. The top image is the polyhedral representation of a studtite chain. The middle image shows the chain in the x,z plane, illustrating the shared peroxide edge. The bottom image shows the chain in the x,y plane, illustrating the bent uranium-peroxide-uranium dihedral angle.

Figure 1.9 A uranyl peroxide ring, \(U_{24R}\) (Sigmon, Weaver, Kubatko, & Burns, 2009), shown in a polyhedral representation (left) and as the graph of the cluster (right), where each vertex represents a uranyl hexagonal bipyramid. \(U_{24R}\) is composed of 24 uranyl hexagonal bipyramids arranged into a ring by the sharing of peroxide edges and hydroxide vertices.

Figure 1.10 Closed uranyl polyoxometalates \(U_{60}\) (a and d), \(U_{24}\) (b and e), and \(U_{24}Pp_{12}\) (c and f) (Qiu & Burns, 2013) where yellow polyhedra represent uranyl polyhedra and purple polyhedra represent pyrophosphate groups. Images a through c show the polyhedral representation of these clusters, while images d through f show the graph of the cluster. In the graph, each vertex is occupied by a uranyl ion. The yellow lines in (f) indicate the bridging by pyrophosphate, while the blue lines show the connectivity of tetrameric rings.

Figure 1.11 Hydrogen bonding environment of uranyl nitrate hexahydrate as studied by Taylor and Mueller using neutron diffraction (Taylor & Mueller, 1965), showing the bond angles between the uranyl center, nitrate groups attached to the uranyl center, and coordinating water molecules. The image indicates hydrogen bonding by dashed lines and the filled black circles indicate hydrogen, while the unfilled circles represent oxygen.

Figure 2.1 Scattering from a Small Sphere (a) and a Large Sphere (b), where \(1\lambda\) is the path difference between two scattered waves and \(2\theta\) is the scattering angle between the vector of the wave prior to scattering and the scattered vector. Maximum scattering occurs when phase differences are minimized (adapted from Glatter & Kratky, 1982).

Figure 2.2 Qualitative Scattering Curves from a Small Sphere (a) and a Large Sphere (b) as pictured in Figure 2.1. The smaller sphere has a wider scattering curve because the path differences occur at smaller angles of \(2\theta\) for the small sphere, while the
path difference for larger spheres occur at larger angles of $2\theta$ (adapted from Glatter & Kratky, 1982).

Figure 2.3 Encapsulation of USAXS samples prepared at the University of Notre Dame and shipped to the Advanced Photon Source. The samples (yellow in the figure) were doubly contained in two Kapton capillaries, the inner shown in orange and the outer shown in amber brown. Each end of the capillary was sealed with epoxy (gray circle) and allowed to dry. The ends of the capillaries were then covered with Kapton tape (light orange rounded square) to ensure that the ends of capillaries were also doubly contained.

Figure 2.4 The mounting of doubly contained capillaries on a metal paddle for USAXS analysis (a), where the individual capillaries are placed on a paddle with machined groves and taped in place. This paddle is then mounted within the instrument (b) on a motorized arm that can move in the x and y directions, and the source and detectors are oriented perpendicular to the paddle in the z direction.

Figure 2.5: Molecular weight dependence on light scattering for a low molecular weight species and a high molecular weight species. A low molecular weight species scatters weakly and at lower intensities than a high molecular weight species (Malvern Instruments Ltd).

Figure 2.6 Schematic of the ion desolvation process, by which an initial droplet evaporates and desolvates in a self-generated electric field to form a quasi-molecular ion. This is the ion that is detected by the mass spectrometer in ESI-MS (adapted from Fenn et. al, 1989).

Figure 3.1 Optical light image of crystals remaining after exposure to ultrapure water for thirty days at ambient temperature and pressure in a sealed container at circumneutral pH, showing dissolution resulting in the rounding of the edges of the crystals. The scale bar shows a size of 0.25 mm. Single crystal X-ray diffraction confirmed that the crystals are U$_{24}$Pp$_{12}$.  

Figure 3.2 Concentration of U$_{24}$Pp$_{12}$ in solution over the thirty-day dissolution period as calculated from uranium concentrations from ICP-OES. The data were fit to a logarithmic curve (solid line). Data with $t > 120$ hr were fit to a line to represent steady state, where the maximum concentration of U$_{24}$Pp$_{12}$ in solution is 69 g/L. Error bars were calculated from the standard deviation of multiple uranium concentration measurements. Uranium concentration measurements in ppm are included in Appendix F.

Figure 4.1 An example of the volume distribution vs. size data obtained using DLS for a aqueous solution of U$_{24}$Pp$_{12}$ at a concentration of 65 g/L, where the single peak indicates a monodisperse solution of particles with a $R_H$ of 0.4 nm.

Figure 4.2 Hydrodynamic radii over time for two samples of U$_{24}$Pp$_{12}$ monitored for a two-week period, where the red circles are average data for the first sample and the blue triangles are average data for the second sample.
the blue circles are average data for the second sample. Error bars were obtained from the standard deviation of multiple measurements of the same solution at a particular time point.

Figure 4.3 Ball and stick (a) and polyhedral (b) representation of $\text{U}_{24}\text{Pp}_{12}$ from crystallographic data, where red balls indicate oxygen atoms, purple balls/polyhedra indicate phosphorus atoms/polyhedra, and yellow balls/polyhedra indicate uranium atoms/polyhedral.

Figure 4.4 Spherical shell model (adapted from Kline & Munter, 1999) where the shell has a thickness $t$ and a density $\rho_{\text{shell}}$, the solvent a density of $\rho_{\text{solvent}}$, and the core has a radius of $r_{\text{core}}$ and a density of $\rho_{\text{core}}$.

Figure 4.5 USAXS Scattering pattern for $\text{U}_{24}\text{Pp}_{12}$ (red circles) with the model (black line) obtained by USAXS where the high-q area data were modeled using a core-shell form factor with a mean size of 7.4 Å and a hard spheres structure factor with a radius of 25 Å and volume fraction of 11%. The low-q data were modeled using a single unified fit of the Porod/Power law slope of approximately 3, indicating a rough surface.

Figure 4.6 Porod law behaviors for a variety of different shapes, where the solid black lines indicate the shape and the red circles indicate the region that the Porod slope describes. The Porod slope is the $n$ in $Q^n$ (from Hammouda, 2009).

Figure 4.7 Guinier approximation determined from small-angle scattering data of a solution of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ (shown in black). The linear region, satisfying the requirement of $(q \times R_g > 1.3)$, is indicated by a solid red line, from which the slope is used to find $R_g$ for particles in solution.

Figure 4.8 A Visual representation of the pair distance function, where the black rings represent a particular distance from the center of a particle and the red arrows represent the paired electrons at a particular pair distance, $r$, from each other. The sum of all these pair distances gives the overall pair distance function.

Figure 4.9: The PDDF derived from SAXS data for a solution of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ (black squares), fit with four distributions using Gauss fit (Table 4.1). The red distribution corresponds to the shell thickness, the green and blue distributions correspond to the cluster itself, and the cyan distribution corresponds to the cluster-Na ion interaction on the outside of the cluster. The magenta curve is the cumulative fit for the four distributions and correlates to the data with a $R^2$ of 0.99997.

Figure 4.10 Geometry to determine the thickness of the shell of $\text{U}_{24}\text{Pp}_{12}$, where a triangle was drawn using the centers of $\text{O}_{\text{y, int}}$ and $\text{O}_{\text{py, free}}$ as two vertices and the third vertex ($z$) is the intersection of the x and y axis of these two atoms, respectively, with an angle of 54.7° for $\text{O}_{\text{py, free}}$-$\text{O}_{\text{y, int}}$-$z$. The tangent of this angle was used to find the leg labeled as $x$ to determine the thickness of the shell of $\text{U}_{24}\text{Pp}_{12}$. 
Figure 4.11 Comparison of USAXS/SAXS scattering profiles for aqueous solutions of $U_{24}Pp_{12}$ at 10 g/L (black squares), 20 g/L (red circles), 30 g/L (green up-triangles), 40 g/L (blue down-triangles), and 50 g/L (magenta left-triangles), which show a characteristic scattering pattern of aqueous solutions of $U_{24}Pp_{12}$ in the high-q region. Jumps in intensity are due to X-ray induced bubbles forming in the capillary, and are not a result of structural changes.........................................................83

Figure 4.12 Change in structure factor parameters from models of data from USAXS experiments on aqueous solutions of $U_{24}Pp_{12}$, where the top graph is the correlation distance and the bottom graph is volume fraction for each solution at five cluster concentrations. The error bars were determined by uncertainty analyses of each parameter at each concentration by Irena macros.............................85

Figure 4.13 PDDFs derived from SAXS data for aqueous solutions of $U_{24}Pp_{12}$ at 10 g/L (black squares), 20 g/L (red circles), 30 g/L (green up-triangles), 40 g/L (blue down-triangles), and 50 g/L (magenta left-triangles). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros.88

Figure 4.14 Peak fit distributions for the $U_{24}Pp_{12}$-Na interaction from the PDDF from SAXS data for aqueous solutions of $U_{24}Pp_{12}$ at 10 g/L (black solid line), 20 g/L (red dotted line), 30 g/L (green small dashed line), 40 g/L (blue large dashed line), and 50 g/L (magenta dot-dash line). As the concentration increases, the distribution width decreases and height increases, indicating a higher probability of the sodium ion being found closer to the cluster.................................................................90

Figure 4.15 (a) A crystal of $U_{24}Pp_{12}$, 1 mm long, in oil immediately after harvesting. The crystal is a translucent yellow with well defined edges. (b) A crystal of $U_{24}Pp_{12}$, 2 mm long, three days after harvesting, dry, and exposed to air. The crystal is opaque and yellow, and has begun to crumble, evidenced by the shards surrounding the large crystal, due to dehydration.................................................92

Figure 4.16 PXRD pattern for ground crystals of $U_{24}Pp_{12}$. Data were collected at ambient conditions over a 2θ range from 5-55°, and the stage with the slide was rotated at a speed of 15 rotations per minute. The resulting powder pattern indicates that the sample is amorphous to X-rays.................................................................93

Figure 4.17 ESI-MS spectra for aqueous solutions of $U_{24}Pp_{12}$ made by dissolving (a) crystals and (b) powder immediately after harvesting or grinding (black), one hour exposure in air before dissolution (blue), and 24 hr of exposure in air before dissolution (red), indicating that cluster material remains after exposure to air....94

Figure 4.18 Micro-Raman spectra for a single crystal of $U_{24}Pp_{12}$ immediately after harvesting (black) and a powder of $U_{24}Pp_{12}$ after one day of exposure to air (gray). The peaks attributed to the uranyl stretch, pyrophosphate stretch, and TEAH stretches are in the same locations, shown by dashed lines. ......................95
Figure 5.1 Volume distribution for DLS data for aqueous solutions of U$_{24}$P_12 after being inoculated with 12.5 μL of monovalent cations. Aqueous solution of U$_{24}$P_12 without added cations (untreated) is shown in black, with added lithium is shown in orange, sodium in blue, potassium in red, rubidium in magenta, cesium in green, and silver is shown in cyan. The distributions of all peaks at approximately the same size, indicating aggregation does not occur immediately after monovalent cations are added to aqueous cluster solutions.

Figure 5.2 Initial hydrodynamic radii of species in aqueous solutions of U$_{24}$P_12 inoculated with increasing amounts of lithium (orange), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). For comparison, untreated U$_{24}$P_12 is shown in black, showing that no aggregation occurs initially as a result of the increasing the amount of monovalent cations added to cluster solution. Error bars are determined by multiple analyses of the same system.

Figure 5.3 The change in hydrodynamic radii over time for species in solutions of U$_{24}$P_12 inoculated with 12.5 μL of lithium (orange), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). For comparison, the R$_H$ of untreated U$_{24}$P_12 is shown by the dashed black line. Aggregation is only present in aqueous solutions of U$_{24}$P_12 with added cesium, with a large increase in R$_H$ three days after cesium was added. The other solutions with added monovalent ions did not induce aggregation over a two-week period.

Figure 5.4 USAXS scattering patterns for aqueous solutions of U$_{24}$P_12 inoculated with lithium (black), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). The characteristic scattering pattern for U$_{24}$P_12 in aqueous solution is present at high-q.

Figure 5.5 Unified Fit model for U$_{24}$P_12 with Cs including fits for a higher-q unified level modeled best as a rod with an R$_g$ of 107 Å and a lower-q unified level that represents agglomeration of these rods into a mass fractal.

Figure 5.6 Comparison of hard sphere structure factor parameters distance between clusters (bottom) and nearest neighbors involved (top) with atomic number for monovalent cations.

Figure 5.7 Guinier Approximations for aqueous solutions of U$_{24}$P_12 with added (a) lithium, (b) sodium, (c) potassium, (d) rubidium, (e) cesium, and (f) silver. The data are shown in color for each figure, and the fit of the linear component, meeting the requirements q×R$_g$<1.3, is shown in black. The slope of the fit gives the R$_g$, and for the solutions of U$_{24}$P_12 with monovalent cations, the respective R$_g$ is approximately 9 Å. This is consistent with U$_{24}$P_12 as the base particle.

Figure 5.8 PDDFs derived from SAXS data for aqueous solutions of U$_{24}$P_12 with added lithium (black), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). Error bars were determined by the analysis within the
Pair Distance Function tool, a part of the Irena macros. The inset is a magnification of the cluster-cation region of the PDDF.

Figure 5.9 Peak fit distributions for the $U_{24}Pp_{12}$-cation interactions from the PDDF from SAXS data for aqueous solutions of $U_{24}Pp_{12}$ with added lithium (black solid line), sodium (blue dotted line), potassium (red short dashed line), rubidium (magenta medium dashed line), cesium (green dot dash line), and silver (cyan long dash line). Systems with added lithium, sodium, potassium, and cesium have a maximum dimension of approximately 23 Å, while systems with added rubidium and silver are shorter.

Figure 5.10 Comparison of ionic radii (open circles), hydrated radii (open triangles), and radii calculated from Eq. 5.1, using data from PDDF for USAXS data of solutions of $U_{24}Pp_{12}$ with added lithium, sodium, potassium, rubidium, silver, and cesium. Atomic number of the added cation is used to allow for comparison of all three radii associated with each added cation.

Figure 5.11 PXRD patterns for precipitates formed from aqueous solutions of $U_{24}Pp_{12}$ with added sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). For comparison, the PXRD pattern for untreated, ground crystals of $U_{24}Pp_{12}$ (black) is shown on the bottom of the figure.

Figure 5.12 The simulated powder diffraction pattern for $U_{24}Pp_{12}$ from the structure of $U_{24}Pp_{12}$ determined using single crystal X-ray diffraction data. The simulated pattern was calculated using Mercury (Macrae et al., 2008).

Figure 5.13 Raman spectra for untreated crystals of $U_{24}Pp_{12}$ (black) and precipitates formed from aqueous solutions of $U_{24}Pp_{12}$ with added sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan) with line 1 through the uranyl mode and line 2 through the pyrophosphate mode for the crystal of $U_{24}Pp_{12}$.

Figure 5.14 Comparison of the red shift in Raman spectroscopy of the uranyl stretch for precipitates formed from solutions of $U_{24}Pp_{12}$ with added monovalent cations. A weak trend may occur for Group I cations. Silver does not follow this trend.

Figure 6.1 Volume distributions for DLS data for aqueous solutions of $U_{24}Pp_{12}$ after being inoculated with 12.5 μL of divalent cations. Aqueous solution of $U_{24}Pp_{12}$ without added cations (untreated) is shown by the solid black line, while the systems with added divalent cations are shown in color. The distributions of all systems with added divalent cations occur at a much larger size than for the untreated system, indicating aggregation occurs immediately after divalent cations are added to aqueous cluster solutions.

Figure 6.2 Initial hydrodynamic radii of species in aqueous solutions of $U_{24}Pp_{12}$ inoculated with increasing amounts of added divalent cations. For comparison, untreated $U_{24}Pp_{12}$ is shown in black, showing that aggregation occurs for all
systems studied regardless of the concentration of divalent cations added to cluster solution. The copper system was polydisperse with two distinct size distributions. Error bars were determined by multiple analyses of the same system.

Figure 6.3 The change in hydrodynamic radii over time for species in solutions of $U_{24}Pp_{12}$ inoculated with 12.5 μL of magnesium (orange), calcium (blue), strontium (red), barium (magenta), lead (green), and copper (cyan). For comparison, the $R_H$ of untreated $U_{24}Pp_{12}$ is shown by the dashed black line. Aggregation is for all systems for the duration of the experiment, except for the system with added barium.

Figure 6.4 USAXS scattering patterns for aqueous solutions of $U_{24}Pp_{12}$ inoculated with magnesium (black), calcium (blue), and strontium (red). The characteristic scattering pattern for $U_{24}Pp_{12}$ in aqueous solution is present at high-q.

Figure 6.5 Unified Fit model for $U_{24}Pp_{12}$ with Sr including fits for a higher-q unified level modeled best as a mass fractal with an $R_g$ of 340 Å and a lower-q unified level that represents agglomeration of these fractals into a larger mass fractal.

Figure 6.6 Comparison of hard sphere structure factor parameters distance between clusters (bottom) and nearest neighbors involved (top) with atomic number for divalent cations.

Figure 6.7 Guinier Approximations for aqueous solutions of $U_{24}Pp_{12}$ with added (a) magnesium, (b) calcium, and (c) strontium. The data are shown in color for each figure, and the fit of the linear component, meeting the requirements $q \times R_g < 1.3$, is shown in black. The slope of the fit gives the $R_g$, and for the solutions of $U_{24}Pp_{12}$ with monovalent cations, the respective $R_g$ is approximately 9 Å. This is consistent with $U_{24}Pp_{12}$ as the base particle.

Figure 6.8 PDDFs derived from SAXS data for aqueous solutions of $U_{24}Pp_{12}$ with added magnesium (orange), calcium (blue), and strontium (red). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros. The inset is a magnification of the cluster-cation region of the PDDF.

Figure 6.10 PXRD patterns for precipitates formed from aqueous solutions of $U_{24}Pp_{12}$ with added magnesium (orange), calcium (blue), strontium (red), barium (magenta), lead (green), and copper (cyan). For comparison, the PXRD pattern for untreated, ground crystals of $U_{24}Pp_{12}$ (black) is shown on the bottom of the figure.

Figure 6.11 Raman spectra for untreated crystals of $U_{24}Pp_{12}$ (black) and precipitates formed from aqueous solutions of $U_{24}Pp_{12}$ with added magnesium (orange), calcium (blue), strontium (red), barium (magenta), and lead (green) with line 1 through the uranyl mode and line 2 through the pyrophosphate mode for the crystal of $U_{24}Pp_{12}$. 
Figure 7.1 Volume distributions for DLS data for aqueous solutions of U$_{24}$P$_{12}$ after being inoculated with 12.5 μL of trivalent cations. Aqueous solution of U$_{24}$P$_{12}$ without added cations (untreated) is shown by the solid black line, and systems with added trivalent cations are shown in color. The distributions of all systems with added trivalent cations occur at a much larger size than for the untreated system, indicating aggregation occurs immediately after trivalent cations are added to aqueous cluster solutions. 171

Figure 7.2 Initial hydrodynamic radii of species in aqueous solutions of U$_{24}$P$_{12}$ inoculated with increasing amounts of added trivalent. For comparison, untreated U$_{24}$P$_{12}$ is shown in black, showing that aggregation occurs for all systems studied regardless of the concentration of trivalent cations added to cluster solution. The copper system was polydisperse with two distinct size distributions. Error bars were determined by multiple analyses of the same system. 173

Figure 7.3 The change in hydrodynamic radii over time for species in solutions of U$_{24}$P$_{12}$ inoculated with 12.5 μL of added trivalent cations. For comparison, the R$_H$ of untreated U$_{24}$P$_{12}$ is shown by the dashed black line. Aggregation is present for all systems for the duration of the experiment, except for the system with added cerium and neodymium. 174

Figure 7.4 USAXS scattering patterns for aqueous solutions of U$_{24}$P$_{12}$ inoculated with lanthanum (orange), europium (green), holmium (cyan), and aluminum (gray). The characteristic scattering pattern for U$_{24}$P$_{12}$ in aqueous solution is present at high-q. 176

Figure 6.5 Unified Fit model for U$_{24}$P$_{12}$ with Al including fits for a higher-q unified level modeled best as a mass fractal with an R$_g$ of 210 Å and a lower-q unified level that represents agglomeration of these fractals into a larger mass fractal... 180

Figure 7.6 Comparison of hard sphere structure factor parameters distance between clusters (bottom) and nearest neighbors involved (top) with atomic number for trivalent cations. 182

Figure 7.7 Guinier Approximations for aqueous solutions of U$_{24}$P$_{12}$ with added (a) lanthanum, (b) europium, (c) holmium, and (d) aluminum. The data are shown in color for each figure, and the fit of the linear component, meeting the requirements qR$_Q$<1.3, is shown in black. The slope of the fit gives the R$_g$, and for the solutions of U$_{24}$P$_{12}$ with monovalent cations, the respective R$_g$ is approximately 9 Å. This is consistent with U$_{24}$P$_{12}$ as the base particle. 183

Figure 7.8 PDDFs derived from SAXS data for aqueous solutions of U$_{24}$P$_{12}$ with added lanthanum (orange), europium (green), holmium (cyan), and aluminum (gray). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros. The PDDF for systems of U$_{24}$P$_{12}$ with added lanthanum, europium, and holmium are typical for the cluster interacting with one cation at a single distance. The PDDF for U$_{24}$P$_{12}$ with added aluminum has...
multiple cation peaks, suggesting that there are cations interacting with the cluster at distances further away from the cluster. ................................................................. 186

Figure 7.9 Peak fit distributions for the \( U_{24}Pp_{12} \)-cation interactions from the PDDF from SAXS data for aqueous solutions of \( U_{24}Pp_{12} \) with added lanthanum (orange solid line), europium (green dotted line), holmium (cyan short dashed line), and aluminum (gray dash-dot line). The fourth peaks for all four systems are centered at the same radius. Aluminum was fit with an additional peak (labeled as 5), which suggests cations interact at multiple distances from the cluster, though more are interacting at closer distances than distances further away from the cluster. ........................................................................................................ 188

Figure 7.10 PXRD patterns for precipitates formed from aqueous solutions of \( U_{24}Pp_{12} \) with added lanthanum (orange), cerium (blue), neodymium (red), and samarium (magenta). For comparison, the PXRD pattern for untreated, ground crystals of \( U_{24}Pp_{12} \) (black) is shown on the bottom of the figure................................. 191

Figure 7.11 Raman spectra for untreated crystals of \( U_{24}Pp_{12} \) (black) and precipitates formed from aqueous solutions of \( U_{24}Pp_{12} \) with added lanthanum (orange), cerium (blue), holmium (cyan), and aluminum (gray) with a dotted line through the uranyl mode at approximately 815 cm\(^{-1}\) and the pyrophosphate mode at approximately 856 cm\(^{-1}\) for the crystal of \( U_{24}Pp_{12} \). In the spectra for the systems with added aluminum and holmium, the two modes of interest are shifted to higher wavenumbers, indicating interactions between the added cations and the uranyl oxygen atoms and pyrophosphate oxygen atoms on the cluster............. 193

Figure 8.1 Average multi-angle DLS distribution data for all species in a 0.5 aqueous solution of \( U_{24}Pp_{12} \) with added potassium at 30°, 45°, 60°, 75°, and 90° showing the angular dependence on size for the system................................................................. 202

Figure 8.2 The Stokes-Einstein relationship from average \( R_h \) values determined from DLS distributions of aqueous solutions of \( U_{24}Pp_{12} \) with added potassium at multiple angles. Error bars are determined from replicate DLS measurements. The linear fit of the data is used to calculate an \( R_{h,0} \) for the system of 79 nm........ 203

Figure 8.3 Partial Zimm (\( R_g \)) analysis of SLS Data of 0.5 g/L aqueous solutions of \( U_{24}Pp_{12} \) with added potassium. A linear fit was applied to the data, and gave \( R_g \) 82 nm. ........................................................................................................................................... 204

Figure 8.4 Average multi-angle DLS distribution data for all species in a 0.5 g/L aqueous solution of \( U_{24}Pp_{12} \) with added cesium at 30°, 45°, 60°, 75°, and 90° showing the angular dependence on size for the system.............................................. 205

Figure 8.5 The Stokes-Einstein relationship from average \( R_h \) values determined from DLS distributions of aqueous solutions of \( U_{24}Pp_{12} \) with added cesium at multiple angles. Error bars are determined from replicate DLS measurements. The linear fit of the data is used to calculate an \( R_{h,0} \) for the system of 49 nm........... 207
Figure 8.6 Partial Zimm ($R_g$) analysis of SLS data of 0.5 g/L aqueous solutions of $U_{24}P_{12}$ with added cesium. A linear fit was applied to the data, from which the $R_g$ was calculated to be approximately 55 nm.

Figure 8.7 Average multi-angle DLS distribution data for all species in a dilute aqueous solution of $U_{24}P_{12}$ with added copper at 30°, 45°, 60°, 75°, and 90° showing the angular dependence on size for the system.

Figure 8.8 The Stokes-Einstein relationship from average $R_h$ values determined from DLS distributions of aqueous solutions of $U_{24}P_{12}$ with added copper at multiple angles. Error bars were determined from replicate DLS measurements. The linear fit of the data is used to calculate an $R_{h,0}$ for the system of 73 nm.

Figure 8.9 Partial Zimm ($R_g$) analysis of SLS data of dilute aqueous solutions of $U_{24}P_{12}$ with added copper. A linear fit was applied to the data, from which the $R_g$ was calculated to be approximately 72 nm.

Figure 9.1 Polyhedral representation of a four-membered ring of uranyl hexagonal bipyramids from the $U_{24}P_{12}$ cluster (yellow), with a Na$^+$ atom (blue) bonded through O$_{uranyl}$ atoms to the interior of the cluster. (a) is a side-on view, where the sodium ion sits below the ring inside the cluster. (b) is a view from the center of the cluster showing the Na-O$_{uranyl}$ interactions on the inner side of the ring.

Figure 9.2 Potential sites for bonding between external sodium ions and O$_{per}$ atoms on (a) concave-in rings and (b) concave-out rings on $U_{24}P_{12}$. Sites 1 and 4 are the peroxide oxygen atoms extending away from the center of tetrameric concave-in and concave-out rings, respectively (referred to as outer O$_{per}$). Sites 2 and 3 are the O$_{per}$ atoms extending toward the center of the tetrameric concave-in and concave-out rings, respectively (referred to as inner O$_{per}$).

Figure 9.3 Potential bonding sites for Na ions to O$_{ur,ex}$ on (a) concave-in rings and (b) concave-out rings of $U_{24}P_{12}$. On the concave-in ring, the O$_{ur,ex}$ atoms extend away from the center of the tetrameric ring. On the concave-out ring, the O$_{ur,ex}$ atoms extend toward the center of the tetrameric ring.

Figure 9.4 Potential bonding sites for Na ions to O$_{py}$ on (a) concave-in rings and (b) concave-out rings of $U_{24}P_{12}$, where sites 1 on either concavity ring are occupied by O$_{py,ab}$ atoms and sites 2 are occupied by O$_{py,bridge}$ atoms.

Figure 9.5 Aggregation summary for concentrated solutions of $U_{24}P_{12}$ with added cations (indicated by blue circles), where systems of untreated solutions are discrete molecules, systems with added monovalent cations generally show only a small increase in size (possible dimers or trimers), and systems with added divalent and trivalent cations induce aggregation into large assemblies.

Figure 9.6 ESI-MS of an aqueous solution of 0.5 g/L $U_{24}P_{12}$ over 62 days showing the equilibration of the cluster in solution and the beginning of fragmentation of the
cluster between measurements on Day 26 and Day 38. Fragmentation is demonstrated by the disappearance of the second marked distribution.

Figure 11.1 A magnified image of a crystal of U$_{24}$Pp$_{12}$ in grease sealed within a Kapton tube that is heat-sealed on the left end. For clarity, the approximate crystal dimensions have been outlined in green. The scale bar indicates 1 mm.

Figure 11.2 Sample mounting arrangement for the TOPAZ single-crystal diffractometer. The arrow points to the sample mounted in Kapton tube on a Hampton base affixed magnetically to the goniometer head. Below the mounted area is the detector array and the cold stream.

Figure 11.3 An example of the detector array for TOPAZ. Each dark brown square represents a detector, which is a two-dimensional energy dispersive Anger camera detector. Currently there are thirteen detectors around the instrument. The blue circle represents the placement of the sample in relation to the detectors, and blue lines from this circle represent diffraction to a particular detector (Hoffman & Wang, 2013).

Figure 11.4 Crystal structure of U$_{24}$Pp$_{12}$ from single-crystal X-ray diffraction structure solution. The orientation of the crystal in the x,y direction is shown in (a) and the orientation in the x,z direction is shown in (b), where the yellow polyhedra are uranyl polyhedra and the purple polyhedra are pyrophosphate groups. The two orientations demonstrate the oblate nature of the cluster, with four of the six uranyl tetramers with concavity towards the center of the cluster (central tetramer in a), the remaining two uranyl tetramers having opposite concavity (central tetramer in b).

Figure 11.5 Crystal structure of U$_{24}$Pp$_{12}$ from single-crystal neutron diffraction data without hydrogen atoms shown. The orientation of the crystal in the x,y direction is shown in (a) and the orientation in the x,z direction is shown in (b), where the yellow polyhedra are uranyl, the purple are pyrophosphate, and the blue are sodium.

Figure B.1 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L U$_{24}$Pp$_{12}$ with added lithium.

Figure B.2 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L U$_{24}$Pp$_{12}$ with added sodium.

Figure B.3 The model (black solid line) for the data from USAXS experiments (red data points) with concentrated U$_{24}$Pp$_{12}$ with added potassium.

Figure B.4 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L U$_{24}$Pp$_{12}$ with added rubidium.
Figure B.5 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added cesium. ...............274

Figure B.6 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added silver. .................275

Figure B.7 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added magnesium. .......276

Figure B.8 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added calcium. ............277

Figure B.9 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added strontium. ...........278

Figure B.10 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added lanthanum. ........279

Figure B.11 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added europium. ..........280

Figure B.12 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added holmium. ..........281

Figure B.13 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added aluminum...........282

Figure C.1 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 10 g/L $\text{U}_{24}\text{Pp}_{12}$. Distributions 1, 2, and 3 correspond to cage of $\text{U}_{24}\text{Pp}_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................284

Figure C.2 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 20 g/L $\text{U}_{24}\text{Pp}_{12}$. Distributions 1, 2, and 3 correspond to cage of $\text{U}_{24}\text{Pp}_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................285

Figure C.3 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 30 g/L $\text{U}_{24}\text{Pp}_{12}$. Distributions 1, 2, and 3 correspond to cage of $\text{U}_{24}\text{Pp}_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................286

Figure C.4 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 40 g/L $\text{U}_{24}\text{Pp}_{12}$. Distributions 1, 2, and 3 correspond to cage of $\text{U}_{24}\text{Pp}_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................287
Figure C.5 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 50 g/L $U_{24}Pp_{12}$. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................288

Figure C.6 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added lithium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................289

Figure C.7 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added sodium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................290

Figure C.8 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added potassium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................291

Figure C.9 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added rubidium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................292

Figure C.10 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added cesium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................293

Figure C.11 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added silver. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................294

Figure C.12 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added calcium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................295

Figure C.13 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added magnesium. Distributions 1, 2, and 3 correspond to cage of $U_{24}Pp_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster. .................................................................296

Figure C.14 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}Pp_{12}$ with added strontium. Distributions 1, 2,
and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4
corresponds to the interaction between the sodium ion and the cluster...........297

Figure C.15 Peak fitting of the distributions for the PDDF (black) from USAXS data for
an aqueous solution of 65 g/L $U_{24}P_{12}$ with added lanthanum. Distributions 1, 2,
and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4
corresponds to the interaction between the sodium ion and the cluster.............298

Figure C.16 Peak fitting of the distributions for the PDDF (black) from USAXS data for
an aqueous solution of 65 g/L $U_{24}P_{12}$ with added europium. Distributions 1, 2,
and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4
corresponds to the interaction between the sodium ion and the cluster.............299

Figure C.17 Peak fitting of the distributions for the PDDF (black) from USAXS data for
an aqueous solution of 65 g/L $U_{24}P_{12}$ with added holmium. Distributions 1, 2,
and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4
corresponds to the interaction between the sodium ion and the cluster.........300

Figure C.18 Peak fitting of the distributions for the PDDF (black) from USAXS data for
an aqueous solution of 65 g/L $U_{24}P_{12}$ with added aluminum. Distributions 1, 2,
and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distributions 4 and 5
correspond to the interaction between the sodium ion and the cluster.........301

Figure D.1 Four DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added potassium at a source-
sample-detector angle of 30°. .................................................................302

Figure D.2 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added potassium at a source-
sample-detector angle of 45°. .................................................................303

Figure D.3 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added potassium at a source-
sample-detector angle of 60°. .................................................................304

Figure D.4 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added potassium at a source-
sample-detector angle of 75°. .................................................................305

Figure D.5 Four DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added potassium at a source-
sample-detector angle of 75°. .................................................................306

Figure D.6 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added cesium at a source-
sample-detector angle of 30°. .................................................................307

Figure D.7 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added cesium at a source-
sample-detector angle of 45°. .................................................................308

Figure D.8 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added cesium at a source-
sample-detector angle of 60°. .................................................................309
Figure D.9 Five DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added cesium at a source-sample-detector angle of 75°.

Figure D.10 Five DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added cesium at a source-sample-detector angle of 90°.

Figure D.11 Six DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added copper at a source-sample-detector angle of 30°.

Figure D.12 Six DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added copper at a source-sample-detector angle of 45°.

Figure D.13 Five DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added copper at a source-sample-detector angle of 60°.

Figure D.14 Five DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added copper at a source-sample-detector angle of 75°.

Figure D.15 Six DLS measurements of 0.5 g/L $U_{24}Pp_{12}$ with added copper at a source-sample-detector angle of 90°.

Figure E.1 $R_H$ data for three concentrations of $U_{24}Pp_{12}$ in 2:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{24}Pp_{12}$ of 0.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of $U_{24}Pp_{12}$ of 3.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The red triangles show data for the highest starting concentration of $U_{24}Pp_{12}$ of 33.3 g of cluster crystal per liter of 2:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.2 $R_H$ data for three concentrations of $U_{24}Pp_{12}$ in 1:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{24}Pp_{12}$ of 0.25 g of cluster crystal per liter of 1:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of $U_{24}Pp_{12}$ of 2.5 g of cluster crystal per liter of 1:1 water-methanol mixture. The red triangles show data for the highest starting concentration of $U_{24}Pp_{12}$ of 25 g of cluster crystal per liter of 1:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.3 $R_H$ data for three concentrations of $U_{24}Pp_{12}$ in 1:2 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{24}Pp_{12}$ of 0.17 g of cluster crystal per liter of 1:2 water-methanol mixture. The blue squares show data for the moderate starting concentration of $U_{24}Pp_{12}$ of 1.67 g of cluster crystal per liter of 1:2 water-methanol mixture. The red triangles show...
data for the highest starting concentration of U$_{24}$Pp$_{12}$ of 16.7 g of cluster crystal per liter of 1:2 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.4 $R_H$ data for three concentrations of U$_{24}$Pp$_{12}$ in 2:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U$_{24}$Pp$_{12}$ of 0.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U$_{24}$Pp$_{12}$ of 2.5 g of cluster crystal per liter of 2:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of U$_{24}$Pp$_{12}$ of 25 g of cluster crystal per liter of 2:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.5 $R_H$ data for three concentrations of U$_{24}$Pp$_{12}$ in 1:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U$_{24}$Pp$_{12}$ of 0.25 g of cluster crystal per liter of 1:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U$_{24}$Pp$_{12}$ of 2.5 g of cluster crystal per liter of 1:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of U$_{24}$Pp$_{12}$ of 25 g of cluster crystal per liter of 1:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.6 $R_H$ data for three concentrations of U$_{24}$Pp$_{12}$ in 1:2 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U$_{24}$Pp$_{12}$ of 0.17 g of cluster crystal per liter of 1:2 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U$_{24}$Pp$_{12}$ of 1.67 g of cluster crystal per liter of 1:2 water-ethanol mixture. The red triangles show data for the highest starting concentration of U$_{24}$Pp$_{12}$ of 16.7 g of cluster crystal per liter of 1:2 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.7 $R_H$ data for three concentrations of U$_{60}$ in 2:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U$_{60}$ of 0.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of U$_{60}$ of 3.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The red triangles show data for the highest starting concentration of U$_{60}$ of 33.3 g of cluster crystal per liter of 2:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.8 $R_H$ data for three concentrations of U$_{60}$ in 1:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The
black diamonds show data for the lowest starting concentration of U\textsubscript{60} of 0.25 g of cluster crystal per liter of 1:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of U\textsubscript{24}P\textsubscript{12} of 2.5 g of cluster crystal per liter of 1:1 water-methanol mixture. The red triangles show data for the highest starting concentration of U\textsubscript{60} of 25 g of cluster crystal per liter of 1:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.9 R\textsubscript{H} data for three concentrations of U\textsubscript{60} in 1:2 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U\textsubscript{60} of 0.17 g of cluster crystal per liter of 1:2 water-methanol mixture. The blue squares show data for the moderate starting concentration of U\textsubscript{60} of 1.67 g of cluster crystal per liter of 1:2 water-methanol mixture. The red triangles show data for the highest starting concentration of U\textsubscript{60} of 16.7 g of cluster crystal per liter of 1:2 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.10 R\textsubscript{H} data for three concentrations of U\textsubscript{60} in 2:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U\textsubscript{60} of 0.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U\textsubscript{60} of 3.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of U\textsubscript{60} of 33.3 g of cluster crystal per liter of 2:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.11 R\textsubscript{H} data for three concentrations of U\textsubscript{60} in 1:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U\textsubscript{60} of 0.25 g of cluster crystal per liter of 1:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U\textsubscript{24}P\textsubscript{12} of 2.5 g of cluster crystal per liter of 1:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of U\textsubscript{60} of 25 g of cluster crystal per liter of 1:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

Figure E.12 R\textsubscript{H} data for three concentrations of U\textsubscript{60} in 1:2 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U\textsubscript{60} of 0.17 g of cluster crystal per liter of 1:2 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U\textsubscript{60} of 1.67 g of cluster crystal per liter of 1:2 water-ethanol mixture. The red triangles show data for the highest starting concentration of U\textsubscript{60} of 16.7 g of cluster crystal per liter of 1:2 water-ethanol mixture.
mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
TABLES

Table 2.1 Mother Solution Compositions for two Uranyl Peroxide Nanoscale Cage Clusters ......................................................................................................................28

Table 2.2 Procedure for the Determination of Crystalline Structures Using X-ray Diffraction.......................................................................................................................44

Table 2.3 Procedure for the Determination of Crystalline Structures Using Neutron Diffraction ..................................................................................................................46

Table 3.1 Concentration of Uranium and U_{24}P_{12} in Solution After 30 Days At Ambient Temperature and Pressure ..........................................................................................60

Table 3.2 Retention Data for U_{24}P_{12} after Ultrafiltration from Concentrations Obtained by ICP-OES ........................................................................................................61

Table 4.1 Nonlinear Curve Fit Gauss data For the PDDF from SAXS Datat of a 65 g/L Solution of U_{24}P_{12} ........................................................................................................80

Table 4.2 Nonlinear Curve Fit Gauss Data for the PDDF from SAXS Data for Solutions of U_{24}P_{12} at Multiple Concentrations .....................................................................89

Table 5.1 Monovalent Cations Added to Aqueous Cluster Solutions of U_{24}P_{12} ........100

Table 5.2 Concentrations of Cations Added to U_{24}P_{12} for USAXS Analysis ..............110

Table 5.3 USAXS Modeling Parameters for U_{24}P_{12} with Monovalent Cations ............112

Table 5.4 Unified Fit Model from USAXS Data for U_{24}P_{12} with Added Cs ..................115

Table 5.5 Guinier Approximation Data for U_{24}P_{12} with Monovalent Cations ..........118

Table 5.6 Nonlinear Curve Fit Gauss Data for the PDDF from SAXS Data for Solutions of U_{24}P_{12} with Monovalent Cations Added ................................................121

Table 5.7 Presence of Precipitate upon Addition of Monovalent Cations to Solutions of U_{24}P_{12} ..............................................................................................................125

Table 5.8 Presence of Elements in XRF Analyses of Precipitates Formed from Solutions of U_{24}P_{12} with Added Monovalent Cations ......................................................129
Table 5.9  Comparison of the Raman Redshift for Aqueous Solutions of U$_{24}$PP$_{12}$ with Added Monovalent Cations .................................................................131

Table 5.10  Extent of Aggregation in concentrated Solutions of U$_{24}$PP$_{12}$ with Monovalent Cations .................................................................134

Table 6.1  Divalent Cations Added to Aqueous Cluster Solutions of U$_{24}$PP$_{12}$.............137

Table 6.2  Concentrations of Cations Added to U$_{24}$PP$_{12}$ for USAXS Analysis .............145

Table 6.3  USAXS Modeling Parameters for U$_{24}$PP$_{12}$ with Divalent Cations .............148

Table 6.4  Unified Fit Model from USAXS Data for U$_{24}$PP$_{12}$ with Added Sr ..........151

Table 6.5  Guinier Approximation Data for U$_{24}$PP$_{12}$ with Divalent Cations ..........154

Table 6.6  Nonlinear Curve Fit Gauss Data for the PDDF from SAXS Data for Solutions of U$_{24}$PP$_{12}$ with Divalent Cations Added ........................................157

Table 6.7  Presence of Elements in XRF Analyses of Precipitates Formed from Solutions of U$_{24}$PP$_{12}$ with Added Divalent Cations ........................................161

Table 6.8  Extent of Aggregation in Concentrated Solutions of U$_{24}$PP$_{12}$ with Divalent Cations .................................................................164

Table 7.1  Trivalent Cations Added to Aqueous Cluster Solutions of U$_{24}$PP$_{12}$...........167

Table 7.2  Concentrations of Cations Added to U$_{24}$PP$_{12}$ for USAXS Analysis ..........175

Table 7.3  USAXS Modeling Parameters for U$_{24}$PP$_{12}$ with Divalent Cations ..........178

Table 7.4  Unified Fit Model from USAXS Data for U$_{24}$PP$_{12}$ with Added Al ..........181

Table 7.5  Guinier Approximation Data for U$_{24}$PP$_{12}$ with Trivalent Cations ..........184

Table 7.6  Nonlinear curve fit Gauss Data for the PDDF from SAXS Data for Solutions of U$_{24}$PP$_{12}$ with Trivalent Cations Added ........................................187

Table 7.7  Presence of Elements in XRF Analyses of Precipitates Formed from Solutions of U$_{24}$PP$_{12}$ with Added Trivalent Cations ........................................192

Table 7.8  Extent of Aggregation in Concentrated Solutions of U$_{24}$PP$_{12}$ with Trivalent Cations .................................................................196

Table 8.1  Cation Addition Information for Dilute Solutions of U$_{24}$PP$_{12}$...............199

Table 8.2  Peak of DLS Distribution Data for 0.5 g/L Aqueous Solutions of U$_{24}$PP$_{12}$ with Added Potassium .................................................................202
Table 8.3  Peak of DLS Distribution Data for 0.5 g/L Aqueous Solutions of U$_{24}$P$_{12}$ with Added Cesium ........................................................................................................................................206

Table 8.4  Peak of DLS Distribution Data for 0.5 g/L Aqueous Solutions of U$_{24}$P$_{12}$ with Added Copper ........................................................................................................................................210

Table 10.1  Final Cluster Concentration in Mixed-Solvent Systems Based on the Initial Cluster Concentration (Top Row) and the Mixture Ratio (Left-Most Column) ..................................................................................235

Table 10.2  Refractive Index of Water-Methanol Mixtures (Herraez & Belda, 2006) ..................................................................................................................................................237

Table 11.1  Selected Bond Distances in the Structure Solution of U$_{24}$P$_{12}$ from Neutron Diffraction Data ........................................................................................................................................259
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xxxiii
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CHAPTER 1:

INTRODUCTION

1.1 Actinides

The actinide series is composed of a group of elements in the f-block of the periodic table, starting with element 89, Actinium, and going through element 103, Lawrencium. The series is composed by elements that have a sequential filling of the 5f orbitals. Few actinides occur in nature, with uranium and thorium being found in appreciable amounts in the environment. Actinium and protactinium have been found in small amounts in nature, often associated with uranium ores. The actinides after uranium, called transuranics, must be produced produced in a reactor. Unlike the other half of the f-block, the lanthanides, all actinides are radioactive and can adopt a wide variety of oxidation states, making study of the chemistry of these elements rich, as well as complicated.

In addition to providing information to complete the chemistry of the periodic table, study of actinides is extremely relevant in society. Actinides provide the fuel for nuclear reactors, were used to make the first nuclear weapons, are important for nuclear non-proliferation, and are exceedingly important for national security. With the development of nuclear weapons and nuclear energy, the environmental impact of actinides also becomes a concern, as they are major radiological and heavy metal...
contaminants. As such, transport of actinides in the environment is an important area of research.

1.2 Nuclear Energy

Although there are many things that separate first-world from second-world countries, the predominant difference involves a country’s ability to generate and supply electricity to the public. According to the World Energy Outlook report from 2012, approximately 1.3 billion people do not have access to electricity. The majority of these people live in developing countries in Asia and Sub-Saharan Africa (IEA, 2012). Furthermore, the demand for electricity is continuously growing, and the demand must be met by the energy infrastructure in place and the newly incorporated energy production systems. Current systems for electricity generation include natural gas, petroleum and other liquid fuels, coal, nuclear, and renewable resources such as wind and solar power.

Since the Kyoto Agreement, energy production should be combined with a decrease in emission of carbon dioxide (CO$_2$). Although energy generation from renewable energy sources has quadrupled in the past two decades, many countries, including the U.S. and the U.K., are well below their potential for renewable energy. For countries such as these, nuclear energy provides an alternative to carbon-based energy sources (natural gas, coal, and petroleum) and renewable energy sources (Wittneben, 2012). Nuclear energy serves as a viable source of energy production in light of the Kyoto Agreement because it is a low-carbon alternative to fossil fuels (Wolde-Rufael, 2010) and is expected to be a valid option in globally sustainable development (Lee &
Chiu, 2011). As of 2012, nuclear energy comprised approximately 14% of the world electricity budget (Dittmar, 2012).

Nuclear energy is produced via the use of nuclear reactors. A nuclear reactor is generally composed of four main parts: the core, control rods, coolant, and heat-utilization system. The core of the reactor holds the fuel, and a neutron moderator is used to slow down the neutrons in the case of thermal nuclear reactors. The control rods regulate the chain reaction by absorbing neutrons, which slows the fission process. The coolant removes the heat that is generated via the fission, which generates neutrons as well as energy. The heat-utilization system in energy production is a generator connected to the grid to allow for the transfer of energy from the plant (Percebois, 2003).

There are two types of nuclear fuel cycles, “open” and “closed”, which differ in the specifics of the back end of the fuel cycle. An example of an open fuel cycle is shown in Figure 1.1, and a closed fuel cycle is shown in Figure 1.3.

The fuel cycle can be divided into three major parts—the front end (blue in figures), irradiation (purple in figures), and the back end (orange in figures) of the fuel cycle. The front end of the fuel cycle deals with mining, conversion, and enrichment of mined natural uranium to fabricate the uranium fuel suitable for the reactor.
Figure 1.1 The Open Fuel Cycle, where the front end of the cycle is shown in blue, irradiation is shown in purple, and the back end is shown in orange. The green arrows indicate natural or depleted uranium ($^{235}\text{U}$ content is less than 0.7%), while the black arrows indicate enriched uranium ($^{235}\text{U}$ content is greater than 0.7%). Currently, the United States has no permanent geologic repository, so the open fuel cycle ends at interim, on-site storage.
Uranium ore is milled and concentrated to form “yellowcake”, a form of isotopically natural uranium. Natural uranium is mostly composed of $^{238}\text{U}$, an isotope that is fertile but not fissile. The fissile isotope of uranium, $^{235}\text{U}$, is present in small amounts (0.7% atomic percent) in the yellowcake. In order to enrich the uranium in $^{235}\text{U}$, the yellowcake must be converted to UF$_6$ gas, which can be enriched either using gaseous diffusion or centrifugation. The enriched UF$_6$ is then converted into enriched uranium dioxide for use in most commercial nuclear reactors, which require uranium to be enriched to around three percent $^{235}\text{U}$ for a sustained fission reaction to occur.

Prior to the irradiation phase, the uranium fuel is placed into fuel rod assemblies, which are subsequently inserted into the reactor. In the reactor, a sustained fission chain reaction occurs by bombardment of neutrons. Fission occurs when the $^{235}\text{U}$ absorbs a neutron creating an unstable species, which splits into two smaller nuclei and emits a few neutrons (Percebois, 2003). The fission yield for $^{235}\text{U}$ is shown in Figure 1.2 (HyperPhysics).
Figure 1.2 Fission Yield for $^{235}\text{U}$, where the curve indicates the percent yield at a particular mass number. Maxima of these distributions occur at mass number 95 (molybdenum) and 137 (barium). A local minimum between these two maxima occurs at mass number 118 (tin). This represents the percent yield of mass that occurs when $^{235}\text{U}$ undergoes fission and the nucleus fragments.
Figure 1.3 The Closed Fuel Cycle, where the front end is shown in blue, irradiation is shown in purple, and the back end is shown in orange. The light green arrows indicate natural or depleted uranium ($^{235}$U content is less than 0.7%), while the black arrows indicate enriched uranium ($^{235}$U content is greater than 0.7%). The dark green arrow indicates a secondary waste stream, from which the uranium has been separated. In a closed cycle, irradiated fuel is reprocessed to recover uranium and plutonium, which can go back to the conversion step and used again.

Once the fuel has been irradiated for about a year (WNA, 2012), the back end of the fuel cycle begins. Fuel rods must be periodically replaced due to the accumulation of fission products and the stability of the fuel assemblies, which helps maintain reactor efficiency. In the back end of the cycle, the fuel is cooled in cooling ponds due to the high temperature and intense radioactivity from fission reactions. Once cooled, the fuel
either undergoes reprocessing (closed cycle) or is stored temporarily with the hopes of transporting the fuel to a long-term geological repository (open cycle). The U.S. currently employs an open fuel cycle. However, no permanent geological repository is currently available, so fuel is stored on site in dry cask storage (NRC).

1.3 Uranium in the Environment

Uranium is one of the naturally occurring actinides and can be found worldwide in low levels in seawater (3 ppb), rock, and soil (0.7 to 11 ppm), at an average crustal concentration of approximately 3-4 ppm (Seko et al., 2004). Besides this natural occurrence in a variety of mineral phases (see Section 1.4), uranium can be found at higher levels due to contamination from mine tailings, the Manhattan Project and Cold War era weapons production, reactor incidents, and possible breach of containment for stored spent nuclear fuel.

Uranium mill tailings are a potential hazard to the environment and public health, not only due to their radioactivity due to the uranium, but also from the presence of radium, which decays into radon gas. Radon gas is listed as an Environmental Protection Agency concern, which is estimated to cause tens of thousands of lung cancer deaths every year (EPA, 2012). Because of this, Congress passed the Uranium Mill Tailings Radiation Control Act of 1978 to handle the disposal, stabilization, and control of mill tailings (NRC, 2006).

Cleaning up nuclear and chemical waste at Manhattan Project and Cold War era legacy sites, such as Hanford, Oak Ridge, and Fernald, is an ongoing process. Sites such as Hanford in Washington State, Oak Ridge in Tennessee, Fernald in Ohio, and Savannah
River in South Carolina were, and still are, contaminated with uranium and transuranic elements from nuclear weapon production during the Manhattan Project and the Cold War. These are examples of sites that are listed as both Nation Priority List and Superfund sites by the Environmental Protection Agency (USEPA, 2012).

With the current use of uranium for the commercial nuclear fuel cycle, concerns arise over contamination of the environment. Nuclear incidents such as Three Mile Island, Chernobyl, and, most recently, Fukushima, can trigger public concern about exposure (Balonov, 2007; Rahu, 2003; Wittneben, 2012). Nuclear incidents can cause release of radioactive materials into the air and water, and radioactive particles can coat the ground (Hammond et al., 2011; Pollanen et al., 1997). The fuel itself can corrode and cause transport of uranium (Armstrong et al., 2012; Burns, et al., 2012).

In addition to nuclear incidents, it is possible that breach of containment of stored nuclear waste can cause release of uranium into the environment. Uranium fuel for reactors is most commonly U(IV), which is less mobile than U(VI). However, when uranium oxide fuel (or simulated fuel) is exposed to oxygenated water, the uranium oxidizes to its more soluble form (Clarens et al., 2004; Corbel et al., 2006; McNamara et al., 2003; McNamara et al., 2005; Sattonay et al., 2001; Shoesmith, 2000; Wronkiewicz et al., 1992; Wronkiewicz et al., 1996).

1.4 Uranium Minerals

Uranium has two primary oxidation states in natural environments—tetravalent (+4) in anoxic environments and hexavalent (+6) in oxygen rich environments. Uranium minerals can be placed into two groups based on these oxidation states, where primary
minerals consist of uranium as U(IV), and secondary minerals consist of uranium as U(VI). Not surprisingly, secondary minerals are formed as alteration products of U(IV) minerals via oxidation and incorporation of secondary ions.

The most important primary uranium mineral is uraninite, UO$_{2+x}$. Uraninite, in Nature, most frequently incorporates lead, thorium, and rare earth element oxides. When uraninite is exposed to an oxygen-rich environment, the mineral forms a corrosion rind of secondary minerals. The secondary minerals that are formed are largely dependent on the presence of anions in the environment. For instance, carbonate rich waters tend to form uranyl carbonate minerals, while phosphate rich waters tend to form uranyl phosphate minerals.

Hexavalent uranium structures are composed predominantly by the nearly linear dioxo uranyl ion. In fact, all U(VI) minerals contain the uranyl ion, which has a +2 formal charge. The uranyl ion has a central U(VI) cation that is strongly bonded to two oxygen atoms in a nearly linear configuration. Because of this, the uranyl bond satisfies most of the bonding requirements for the uranyl oxygen atoms, seldom allowing for strong bonds between the O$_{ur}$ and other cations. Uranyl oxygen atoms can, however, form bonds with Group I or Group II metals and accept some H bonds (Burns, 1997).

In uranyl U(VI) structures, the uranyl ion can be further coordinated by four, five, or six oxygen atoms in the equatorial plane to form square, pentagonal, and hexagonal bipyramids, respectively. The equatorial O atoms that form the vertices of the bipyramids can correspond to O, OH, H$_2$O, and oxyanions. These polyhedra can form an extended structure by the sharing of mostly edges or vertices to form a larger overall structure.
Of the 368 inorganic uranyl compounds described in the hierarchy of U(VI) minerals and inorganic compounds, 89 were minerals (Burns, 2005). The majority of these 89 minerals consisted of sheets of uranyl polyhedra (~77.5%). The remaining structures include clusters (~7.9%), chains (~11.2%), and frameworks (~3.4%). These structures often include oxyanions, such as phosphate, silicate, carbonate, and molybdate, which are essential to the mineral structures (Burns, 2005). Because the uranyl ion is essentially terminal, most of the uranyl U(VI) structures only share edges or vertices in the equatorial plane, favoring the formation of sheets and chains. The use of non-bridging, chelating ligands—such as carbonate in the uranyl tricarbonate structures—form isolated clusters.

Uranyl minerals follow general trends for solubility. In general, uranyl tricarbonates are the most soluble, with solubility products ranging from $10^{-85.5}$ to $10^{-36.6}$ (Alwan & Williams, 1980; O’Brien & Williams, 1983). Uranyl sulfate minerals are also readily soluble in acidic waters. Less soluble minerals include arsenates, vanadates, and phosphates. Studies on uranium mineral solubilities and thermodynamics have been reported primarily for the carbonates and oxide hydrates. (Gorman-Lewis et al., 2008; Burns, 2006). However, some uranyl mineral groups, such as the phosphates, are lacking significant data.
Figure 1.4 Relative Solubilities of Uranyl Minerals where the thick box borders are the mineral phases that form upon introduction of the dissolved uranyl ion to the conditions described by the boxes with dotted line borders. Minerals located at the top of the diagram are more soluble, and minerals located at the bottom of the diagram are more soluble (adapted from *Reviews in Mineralogy*, 1999).
1.5 Transition Metal Polyoxometalates

Polyoxometalates (POMs) have been defined as nanometer-sized assemblies of transition metal oxides containing sub-units of metal oxides, MOₓ. (Pigga et al., 2010). These subunits form polyhedra with oxygen atoms at the vertices, which form a larger POM structure by the sharing of edges or vertices. These POM structures self-assemble via condensation of metal oxides. For example, five sub-units can be joined to form a pentagonal ring, or a pentamer (Figure 1.5 a). These pentamers can share edges to form a three-dimensional array as open (Figure 1.5 b) or closed polyhedra (Figure 1.5 c), such as a dodecahedron. The pentamers can also expand (Figure 1.5 d) by the use of a ligand as a linker, which gives an extended polyhedron (Figure 1.5 e) that retains the symmetry of the closed polyhedron. (Muller, Kogerler, & Dress, 2001) This is shown in Figure 1.3 below, where the pentagons represent the pentameric unit of the POM with metal atoms at each vertex, and the grey balls represent the ligand linker (Figure 1.5e).
Most POMs consist of molybdenum, tungsten, vanadium, or niobium, but POMs also contain lanthanide and actinide metals (Burns, 2011; Long et al., 2010; Sigmon et al., 2009). The earliest documented POM is a Keggin- type ammonium phosphomolybdate POM reported by Berzelius in 1826 (Berzelius, 1826). POMs also exist as anions in solution, making POMs model systems for soluble macroions (Pigga et al., 2010). Five basic polyoxometalates are shown in Figure 1.6, including the Lindqvist, Anderson, Keggin, Wells-Dawson, and Pressler polyoxoanions.
One particular example of a POM structure is the Lindqvist ion. The Lindqvist ion (Figure 1.6 a) is the most common geometry for alkaline-based POMs (Nyman & Burns, 2012). The Lindqvist ion has the formula \([\text{M}_6\text{O}_{19}]^{n-}\), where the six metal atoms (Ta or Nb) are octahedrally coordinated. The Lindqvist ion has no central cation, also called a heteropolyion, but this is not always the case.

Another example of a POM structure is the Keggin ion, following the general formula \([\text{XM}_{12}\text{O}_{40}]^{n-}\) (Figure 1.6 c). The X in the Keggin structure represents a heteropolyion. Larger simple POMs with a heteropolyion structure include the Wells-
Dawson ion, with the general formula $[\mathrm{XM}_{18}\mathrm{O}_{62}]^{n-}$ (Briand et al., 2003). This is shown in Figure 1.6.d.

Polyoxometalates self-assemble in solution and can self-aggregate to form larger structures (Fielden et al., 2006). Macroions, or aggregates, of POMs are intermediate in size, between simple inorganic ions and colloidal suspensions. As such, they cannot be described using Debye-Hückel theory or DVLO theory for colloids. Debye-Hückel theory is invalid due to the large size of the POM anions in comparison to the cations (Pigga, et al., 2010). DVLO is invalid because van der Waals forces are not the primary attractive forces in blackberry formation (Liu et al., 2006).

Aggregates of POMs include films, tubes, wires, fibers, micelles, dots and blackberry structures with a hollow spherical shape (T. Liu, 2009, 2010; Veen & Kegel, 2009; Yin, Li, & Liu, 2011). The phenomenon of self-aggregation begins with a single ion (0.1 nm) that self-assembles into a POM (~1 nm), as shown in Figure 1.6. This POM then assembles into larger structures ranging from 10-100nm based on the dielectric constant of the solvent (T. Liu, 2009). Aggregation may prove important for applications in fields such as energy, molecular electronics, nanowires, biomedicine, catalysis, optical, nanofluids, and quantum dots. Assembly of nanoclusters into aggregates is unique because the assembly process is not primarily based on hydrophobic interactions, van der Waals forces, or chemical interactions. Instead, the process is based on the counter-ion effect and hydrogen bonds. To a small extent, van der Waals interactions are also involved in aggregation (Kistler et al., 2010).
One example of POM self-aggregation has been documented for the wheel-shaped Mo$_{154}$ structure. This structure can undergo aggregation in solution to form a structure composed of approximately 1200 of the wheel clusters arranged in a hollow sphere called a blackberry. (T. Liu, 2010). Liu et al. hypothesized that self-aggregation is thermodynamically favorable with an oligomeric transitional state (G. Liu & Liu, 2005).

Aggregate size can be tuned by changing the solvent concentration or POM charge density. Examples of changing solvent concentrations include those with molybdenum-oxide nanoacids in water/organic solvent mixtures (Kistler et al., 2009) (Kistler, et al., 2007). Charge density can be changed by pH (T. Liu et al., 2006) or by the addition of metal cations (Pigga et al., 2010).
Because counterion-mediated attraction is important for blackberry formation, countercations may play an important role in blackberry formation (Pigga et al., 2010). Studies have shown that TM-POMs can aggregate when a metal cation is added to solution (Abbas, et al., 2005; G. Liu, et al., 2006; Yao, et al., 2010). Anionic POMs have ideal structures for binding and associating with metal cations due to ion pairing (Antonio, Nyman, & Anderson, 2009). The self-assembly of POMs may depend on the size and degree of hydration of the counter cations. Alkali metal ions with larger ionic radii have lower hydrated radii, enabling them to form more intimate ion pairs (Pigga et al., 2010).

Additionally, POMs can aggregate upon addition of an organic linker. Cooper et al. predicted that controlled aggregation into nanotubules could be achieved by varying the organic ion solubility and POM solubility, resulting in osmotically driven crystal morphogenesis (Cooper et al., 2007). Controlled assembly of aggregates allows for nanofabrication of material architectures specific to applications, such as the assembly of tubular macromolecules (Long et al., 2010).

Mechanisms of aggregation have been attributed to hydrogen-bond formation in certain cases. In a study by Sawada et al. (2012), three Coulombic aggregations of Keggin-type POMs showed that hydrogen bonding allowed for aggregation into sheets and chains (Sawada et al., 2012). Further studies in mixed-POM systems with ruthenium photosensitizers and molybdenum POMs have shown that aggregation can also occur by hydrogen bonding, which can be inhibited by the addition of an ion-pair-forming cation. (Huessner et al., 2011)
POMs have been shown to aggregate by self-assembly, the addition of metal ions, and the addition of organic ligands. Aggregation has been documented as occurring when thermodynamically favorable (G. Liu & Liu, 2005). Although much less is known about the aggregation behavior of actinyl-POMs, TM-POMs may provide useful in understanding actinyl-POM behavior.

1.6 Uranyl Polyoxometalates

Uranyl polyoxometalates (U-POMs), also known as cage clusters or nanoclusters, are one component of the structural hierarchy of U(VI) compounds. The basic subunit of U-POMs is the uranyl unit coordinated by six oxygen atoms, forming uranyl hexagonal bipyramids. Like TM-POMs, U-POMs are composed of rings of multiple subunits, usually 4, 5, or 6.

As mentioned previously, U(VI) structures have a tendency to form sheets due to the terminal nature of the uranyl moiety, demonstrated by the uranyl hierarchy (Burns, 2005). In order to synthesize U-POMs, the tendency of uranyl structures to form sheets must be overcome. In 2003, Burns and Hughes reported the structure of studtite, [(UO$_2$)(O$_2$)(H$_2$O)$_2$](H$_2$O)$_2$ (Figure 1.8), a mineral species consisting of chains of uranyl ions linked by bidentate peroxide ligands (Burns & Hughes, 2003; Walenta, 1974). The corrugated nature of the chains is due to the peroxide-uranium-peroxide dihedral angle, which is inherently bent. This induction of curvature was the inspiration behind the synthesis of U-POMs (Vlaisavljevich, Gagliardi, & Burns, 2010).
Figure 1.8 The crystal structure of studtite (Burns & Hughes, 2003), where the uranium atoms are shown in yellow, uranyl oxygen atoms in light red, equatorial oxygen atoms in red, and hydrogen atoms in white. The top image is the polyhedral representation of a studtite chain. The middle image shows the chain in the x,z plane, illustrating the shared peroxide edge. The bottom image shows the chain in the x,y plane, illustrating the bent uranium-peroxide-uranium dihedral angle.

To date, over 50 uranyl polyoxometalates have been published, and even more remain to be published (Qiu & Burns, 2013). The uranyl polyhedra of U-POMs contain hexagonal or pentagonal bipyramids that are often linked through bidentate peroxide groups that self assemble in aqueous solution (Sigmon et al., 2009). Diperoxo bipyramids contain two peroxide groups in a cis arrangement, with the third edge of the uranyl hexagonal bipyramid defined by two oxygen atoms, which can come from another bidentate ligand or two monodentate ligands. Triperoxo bipyramids have three peroxide
bidentate groups forming all six edges of a bipyramid, three of which correspond to the O-O bonds (Burns, 2005).

U-POMs can be divided into two major groups: open clusters and closed cage polyoxometalates. Open clusters can form a bowl-shape or a ring/crown-shape. An example of an open cluster is $U_{24R}$, which is composed of 24 uranyl polyhedral arranged in hexameric rings (Figure 1.9).

![Figure 1.9 A uranyl peroxide ring, $U_{24R}$ (Sigmon, Weaver, Kubatko, & Burns, 2009), shown in a polyhedral representation (left) and as the graph of the cluster (right), where each vertex represents a uranyl hexagonal bipyramid. $U_{24R}$ is composed of 24 uranyl hexagonal bipyramids arranged into a ring by the sharing of peroxide edges and hydroxide vertices.]

Closed polyoxometalates are spherical or spheroid in nature, corresponding to three-connected topological graphs with squares and/or pentagons or hexagons. These U-POMs can be grouped into structures containing only uranyl bipyramids and those containing additional linkers. Possible linkers include phosphate, pyrophosphate, oxalate, nitrate, transition metals, and arsenate groups (Adelani, Sigmon, & Burns, 2013; Burns, 2011; Ling et al., 2014; Ling et al., 2012; Ling et al., 2010; Qiu & Burns, 2013).
1.10 shows three closed cage structures—$U_{60}$ (a and d), $U_{24}$ (b and e), and $U_{24}P_{12}$ (c and f). Parts a–c show the polyhedral representation, where the yellow polyhedra indicate uranyl bipyramids and the purple polyhedra represent pyrophosphate groups.

Figure 1.10 Closed uranyl polyoxometalates $U_{60}$ (a and d), $U_{24}$ (b and e), and $U_{24}P_{12}$ (c and f) (Qiu & Burns, 2013) where yellow polyhedra represent uranyl polyhedra and purple polyhedra represent pyrophosphate groups. Images a through c show the polyhedral representation of these clusters, while images d through f show the graph of the cluster. In the graph, each vertex is occupied by a uranyl ion. The yellow lines in (f) indicate the bridging by pyrophosphate, while the blue lines show the connectivity of tetrameric rings.

Unlike TM-POMs, properties and aggregation of U-POMs have not been well studied. However, TM-POMs provide comparison and insight. Studies of U-POMs are important for potential applications in the nuclear fuel cycle, and their spontaneous assembly when uranium and peroxide are present over a wide pH range. Furthermore, U-
POMs may form in various nuclear accident scenarios, such as in water after the nuclear incident at Fukushima (Armstrong et al., 2012; Burns et al., 2012).

1.7 Neutron Diffraction of Uranyl Compounds

The idea of using neutrons as an analytical probe was announced just as parts of the Manhattan Project research were declassified in 1946. Shortly after the American Physical Society met in Chicago in 1946, an article titled “New Toys” appeared in TIME magazine and described neutrons as the “new toy” for scientists. Scientist Walter H. Zinn had discovered that neutrons, like electrons, subscribed to the wave mechanics theory, producing a diffraction pattern when a crystal was bombarded with neutrons ("New Toys," 1946). Based on these results, Zinn believed that neutrons could be used similar to X-rays to probe the structural information for molecules.

Neutron diffraction is an analytical method by which a neutron beam interacts with the nuclei of a sample to give structural information. Similar to X-ray crystallography, both powder and single crystal diffraction techniques can be used in elucidation. Unlike, X-ray crystallography however, there is no bias towards heavier elements, so light elements, such as hydrogen, can be located. The instrumental method of single crystal neutron diffraction will be detailed in the materials and methods section (Chapter 2).

As early as 1951, research was published on the neutron powder diffraction of uranium compounds (Rundle, 1951). Further studies using neutron powder diffraction data were conducted in 1958, when neutron diffraction was used to confirm the NaCl-like structure of uranyl nitrate (Mueller & Knott, 1958). In 1965, researchers at ANL reported
results on the single crystal structure of uranyl nitrate hexahydrate as obtained using three-dimensional neutron diffraction (Taylor & Mueller, 1965).

Figure 1.11 Hydrogen bonding environment of uranyl nitrate hexahydrate as studied by Taylor and Mueller using neutron diffraction (Taylor & Mueller, 1965), showing the bond angles between the uranyl center, nitrate groups attached to the uranyl center, and coordinating water molecules. The image indicates hydrogen bonding by dashed lines and the filled black circles indicate hydrogen, while the unfilled circles represent oxygen.

Since the early studies of uranium compounds with neutron diffraction, many studies have been conducted on uranium materials utilizing neutrons (Vogel, 2013). Research areas include characterization of both ceramic (Andersen, 1958; Bevan, Grey, & Willis, 1968; Loopstra, 1964; Loopstra, Taylor, & Waugh, 1977; Willis, 1963) and
metallic nuclear fuels (Birtcher, Richardson, & Mueller, 1997; Brown et al., 2009; Lander & Mueller, 1997; Lawson et al., 1988; Lee, Kim, & Em, 2000; Sears et al., 2011; Seong et al., 2000) and waste forms, especially pyrochlores (James et al., 2010; Zhang et al., 2013). However, very little has been studied in regard to actinide-bearing minerals (Vogel, 2013), and uranium nanoscale cage clusters have not been studied using neutron diffraction previously.

1.8 Dissertation Overview

Despite the usage of uranium as a nuclear fuel in the advanced fuel cycle, much is still not understood in the realm of actinide chemistry. With the demands of energy generation and a call for decreased dependence on fossil fuels, the prevalence of nuclear energy will likely increase in the United States and elsewhere. To meet such needs safely and efficiently, basic research is needed to determine the interactions of uranium with the environment, particularly in its hexavalent oxidation state. This research has the potential to impact the future of nuclear energy, from the production and processing of fuel materials to the recycling and storage of used nuclear materials.

This dissertation examines some aspects of uranium chemistry in both the crystalline and aqueous states. The unifying theme of this research is the characterization of uranium materials with potential applications for an advanced nuclear fuel cycle and storage of used nuclear fuel. First, I report the aqueous behavior of uranyl peroxide nanoscale cage clusters under normal (U_{24}P_{12}) and altered solution conditions (U_{24}P_{12} and U_{60}). These studies of nanoclusters extend beyond the early characterization of materials, beginning with Burns et al. (2005), and leading to the discovery of a large
family of uranium-based polyoxometalates. The aqueous solution behavior of uranyl clusters has potential applications for the back end of the nuclear fuel cycle, and this research helps develop principles by which we can understand the intricate interactions between the clusters and other species in solution after fuel is irradiated. Second, I report advancements in the structural properties of uranyl peroxide nanoscale cage clusters using single crystal neutron diffraction. This work utilizes a previously published crystal structure collected using single-crystal X-ray diffraction and adds additional structural information, such as the atomic locations of previously undetermined hydrogen atoms and lighter alkali and alkaline earth ions.

Twelve chapters detail this research. Chapter 1 introduces nuclear energy and uranium chemistry. The remainder of this dissertation is outlined as follows:

- Chapter 2 discusses the materials and methods used in this research.
- Chapter 3 examines the aqueous solubility of a uranyl peroxide pyrophosphate nanoscale cage cluster, $\text{U}_{24}\text{P}_{12}$, at room temperature.
- Chapter 4 presents characterization studies of the aqueous behavior $\text{U}_{24}\text{P}_{12}$ under ambient conditions.
- Chapters 5-7 examine the concentration and time dependence on the aggregation of $\text{U}_{24}\text{P}_{12}$ with added mono-, di-, and trivalent cations in concentrated aqueous cluster solutions.
- Chapter 8 examines the aggregation behavior of $\text{U}_{24}\text{P}_{12}$ with added mono-, di-, and trivalent cations in dilute solutions of the cluster.
- Chapter 9 introduces a model for aggregation of $\text{U}_{24}\text{P}_{12}$.
- Chapter 10 examines and compares the aggregation behavior of $\text{U}_{60}$ and $\text{U}_{24}\text{P}_{12}$ in mixed solvent systems.
- Chapter 11 focuses on preliminary single-crystal neutron diffraction of uranyl peroxide nanoscale cage clusters.
- Chapter 12 summarizes the research in this dissertation.
CHAPTER 2: 
MATERIALS AND METHODS

2.1 Synthesis of Uranyl Peroxide Pyrophosphate Nanoclusters

Detailed descriptions of the structures and compositions of U_{24}P_{12} and U_{60} are given in chapters 4 and 10 respectively. Both clusters contain uranyl hexagonal bipyramids arranged into rings, which, in addition to peroxide linkages, are further linked by pyrophosphate (P_2O_7^{4-}) groups in the case of U_{24}P_{12} or hydroxide groups in the cases of U_{60}. The clusters self-assemble in aqueous solution under ambient conditions from mother solutions containing uranyl nitrate, hydrogen peroxide, base, alkali earth salts (U_{60}) or pyrophosphate salts and an acid (U_{24}P_{12}) (Sigmon et al., 2009; Ling et al., 2010). The mother solutions are left open to air, and evaporation allows for crystals of the cluster to form. The compositions of the mother solutions used for each cluster are listed in Table 2.1.
TABLE 2.1
MOTHER SOLUTION COMPOSITIONS FOR TWO URANYL PEROXIDE NANOSCALE CAGE CLUSTERS

<table>
<thead>
<tr>
<th>Mother Solution Component</th>
<th>U$<em>{24}$P$</em>{12}$</th>
<th>U$_{60}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Uranium phase</strong></td>
<td>0.5 M Uranyl Nitrate</td>
<td>0.5 M Uranyl Nitrate</td>
</tr>
<tr>
<td><strong>Peroxide phase</strong></td>
<td>30% Hydrogen Peroxide</td>
<td>30% Hydrogen Peroxide</td>
</tr>
<tr>
<td></td>
<td>40% Tetraethyl</td>
<td>3 M Lithium Hydroxide Monohydrate</td>
</tr>
<tr>
<td><strong>Base phase</strong></td>
<td>0.1 M Sodium Hydroxide</td>
<td>0.1 M Sodium Pyrophosphate</td>
</tr>
<tr>
<td><strong>Other Phase</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Acid phase</strong></td>
<td>0.5 M Iodic Acid</td>
<td>Nitric Acid (as needed)</td>
</tr>
<tr>
<td><strong>Salt phase</strong></td>
<td></td>
<td>0.4 M KCl</td>
</tr>
</tbody>
</table>

2.2 Small Angle X-ray Scattering

Small angle X-ray Scattering (SAXS) is an analytical technique using elastic scattering of X-rays to determine properties such as size, shape, and structural features at a nanometer scale. Monochromatic X-rays are emitted from a source with an incident frequency ($f_0$). When the incident beam strikes the sample, the electrons resonate at an identical frequency to $f_0$ and coherent waves are emitted. These secondary waves undergo constructive or destructive interference depending on the shape of the structure and the electron configurations (Glatter & Kratky, 1982).

The simplest example of scattering from a nanoscale particle is that of a sphere. The path difference, or the distance traveled by two waves to a given point, is indicated in blue and equal to $1\lambda$ in Figure 2.1. The minimum scattering angle is $2\theta$, where the waves interfere destructively with one another to produce essential no scattering. However, as the scattering angle decreases from $2\theta$ (approaching zero), the waves become coherent.
due to smaller phase differences, and scattering is noted. Maximum scattering occurs at zero scattering angle, where all waves are in phase.

Figure 2.1 Scattering from a Small Sphere (a) and a Large Sphere (b), where $1\lambda$ is the path difference between two scattered waves and $2\theta$ is the scattering angle between the vector of the wave prior to scattering and the scattered vector. Maximum scattering occurs when phase differences are minimized (adapted from Glatter & Kratky, 1982).

In Figure 2.1, two spheres of different sizes (a) and (b) are compared using the same incident wavelength. Due to the difference between sizes of the spheres, different scattering curves are produced, as shown in Figure 2.2. Due to destructive interference, the intensity (I) decreases as scattering angle ($2\theta$) increases. The smaller sphere (a) has a wider scattering curve than the larger sphere (b) because path differences of $1\lambda$ occur at larger angles of $2\theta$ for the larger sphere.

Scattering is characterized by a reciprocity law, where particle size is inversely related to scattering angle. Thus, as the size of the scatter increases, information about the
system is shifted to smaller scattering angles. When the size of the scatterer greatly exceeds the X-ray wavelength, small angle scattering occurs (Glatter & Kratky, 1982).

![Figure 2.2 Qualitative Scattering Curves from a Small Sphere (a) and a Large Sphere (b) as pictured in Figure 2.1. The smaller sphere has a wider scattering curve because the path differences occur at smaller angles of $2\theta$ for the small sphere, while the path difference for larger spheres occur at larger angles of $2\theta$ (adapted from Glatter & Kratky, 1982).](image)

Although the example given above is in regards to a sphere, the same principle can be applied to particles of other shapes and sizes. As the anisotropy of the scatterer increases, the scattering must be averaged over all orientations. With small inhomogeneities, uniform electron density can be assumed because the shift in electron distances is small in comparison to the overall size of the scatterer (Glatter & Kratky, 1982).

In general, a SAXS instrument is composed of an X-ray source, collimator, sample chamber, and detector. The X-ray beam, generally monochromatic, passes through line or whole collimators to focus the beam. The beam then strikes the sample
and some of the beam is scattered, while the remainder of the beam passes through. The scattered X-rays strike the detector, which is generally perpendicular to the direction of the incident beam. X-rays that are not scattered are blocked using a beam stop.

SAXS samples at the University of Notre Dame were introduced into the instrument via a flow cell system. SAXS patterns were collected using a Bruker AXS Nanostar with a Cu microfocus X-ray source (~8keV), Montel multilayer optics, and a HiSTAR multiwire detector (~25um pixel size). The sample chamber was kept under vacuum. Scattering data were collected at a sample-to-detector distance of 25 cm, yielding a scattering vector (q) of approximately 0.3-0.85 Å⁻¹. For intensity calibration, a glassy carbon standard was used. A separate measurement was collected using water in the flow cell to obtain the background.

After data collection, the data were integrated over a 2θ range of 0.8-12° (0.08-1.31 in q). Data were plotted as log(I) vs. log(q) using Irena SAS macros (Ilavsky & Jemian, 2009) for Igor Pro (Wavemetrics). The experimental data were modeled using a core-shell form factor in the Modeling II tool for Irena. Error analysis between the fit of the Modeling II generated scattering pattern and the experimental data were analyzed using an option within the tool for χ² minimization.

In addition to the Modeling II tool, the Pair Distance Function Tool was used to determine the distance between paired sets of electrons in a molecular structure. The pair distance function produces a series of distributions that can be fit to describe the particle in solution. Core-shell species, like the uranyl nanoclusters, result in an asymmetric pair distance function that is an averaging of multiple distributions consistent with the shell thickness and maximum paired distance of the function. The higher the function value
P(R) at a particular distance R, the higher the probability to find paired electrons at that particular distance. The pair distance function from SAXS data is addressed further in Chapter 4.

In addition to the modeling of scattering data and the pair distance function, SAXS analyses also provide information about the size of a base particle in solution from the Guinier approximation. The radius of gyration (R_g) for the species of solution is determined from a plot of the scattering angle squared (q^2) and the natural logarithm of the scattering intensity (ln I). The Guinier approximation will be discussed in more detail in Chapter 4.

2.3 Ultra Small Angle X-ray Scattering

Synchrotron-based ultra-small angle X-ray scattering (USAXS) is used for particle characterization when the particle size exceeds approximately 20 nm, the range for conventional SAXS. USAXS provides structural information for species between approximately 1-100 nm (Ilavsky, 2009). The USAXS instrument can be combined with a pinhole SAXS (pin-SAXS) for the same sample, which broadens the sampling range.

In the experiments described herein, USAXS and pinhole SAXS patterns were collected at the 15-ID-D beamline (ChemMat CARS) at the Advanced Photon Source at Argonne National Laboratory. USAXS and pin-SAXS were run sequentially, yielding a q-range from 0.001 to 1.2 Å⁻¹ (Ilavsky, 2009), allowing for sample analysis for species from approximately 1 nm to those exceeding 1 μm.

The USAXS system allows for analysis of larger particles due to elimination of a beam stop. The monochromatic beam is produced by a synchrotron beam passing through
a monochromator, which is then passed through beam-defining and collimating crystal slits to remove parasitic scattering. The beam passes through an ion chamber that is used to monitor intensity before striking the sample. In lieu of a beamstop, the scattered beam passes through analyzing crystals, which reflect the beam onto the detector (Ilavsky, 2009).

The USAXS detector and analyzing crystals can be moved out of the beam line and replaced with the pin-SAXS detector. This allows for sequential analysis of the same sample without altering the sample or sample mount. The pin-SAXS detector is similar to that of the Bruker Nanostar. Data sets from the USAXS can be merged with the pin-SAXS data to produce a single data set with a larger q range using the USAXS and Nika macros for the Igor software platform.

For all experiments, samples were doubly contained in two Kapton capillaries sealed with epoxy on both ends, as shown in Figure 2.3. In order to model the background, capillaries filled with water were also analyzed. The concentrations of cations added to the cluster solutions are specified in Chapter 4.
Figure 2.3 Encapsulation of USAXS samples prepared at the University of Notre Dame and shipped to the Advanced Photon Source. The samples (yellow in the figure) were doubly contained in two Kapton capillaries, the inner shown in orange and the outer shown in amber brown. Each end of the capillary was sealed with epoxy (gray circle) and allowed to dry. The ends of the capillaries were then covered with Kapton tape (light orange rounded square) to ensure that the ends of capillaries were also doubly contained.

Samples were mounted on a metal paddle, as shown in Figure 2.4. Nika software was used for background subtraction with the appropriate blank (Ilavsky & Jemian, 2009). USAXS data and pin-SAXS data were merged using the Data Manipulation tool in Irena (Ilavsky & Jemian, 2009). Data were plotted as log(I) vs. log(q) using Irena SAS package for Igor Pro (Wavemetrics).
2.4 Dynamic Light Scattering

Dynamic light scattering (DLS) is an analytical technique used to measure the size of nanoparticles and their aggregates in aqueous solution. In DLS, a monochromatic laser beam is incident upon a sample cell, and light is scattered in all directions by the particles in solution. The resulting scattering fluctuates in a time-dependent manner due to Brownian motion and the constant change in the distance between scatterers. With multiple scatterers in solution, the light scattered interferes either constructively or destructively with neighboring particles. The resulting scatter passes to the detector, which is held at a fixed position. Information available from the scatter includes the time.
scale of motion, which is related to the sizes of particles in the analyte (Goldburg, 1999). The radius of hydration, $R_h$, is obtained using DLS.

Two different instruments were used to analyze the DLS of samples. The first of these two instruments was a Malvern Zetasizer Nano S at the University of Notre Dame. The instrument contains a He-Ne laser, with a wavelength of 633 nm. Scattering was detected using a backscatter detector that is nearly perpendicular to the incident beam, yielding an intensity autocorrelation function based on Rayleigh scattering. Volume functions can be produced using the intensity functions.

Particle size for the nearly linear angle was recorded based on the intensity function, which is the most accurate measure of particle size. However, the intensity autocorrelation function is sized-biased, as the intensity of scattering scales as a function of particle diameter to the sixth power. Thus, the relative quantities (percentage) of scatterers at a particular size were determined using the volume functions, which are spherically based.

Prior to DLS analysis, samples were prepared in a manner that eliminated most unwanted material from the sample volume. All samples were mixed using a vortex mixer and centrifuged for three minutes at 14000 rcf. Following centrifugation, the samples were filtered using a 0.2 μm polytetrafluoroethylene (PTFE) filter to ensure that any dust or precipitates were removed from solution, with the exception of solutions resulting in large aggregates exceeding the pore size of the filter. Between 150 to 500μL of the resulting solution was injected into a polystyrene cuvette for analysis. The concentration of nanoclusters in solution was approximately 65 g/L.
Each sample was used for four measurements, with each measurement composed of 10 runs. Each run was 30 seconds long, and the average of these runs composed one measurement. Samples were allowed to equilibrate within the DLS sample chamber at the set temperature before instrumental optimization. This optimization was auto-controlled within the instrumental software. Errors for single-angle DLS data do not propagate instrumental error.

The second instrument used was a Brookhaven Instruments BI200-SM commercial light scattering system with a BI 9000 correlator at the University of Akron. The instrument is equipped with a JDS Uniphase 50-mW diode-pumped solid-state green laser (λ = 532 nm) and a moveable detector that can be used over the angular range of 8-165°. For each sample, DLS measurements were taken at 30°, 45°, 60°, 75°, and 90°.

For each angle, a value for the linewidth (Γ) is obtained using the CONTIN software (Provencher, 1982) to determine the half-width at half-maximum of the light scattered spectrum, or linewidth (Γ). From Γ, \( R_h \) is obtained by dividing the CONTIN division function (CDF) by the linewidth for a given angle. The CDF is given in Eq. 2.1 below.

\[
CDF = \frac{16 n^2 k_B T_K \sin \left( \frac{\text{rad}}{2} \right)^2}{6 \eta^2 \text{rad}}
\]

Equation 2.1

The CDF is dependent on \( n \), the solution index of refraction (1.334 for water), \( k_b \) is Boltzmann’s constant, \( T_K \) is the temperature in K (298.15 K for our experiments), \( \text{rad} \) refers to the source-sample-detector angle in radians, \( \eta \) is the dynamic viscosity of the
solvent \((8.9\times 10^{-4}\text{ Pa s})\), and \(\lambda\) is the incident wavelength of the laser in m \((0.000000532 \text{ m})\).

In this type of DLS, we can obtain the absolute average size of particles in solution by determining the angular dependence on size of particles by the Stokes-Einstein equation. From the plot of the data, it is possible to calculate \(R_{h,0}\), the hydrodynamic radius where the source-sample-detector distance is zero. Since this cannot be measured directly, the value is obtained by examining the dynamic scattering behavior at a variety of angles and a plot of the inverse of \(R_h\) versus \(q^2\), where \(q\) is obtained using Eq. 2.2. The y-intercept of this plot is the inverse of \(R_{h,0}\).

\[
q = \frac{4 \sin \frac{rad}{2}}{l}
\]

Equation 2.2

Prior to DLS analysis, 7 mL of 0.5 g/L cluster solution was filtered using a 0.2 \(\mu\text{m}\) PTFE filter to remove any dust or particulate that could interfere with the measurements. Then cation solutions or an additional solvent were added to the cluster solution to yield three concentrations, with respect to the cations. The total concentration of cation in the cluster solution was as follows: monovalent \((3 \text{ mM}, 4\text{mM}, 5\text{mM})\), divalent \((0.2 \text{ mM}, 0.3 \text{mM}, \text{and} 0.4 \text{ mM})\), and trivalent \((0.0125 \text{ mM}, 0.025 \text{mM}, 0.05 \text{mM})\). Concentrations of additional solvents, methanol and ethanol, did not exceed 5%. Samples were then placed in glass vials cleaned with acetone vapor and data were collected.
2.5 Static Light Scattering

Static light scattering (SLS) is an analytical technique that is used to measure absolute molecular weight and radius of gyration, $R_g$, of a species in solution. Similar to DLS, SLS is highly dependent on Rayleigh scattering. In SLS, the intensity of the scattered light is related to a molecule’s molecular weight and radius of gyration (Rarity et al., 1989; Yin et al., 1989). This is shown in Figure 2.5.

Figure 2.5: Molecular weight dependence on light scattering for a low molecular weight species and a high molecular weight species. A low molecular weight species scatters weakly and at lower intensities than a high molecular weight species (Malvern Instruments Ltd).
The molecular weight-intensity relationship is especially important in the case of aggregates. When aggregates form in solution, the scattering is considered to be coherent, causing the scattered intensity to increase. For example, when dimerization occurs, the coherent scattering causes a doubling in the intensity, which is expected because dimerization doubles the molecular weight of the species.

Some molecules are smaller than the incident beam and can be considered point scatterers. However, in the case of macromolecules and aggregates, point scattering is invalid and phase variations occur as different parts of the macromolecule are analyzed, leading to constructive or destructive interference in the emitted intensity. Therefore, the size of the macromolecule is dependent on the angle of the detector in relation to the incident beam.

In order to counter this effect, multiple angles are used in SLS to determine the root mean square radius (rms radius). The rms radius is a measure of size weighted by the mass distribution around a center of mass. In this way, SLS allows for a decoupling of size from scattering angle.

The same samples that were analyzed for DLS using the Brookhaven Instrument were also used for SLS. The samples contained approximately 6 mL of cluster solution with low concentrations of the selected salt. The concentration of cluster in solution for SLS analysis was 0.5g/L.

The same instrument that was used for DLS of dilute samples, the Brookhaven Instruments commercial laser light scattering system, was used for SLS. During SLS, a sweeping scan was performed over a range of angles from 20-80°, with a step size of two
degrees. A minimum of five intensity measurements were taken at each angle, based on the requirements of the Brookhaven SLS software.

The software automatically generates a plot relating intensity ($I$) to $q$ by a variety of functions to determine the radius of gyration, $R_g$. The type of plot, and thus the relationship between $I$ and $q$, can be altered by adjusting parameters. The plot used for the purposes of this experiment is the partial Zimm plot. A partial Zimm analysis is generated by plotting the inverse of intensity versus $q$-squared.

The overall equation for a Zimm Plot is given in Equation 2.3, where $K_w$ is the material constant, $R_{ex}$ is the excess Rayleigh Ratio, $M$ is the molecular weight, $R_g$ is the radius of gyration, and $B_2$ is the second virial coefficient. In order for a Zimm plot to be applicable, only dilute solutions may be used.

$$
\frac{K_w}{R_{ex}} = \frac{1}{M} \left( 1 + \frac{R_g^2}{3} q^2 \right) (1 + 2B_2)
$$

Equation 2.3

A Zimm plot gives information about the molecular weight and $R_g$ for particles in a light scattering experiment by varying concentration and S-S-D angle. A partial Zimm plot can be used to get either the molecular weight, by varying concentration, or $R_g$, by changing the angle. For the purposes of these experiments, a partial Zimm is constructed using intensity and angular information in a simplification of Equation 2.3, given in Equation 2.4. For the partial Zimm ($R_g$), the y-intercept of the fit is $1/M$, y is the inverse intensity, and x is $q^2$. $R_g$ is the square root of three times the slope over the y-intercept. In Zimm plots, scatterers are analyzed as point scatterers. The Zimm plot is also bound by
the restrictions of the Guinier plot, where \( q \times R_g < 1.3 \), so at higher \( q \), a linear fit cannot be applied to the data.

\[
I^{-1} = \frac{1}{M} + \frac{R_g^2}{3M} q^2 \quad \text{Equation 2.4}
\]

\[
I^{-1} = \frac{1}{M} + \frac{R_g^2}{3M} q^2 \quad \text{Equation 2.4}
\]

2.6 Single Crystal X-ray Diffraction

Single crystal X-ray diffraction is the primary technique for identifying the structure of crystalline material and is facilitated by monochromatic radiation. When the monochromatic X-ray beam irradiates a sample, elastic scattering by the electrons of each atom occurs. This elastic scattering results in the emission of a spherical wave from each atom, which combine to form the overall scattering pattern (Massa, 2004). The emitted X-rays can interfere with one another, either constructively or destructively, depending on the angle of the incident beam, the direction of the diffracted beam, and the distribution of atoms within the crystal lattice.

Where constructive interference occurs, a set of planes within the crystal can be described using Bragg’s law, shown in Equation 2.5. In this equation, \( n \) is the order of reflections, \( \lambda \) is the wavelength, \( d \) is the lattice spacing, and \( \theta \) is the angle of incidence, otherwise known as the Bragg angle (Massa, 2004).

\[
n\lambda = 2d \sin \theta \quad \text{Equation 2.5}
\]

The fixed wavelength of the incident beam is chosen based on the material being studied. For our experiments with small molecules, \( \lambda \) is fixed by using a molybdenum
target and monochromator. The fixed wavelength given is 0.7107Å. In order to produce diffraction events, the crystal is rotated through three-dimensional space relative to this beam. The intensity of the resulting reflections is a function of the number of electrons of each atom within the compound and the distribution of the atoms within the unit cell. The diffracted intensity can be further affected by a number of factors including polarization, multiplicity, Lorenz factor, absorption, and background effects. The equation for the structure factor is given in Equation 2.6, where \( h, k, \) and \( l \) are the Miller indices of scattering planes \( x, y, \) and \( z. \)

\[
F_{(h,k,l)} = \sum_n f(n) \exp[2\pi i (hx_n + ky_n + lz_n)]
\]

Equation 2.6

For the crystal structure determinations described herein, crystal structures were analyzed using a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized MoK\(\alpha\) radiation at a temperature of 100K. The Bruker SHELXL suite of programs was used to solve and refine the crystal structures. CrystalMaker v8.7.2 was used to develop crystal structure diagrams. Table 2.2 outlines the procedure for the determination of crystal structures by X-ray diffraction.
### TABLE 2.2

**PROCEDURE FOR THE DETERMINATION OF CRYSTALLINE STRUCTURES USING X-RAY DIFFRACTION**

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Synthesize crystals</td>
<td>Slow evaporation technique</td>
</tr>
<tr>
<td>2. Select crystal for analysis</td>
<td>Polarizing microscope</td>
</tr>
<tr>
<td>3. Mount crystal</td>
<td>Mounted on a Cryo-loop in Infinium gel</td>
</tr>
<tr>
<td>4. Determine unit cell/ Matrix collection</td>
<td>APEX II</td>
</tr>
<tr>
<td>5. Collect full data set</td>
<td>APEX II</td>
</tr>
<tr>
<td>6. Integrate data</td>
<td>APEXII</td>
</tr>
<tr>
<td>7. Determine space group</td>
<td>XPREP</td>
</tr>
<tr>
<td>8. Apply absorption correction</td>
<td>XPREP/SADABS</td>
</tr>
<tr>
<td>9. Solve structure by Direct Methods</td>
<td>XS</td>
</tr>
<tr>
<td>10. Refine structure using Least Squares</td>
<td>XL</td>
</tr>
<tr>
<td>11. Check for higher symmetry/Confirm structure</td>
<td>PLATON/CIFcheck</td>
</tr>
<tr>
<td>12. Prepare for publication</td>
<td>EnCIFer</td>
</tr>
<tr>
<td>13. Prepare images of structure</td>
<td>CrystalMaker</td>
</tr>
</tbody>
</table>

#### 2.7 Single Crystal Neutron Scattering

Single crystal neutron diffraction is an analytical method very similar to single crystal X-ray diffraction, facilitated by a neutron beam instead of a monochromatic X-ray radiation source (Zinn, 1947). Because X-rays interact with the electron cloud of an atom, single crystal X-ray diffraction is biased toward heavy elements, such as uranium. The locations of light elements such as H and Li, which are important to the structure of uranyl peroxide nanoscale cage clusters, cannot be resolved using X-ray techniques. Neutrons, however, interact with the nuclei of atoms, allowing for determination of the locations of ordered light atoms in the crystal.
The principles behind single crystal neutron diffraction are the same as those for single crystal X-ray diffraction. Bragg’s law applies to neutron diffraction in the same way, and neutrons are recognized as having a wave-particle duality similar to X-ray radiation. Single crystal neutron diffraction is an application of coherent neutron scattering, which takes place over much smaller length scales that are seen with X-rays (Artioli, 2002; Dove, 2002; *Neutron Scattering in Earth Sciences*, 2006).

For the experiments described herein, single crystal neutron diffraction studies were conducted at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory in Tennessee. The instrument used was TOPAZ (beamline 12), which is a wavelength resolved Laue neutron single crystal diffractometer. The instrument is equipped with 13 detectors, which cover a 2θ range of 20-160°. The neutron beam size is fixed to 2.5 mm in diameter. Depending on the crystal symmetry, a single data collection can take anywhere from four to six days, including instrumental setup. The procedure for structural determination by neutron diffraction is outlined in Table 2.3.
**TABLE 2.3**

**PROCEDURE FOR THE DETERMINATION OF CRYSTALLINE STRUCTURES USING NEUTRON DIFFRACTION**

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Additional Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Synthesize crystals</td>
<td>Slow evaporation technique</td>
</tr>
<tr>
<td>2. Select crystal for analysis</td>
<td>Polarizing microscope</td>
</tr>
<tr>
<td>3. Mount crystal</td>
<td>Mounted on Hampton bases with stainless steel pin insert in vacuum grease, encapsulated in heat-sealed Kapton tubing</td>
</tr>
<tr>
<td>4. Realtime Data Observation</td>
<td>ISAW</td>
</tr>
<tr>
<td>5. Planning of Orientations</td>
<td>CrystalPlan</td>
</tr>
<tr>
<td>6. Determine unit cell/ Matrix collection</td>
<td>MantidPlot</td>
</tr>
<tr>
<td>7. Collect full data set</td>
<td></td>
</tr>
<tr>
<td>8. Integrate data</td>
<td>Python/MantidPlot</td>
</tr>
<tr>
<td>9. Determine space group</td>
<td>From Single Crystal/MantidPlot</td>
</tr>
<tr>
<td>10. Apply absorption correction</td>
<td>ANVRED2X</td>
</tr>
<tr>
<td>11. Solve structure by Direct Methods</td>
<td>SHELX</td>
</tr>
<tr>
<td>12. Refine structure using Least Squares</td>
<td>SHELX</td>
</tr>
<tr>
<td>13. Check for higher symmetry/Confirm structure</td>
<td>PLATON/CIFcheck</td>
</tr>
<tr>
<td>14. Prepare for publication</td>
<td>EnCIFer</td>
</tr>
<tr>
<td>15. Prepare images of structure</td>
<td>CrystalMaker</td>
</tr>
</tbody>
</table>

**2.8 Powder X-ray Diffraction**

Powder X-ray diffraction (PXRD) is a diffraction technique that allows for phase analysis of microcrystalline and powder samples. Based on Bragg’s law, characteristic peaks at particular d-spacings or 2θ can be used to identify phases within a sample. In the experiments described in the following chapters, PXRD was used for powder samples. These patterns were compared to known patterns (d-spacing) for identification of phases within the samples.
2.9 Electrospray Ionization Mass Spectrometry

Electrospray Ionization Mass Spectrometry (ESI-MS) is a soft-ionization analytical method, by which large molecules in a solution are ionized in a non-destructive manner. In ESI-MS, the sample is injected using a steel needle that has a specific voltage in regards to the chamber around it. As the sample leaves the needle, the droplets become charged and are driven towards a capillary by the electric field.

The resulting aerosol droplets get smaller and smaller through a process of desolvation, which increases the surface charge beyond the Rayleigh limit. When the surface charge approaches or exceeds the surface tension, the droplet becomes smaller and continues to desolvate until the resulting droplet is small enough. The desolvation process, shown in Figure 2.6, results in formation of a quasi-molecular ion that is suitable for analysis by a mass spectrometer (Fenn et al., 1989).
Figure 2.6 Schematic of the ion desolvation process, by which an initial droplet evaporates and desolvates in a self-generated electric field to form a quasi-molecular ion. This is the ion that is detected by the mass spectrometer in ESI-MS (adapted from Fenn et al., 1989).

Through data reduction, ESI-MS data are normally reduced to discrete mass over charge numbers indicative of the charged states of the molecule. However, with the complexity of nanoclusters comes the increasing complexity of deconvolution. For the experiments described herein, ESI-MS is used to fingerprint a cluster and demonstrate the presence of a particular cluster in solution after TEM analysis.

To prepare samples for fingerprinting, crystals of the cluster were harvested in ultrapure water to create a dilute solution. A spectrum was collected using a time-of-flight (TOF) Bruker microTOF-Q high-resolution quadrupole mass spectrometer in negative ion mode with analysis over a mass to charge ratio range of 500-3000. The resulting spectrum serves as a fingerprint for the cluster.
2.10 Raman Spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique used to probe the bonding within a material. Raman spectroscopy is based on the inelastic scattering of a monochromatic excitation source, usually a laser. The excitation source excites the molecule, which causes vibration of the bonds. Whether or not a bond will be Raman active is generally dictated by symmetry.

From a source, two types of scattering are possible. Rayleigh scattering, the type of scattering that DLS, SLS, and infrared spectroscopy are based on, is a very strong scattering at the same frequency as the incident beam. The second type of scattering is called Raman scattering, where the scattering is very weak and of a frequency that is either increased or decreased by the vibrational frequency of the molecule. If the frequency of the scattering is less than the incident frequency, the scattering is called Stokes scattering. An increase in the scattering frequency in respect to the incident frequency is called Anti-Stokes scattering (Ferraro, Nakamoto, & Brown, 2002).

Bonds within a molecule have characteristic Raman active vibrational modes, so Raman can be used as a technique to fingerprint a molecule in the solid state or in solution (Ferraro et al., 2002). For experiments with the uranyl peroxide pyrophosphate nanocluster, $U_{24}P_{12}$, the uranyl vibrational mode and the pyrophosphate vibrational modes are important for fingerprinting the cluster. The vibrational mode for the bound uranyl mode is around 815 cm$^{-1}$ (Amme et al., 2002) and the bound pyrophosphate mode is around 855 cm$^{-1}$ (Rudolph, 2012).
2.11 X-ray Fluorescence Spectrometry

X-ray fluorescence spectrometry (XRF) is an analytical technique for elemental analysis of a sample. In XRF, an X-ray excitation source is used to eject an inner-shell electron from an atom. The ejected electron is replaced by relaxation of an electron from another shell, resulting in the release of a fluorescent photon. The emitted photon energies (keV) are characteristic for a particular element, allowing for elemental analysis of a sample. In the experiments in the following chapters, XRF was used to determine the elemental composition of precipitates of nanocluster solutions containing uranium, phosphorus, and a variety of other metal ions introduced to the aqueous system.

2.12 Inductively Coupled Plasma Optical Emission Spectroscopy

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is an analytical technique that is used to determine the apparent concentration of analytes in the parts per million (ppm) range. The instrument is composed of an ICP torch and the spectrophotometer. Liquid samples are aspirated and broken into constituent elements or ions, each emitting light a particular wavelength when excited and the intensities at specific wavelengths are measured. Using a standard curve, the intensities can be converted into measured concentrations of particular elements in solution.

For ICP-OES experiments described herein, the Perkin Elmer Optima 8000 ICP-OES in the Center for Environmental Science and Technology was used. Standards were made using known amounts of stock solutions with concentrations of approximately 1000 ppm. The standard concentrations were chosen to ensure the concentration of our
analytes was contained within the standard range for a suitable calibration curve. For the standards and where dilutions were needed, five percent nitric acid was used. The analytes include uranium as well as other constituents in mineral solubility experiments and uranyl pyrophosphate nanoclusters. Yttrium was added to monitor and correct for instrumental drift.
CHAPTER 3:
SOLUBILITY OF U$_{24}$PP$_{12}$

3.1 Introduction

Uranyl peroxide nanoclusters include a diverse family of nanoscale-sized cage clusters that can incorporate a variety of ligands into their structure (Qiu & Burns, 2013). The solution behavior of these clusters is of particular importance for future applications of uranyl clusters in an advanced nuclear fuel cycle, where uranium, peroxide, and water are present (Armstrong et al., 2012; Burns et al., 2012; Wylie et al., 2014). Despite this importance, essentially no information is available on the solubility of these clusters.

In particular, uranyl peroxide pyrophosphate clusters are interesting due to their connection to mineralogy. U$_{24}$Pp$_{12}$ is a cluster formed by uranyl polyhedra linked by phosphate tetrahedra (as pyrophosphate), in a similar way that the autunite group structure is composed of uranyl polyhedra linked by phosphate tetrahedra. Autunite group minerals, however, are only slightly soluble, with a uranium solution concentration of less than 100 ppb at pH 7 (Wellman et al., 2006). Under similar conditions, U$_{24}$Pp$_{12}$ appears to have a much greater solubility in solution.

In this chapter, solubility studies for U$_{24}$Pp$_{12}$ are reported to determine the maximum concentration of this cluster in aqueous solution—providing insight into the aqueous chemistry of uranyl clusters. Solutions of U$_{24}$Pp$_{12}$ were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) to determine
uranium concentration. Using this concentration, the concentration of clusters in solution was determined over time.

3.2 Experimental Procedure

3.2.1 Synthesis of $\text{U}_{24}\text{Pp}_{12}$

$99+\% \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (International Bioanalytical Industries, Inc.), $30\% \text{H}_2\text{O}_2$ (EMD), $40\% (\text{C}_2\text{H}_5)_4\text{N(OH)}$ (Aldrich), $95+\% \text{Na}_4\text{P}_2\text{O}_7$ (Alpha Aesar), $99\% \text{HIO}_3$ (Alfa Aesar), and Millipore-filtered ultrapure water ($18\text{M}\Omega$ resistance) were used in all reactions.

Crystals of $\text{Na}_{30}[\text{(UO}_2)_{24}(\text{O}_2)_{24}(\text{HP}_2\text{O}_7)_6(\text{H}_2\text{P}_2\text{O}_7)_6] \cdot n\text{H}_2\text{O}$ ($\text{U}_{24}\text{Pp}_{12}$) were synthesized by mixing $0.5 \text{ mL}$ of an aqueous solution of $0.5\text{M UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $0.5 \text{ mL}$ $30\% \text{H}_2\text{O}_2$ in a $20 \text{ mL}$ dram vial to produce a cloudy, yellow solution. $0.5 \text{ mL}$ of $40\% (\text{C}_2\text{H}_5)_4\text{N(OH)}$ in water was added to the solution, which was allowed to off-gas for twenty minutes, yielding a transparent, amber-colored solution. $1.5 \text{ mL}$ of aqueous $0.1\text{M Na}_4\text{P}_2\text{O}_7$ was added, producing a light orange solution. $1.5 \text{ mL}$ of $0.5\text{M aqueous HIO}_3$ was added in three aliquots of $0.5 \text{ mL}$. The resulting transparent, yellow solution had a pH of approximately 8, and was allowed to evaporate uncovered at room temperature for two weeks. After approximately two weeks, translucent yellow crystals of $\text{U}_{24}\text{Pp}_{12}$ formed at the bottom of the vial. X-ray diffraction data showed that the crystals were tetragonal ($\text{P}4/\text{mnm}$). Due to formation of an unidentified secondary phase, solutions were not allowed to evaporate to dryness. Single crystal X-ray diffraction was attempted on the secondary phase, but the diffraction was poor. Each vial yielded approximately
20-40 mg of U$_{24}$Pp$_{12}$ crystals, incorporating 0.3 to 0.5% of the uranium from the uranyl nitrate.

Crystals were extracted from their mother solution, vacuum filtered, and rinsed using ultrapure (18 MΩ) water to remove trace amounts of mother solution. The crystals were then collected from the filter membrane, weighed, and placed in ultrapure water to obtain a cluster concentration of approximately 100 g/L if complete dissolution occurred, for a total volume of 4 mL. The solution was capped to limit evaporation during the 30-day analysis.

The solution was agitated approximately once a day to allow exposure of the entire 400 mg of crystals to water. The solution was sampled for thirty days, with multiple samples taken the first day of the experiment and less frequently after the initial three days. At the end of the sampling period, samples were diluted and acidified (2 μL cluster solution in 10 mL of 5% nitric acid) for further analysis. Samples were obtained by removing 20 μL of solution from the liquid layer and analyzed as collected, without filtration or centrifugation.

### 3.2.2 Inductively Coupled Plasma- Optical Emission Spectroscopy

Solutions of U$_{24}$Pp$_{12}$ were analyzed using a Perkin-Elmer 8000 inductively coupled plasma- optical emission spectroscopy (ICP-OES) instrument. Eight standards containing uranium and phosphorus at concentrations from 0.1 to 10 ppm were used to create a calibration curve based on known concentration and intensity. The intensity derived from samples with unknown concentrations at the wavelength corresponding to an element was compared to the calibration curve to determine the concentration of
analyte in the solution. The final concentration was corrected using a dilution factor to account for any dilution during the ICP-OES sample preparation process.

3.2.3 Ultrafiltration

Ultrafiltration was used to determine the percentage of total uranium in solution attributable to cluster material (Wylie et al., 2014). The diluted solutions from the solubility experiments prior to filtration of U$_{24}$P$_{p12}$ had a aqueous cluster concentration of 13 g/L. Higher concentrations were avoided to ensure that precipitation would not occur if the solution reached saturation. The initial solution was placed in a stirred cell with a General Electric water GK series membrane (GEGK). The molecular weight cut off of the membrane is 3500 Da relative to proteins—small enough to retain U$_{24}$P$_{p12}$ (MW ~10,000 Da), but large enough to allow cluster fragments or other uranium species to pass through. Using a gas pressure of approximately 35 psi and a stir speed of 200 rpm, the solution of U$_{24}$P$_{p12}$ was concentrated by allowing half the volume (by mass) to filter through the membrane. The retentate and permeate for each filtration were diluted and acidified for ICP-OES analysis.

3.3 Uranium Concentration in Solution Over Time for U$_{24}$P$_{p12}$

After thirty days of sampling the solution above the crystals of U$_{24}$P$_{p12}$ at ambient temperature, the dissolved cluster solution was removed from the solid phase (Figure 3.1). A solid phase was present for the entire duration of the experiment despite the mixing, which indicates saturation of U$_{24}$P$_{p12}$. The solid phase was verified to be U$_{24}$P$_{p12}$ using single crystal X-ray diffraction. The unit cell of the treated crystal was identical to
that previously collected, with unit cell edge lengths 21.7, 21.7, 31.8 Å and unit cell angles \( \alpha=\beta=\gamma=90^\circ \).

Figure 3.1 Optical light image of crystals remaining after exposure to ultrapure water for thirty days at ambient temperature and pressure in a sealed container at circumneutral pH, showing dissolution resulting in the rounding of the edges of the crystals. The scale bar shows a size of 0.25 mm. Single crystal X-ray diffraction confirmed that the crystals are \( \text{U}_2\text{Pp}_2 \).

The cluster solution was analyzed using ICP-OES. The concentration of \( \text{U}_{24}\text{Pp}_{12} \) in solution at each data point was calculated using the concentration of uranium as determined by ICP-OES and the crystallographic molecular weight for \( \text{U}_{24}\text{Pp}_{12} \). The cluster concentration in g/L was plotted against time (Figure 3.2). The overall solubility curve was plotted using a logarithmic fit for the data points (solid line in Figure 3.2). Additionally, data in the steady state region (\( t > 120 \text{ hrs} \)) was fit linearly. The slope in this region is small (0.0035 g/L/hr), which indicates that this represents a steady state.
with a y-intercept of 69 g/L, the maximum concentration in solution for $\text{U}_{24}\text{P}_{12}$. The uranium concentrations at steady state may vary due to the uptake of crystals during sampling.
Figure 3.2 Concentration of $\text{U}_2\text{P}_{12}$ in solution over the thirty-day dissolution period as calculated from uranium concentrations from ICP-OES. The data were fit to a logarithmic curve (solid line). Data with $t > 120$ hr were fit to a line to represent steady state, where the maximum concentration of $\text{U}_2\text{P}_{12}$ in solution is 69 g/L. Error bars were calculated from the standard deviation of multiple uranium concentration measurements. Uranium concentration measurements in ppm are included in Appendix F.
To verify the maximum concentration of U$_{24}$P$_{12}$ in solution as calculated above, 12 samples were prepared by placing approximately 100 mg of U$_{24}$P$_{12}$ crystals into 1 mL of ultrapure water, a smaller scale of the bulk solubility experiment. Using the same parameters of ambient temperature and pressure as the bulk solubility experiments, the solutions were sealed and agitated daily to allow exposure of the entire 100 mg of U$_{24}$P$_{12}$ crystals to ultrapure water. After thirty days, the saturated solutions were removed from the excess crystals, diluted, and acidified using 5% nitric acid. The samples were analyzed for uranium using ICP-OES. These concentrations and the crystallographic molecular weight of U$_{24}$P$_{12}$ were used to calculate the concentration of U$_{24}$P$_{12}$ in solution (g/L). For the 12 samples, the average concentration of U$_{24}$P$_{12}$ in solution was calculated to be 69 ± 7 g/L, with a range of 56 to 84 g/L and a standard error of 2 g/L. The ICP-OES and calculated concentrations are shown in Table 3.1. Calculations of the cluster concentration using phosphorus concentrations were in agreement with uranium concentration data.
TABLE 3.1

CONCENTRATION OF URANIUM AND U$_2$Pp$_{12}$ IN SOLUTION AFTER 30 DAYS
AT AMBIENT TEMPERATURE AND PRESSURE

<table>
<thead>
<tr>
<th>Solution Number</th>
<th>[U] (M)</th>
<th>[U$<em>2$Pp$</em>{12}$] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>60</td>
</tr>
<tr>
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<td>63</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>0.17</td>
<td>66</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>11</td>
<td>0.18</td>
<td>76</td>
</tr>
<tr>
<td>12</td>
<td>0.20</td>
<td>84</td>
</tr>
</tbody>
</table>

3.4 Ultrafiltration of Concentrated Solutions of U$_2$Pp$_{12}$

For ultrafiltration, the initial aqueous solutions of U$_2$Pp$_{12}$ had a concentration of 13 g/L. This solution was placed in a stirred cell with a GEGK and the solution of U$_2$Pp$_{12}$ inside the cell (retentate) was concentrated by allowing half the volume (by

---

1 Rounding to significant figures was not done until the end of the calculation. Concentrations of uranium in solution used to calculate the concentration of U$_2$Pp$_{12}$ had six significant figures, but were rounded to two significant digits for Table 3.1
mass) to filter through the membrane (permeate). The retentate and permeate for each filtration were diluted and acidified (Retentate: 5.77 μL solution in 10 mL of 5% nitric acid, Permeate: 1 ml of solution in 9 mL of 5% nitric acid) for ICP-OES analysis. The concentration of uranium in each was determined by comparing experimental intensities from ICP-OES to a calibration curve of standards of known concentration. The retention data is shown in Table 3.2. The average retention rate was 99 ± 0.1%, indicating that 98% of the uranium present in the system is present as cluster material, which was rejected by the membrane.

**TABLE 3.2**

RETENTION DATA FOR U$_{24}$Pp$_{12}$ AFTER ULTRAFILTRATION FROM CONCENTRATIONS OBTAINED BY ICP-OES

<table>
<thead>
<tr>
<th>Solution-Replicate</th>
<th>Percent Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>98.9</td>
</tr>
<tr>
<td>1-2</td>
<td>98.9</td>
</tr>
<tr>
<td>2-1</td>
<td>99.3</td>
</tr>
<tr>
<td>2-2</td>
<td>99.0</td>
</tr>
<tr>
<td>3-1</td>
<td>98.9</td>
</tr>
<tr>
<td>3-2</td>
<td>98.7</td>
</tr>
</tbody>
</table>

3.5 Discussion

A thirty-day solubility study of saturated solutions of U$_{24}$Pp$_{12}$ gives a maximum solution concentration for the cluster of approximately 69 g/L. Throughout the entire experiment, a solid phase is observed. At the end of the experiment, this phase was verified as U$_{24}$Pp$_{12}$ by single crystal X-ray diffraction. These solubility studies for individual clusters are important for a greater understanding of the aqueous behavior of
clusters, and demonstrate that in the case of U$_{24}$Pp$_{12}$, the cluster material is much more soluble than its mineralogic counterpart Na-metaautunite.

\[ \text{Na}_2(\text{UO}_2)(\text{PO}_4)_2 \cdot \Box n \text{H}_2\text{O} \leftrightarrow \text{2Na}^+ + 2 \text{UO}_2^{2+} + 2 \text{PO}_4^{3-} + n \text{H}_2\text{O} \quad \text{Reaction 3.1} \]

It is not clear what specifically causes the solubility of U$_{24}$Pp$_{12}$ to be so much greater than autunite group minerals, but it is possible that part of the increased solubility may be due to the types of bonds required to be broken during the dissolution process. In mineral dissolution, as is the case with Na-metaautunite, dissolutions results in the breaking down of the mineral into the solution components of sodium, uranyl, and phosphate ions (Reaction 3.1) until the solution because saturated with these ions.

In dissolution of crystals of U$_{24}$Pp$_{12}$, the network of bonds between clusters and sodium counterions in the crystal break to give the solution species (Reaction 3.2). The exact solution species during U$_{24}$Pp$_{12}$ dissolution is unknown, and there may be multiple cluster species based on the number of sodium bonded to a particular cluster in solution. However, from electrospray ionization mass spectrometric analysis of U$_{24}$Pp$_{12}$ solutions, dissolution does not result in the breaking of cluster bonds to form simple ions.

\[ \text{Na}_{30}[(\text{UO}_2)_{24}(\text{O}_2)_{24}(\text{HP}_2\text{O}_7)_6(\text{H}_2\text{P}_2\text{O}_7)_6] \cdot \Box n \text{H}_2\text{O} \leftrightarrow \]

\[ (30-m) \text{Na}^+ + \text{Na}_m[(\text{UO}_2)_{24}(\text{O}_2)_{24}(\text{HP}_2\text{O}_7)_6(\text{H}_2\text{P}_2\text{O}_7)_6] + n \text{H}_2\text{O} \quad \text{Reaction 3.2} \]

Because dissolution of Na-metaautunite requires more extensive breaking of bonds than dissolution of U$_{24}$Pp$_{12}$, dissolution of the mineral may be less energetically
favorable. This may be part of the reason the solubility is lower for the mineral species. Calorimetric measurements for both Na-metaautunite and $U_{24}P_{12}$ may provide more insight into each material’s respective solubility.
CHAPTER 4:
CHARACTERISTIC STUDIES OF $\text{U}_{24}\text{Pp}_{12}$

4.1 Introduction

$\text{U}_{24}\text{Pp}_{12}$ is one member of a diverse family of nanoscale cage clusters containing uranium. These clusters can be synthesized across much of the pH range and contain 18 to 124 uranyl polyhedra (Qiu & Burns, 2013). Although multiple efforts have been focused on the crystal chemistry of these clusters (Adelani et al., 2013; Burns, 2011; Krivovichev et al., 2007; Ling et al., 2012; Ling et al., 2010; Qiu & Burns, 2013; Sigmon et al., 2009), little is known about how these clusters behave in aqueous solution. In this chapter, studies of $\text{U}_{24}\text{Pp}_{12}$ are conducted to better characterize the behavior of this cluster in aqueous solution. Experimental methods include solution techniques, such as dynamic light scattering, ultra-small angle X-ray scattering, and electrospray ionization-mass spectrometry, in combination with solid-state techniques, such as Raman spectroscopy and powder X-ray diffraction.
4.2 Experimental Procedure

4.2.1 Synthesis of U$_{24}$Pp$_{12}$

Crystals of U$_{24}$Pp$_{12}$ were grown using the synthesis method described in Chapter 3. The cluster crystals were extracted from their mother solution, vacuum filtered, and rinsed using ultrapure (18 MΩ) water to remove trace amounts of mother solution. The crystals were then collected from the filter membrane, weighed, and dissolved in ultrapure water to obtain a cluster concentration of approximately 65 g/L. The total volume of solution prepared varies from experiment to experiment.

4.2.2 Dynamic Light Scattering

Dynamic light scattering (DLS) data were collected using a Malvern Zetasizer Nano Series instrument. The samples, containing the U$_{24}$Pp$_{12}$ solution, were placed in a disposable plastic uvette (Eppendorf) and capped to decrease evaporation. DLS measurements were taken at 25°C in sets of ten scans, with each scan lasting 30 seconds. These measurements were repeated four times to evaluate reproducibility and ensure that the system was not rapidly changing. Prior to analysis, each sample was centrifuged for 3.5 minutes at 14000 relative centrifugal force and filtered using a 0.2 μm wettable PTFE syringe filter. The samples were monitored using DLS multiple times over a two-week period to assess any changes in aggregation behavior.

The radius of hydration, or Stokes-Einstein radius ($R_H$), is the radius of a hard sphere diffusing at the same rate as the particle in solution and is attained using DLS. $R_H$ values for each sample were derived from the intensity distribution curve. Though the intensity distribution, based on Rayleigh scattering, is the most accurate measure of size
at a given angle, the intensity is highly biased towards larger particles in solution. The volume distribution is used for determining the major size population for $U_{24}Pp_{12}$ in its normal aqueous state because of the small size of the cluster. For the purposes of this research, the particles, in this case clusters, in a solution are assumed to be monodisperse if only one population appears in the volume distribution, even if multiple appear in the intensity distribution. For example, a single, large particulate in a sample can indicate a second population in the intensity distribution due to the size bias. The volume distribution is not based on size, so a single particle does not give a second population in the volume distribution.

4.2.3 Small Angle X-ray Scattering

Combination ultra-small angle X-ray scattering and small angle X-ray scattering (USAXS/SAXS) data for the aqueous solutions of $U_{24}Pp_{12}$ were collected at the Advanced Photon Source (APS) at Argonne National Laboratory. Solutions were prepared as described in section 3.1.2. Samples were loaded into doubly contained Kapton capillaries at the University of Notre Dame and shipped to the APS at Argonne National Laboratory. Approximately one week passed from harvesting the crystals and dissolution in water to the analysis at the APS. Details of the experimental setup are outlined in Chapter 2. The data from these experiments were analyzed using the Irena tool suite for Igor Pro (Ilavsky & Jemian, 2009). Data were fitted to a calculated model, yielding information on the size of the nanocluster in solution.
4.3 Light Scattering of U$_{24}$P$_{12}$

Twenty-five samples of U$_{24}$P$_{12}$ were prepared using approximately 65 mg crystals per milliliter of 18 MΩ water and analyzed using dynamic light scattering (DLS). One example of the volume distribution of U$_{24}$P$_{12}$ is shown in Figure 4.1. The other 24 samples were consistent with this distribution pattern, and R$_H$ of the samples was found to be approximately 0.42 ± 0.01 nm for the 25 samples. The single, sharp peak at 0.4 nm indicates that the solutions are monodisperse. The R$_H$ for U$_{24}$P$_{12}$ is smaller than the crystallographic radius of 0.9 nm from the center of oxygen atoms across the structure, but real U$_{24}$P$_{12}$ is not an impenetrable, hard sphere.

Figure 4.1 An example of the volume distribution vs. size data obtained using DLS for an aqueous solution of U$_{24}$P$_{12}$ at a concentration of 65 g/L, where the single peak indicates a monodisperse solution of particles with a R$_H$ of 0.4 nm.
Aqueous solutions of 65 g/L $U_{24}P_{12}$ were monitored using DLS to determine the effect of time on the particle size in solution. Two samples of $U_{24}P_{12}$ at a concentration of 65 mg/mL were analyzed over a two-week period. Figure 4.2 shows the $R_H$ values collected over the two-week period. Over time the change is negligible. The $R_H$ of $U_{24}P_{12}$ is very close to the detection limit of the instrument (0.1 nm). Based on this data, no aggregation is occurring. In fact, samples after three months still have a small $R_H$, indicating the clusters are discrete macromolecules in solution and not aggregates.

Figure 4.2 Hydrodynamic radii over time for two samples of $U_{24}P_{12}$ monitored for a two-week period, where the red circles are average data for the first sample and the blue circles are average data for the second sample. Error bars were obtained from the standard deviation of multiple measurements of the same solution at a particular time point.
4.4 Small Angle X-ray Scattering of U₂₄P₁₂

The crystallographic structure of U₂₄P₁₂ is shown in Figure 4.3. Since U₂₄P₁₂ is oblate, there are three crystallographic diameters measured from the centers of oxygen atoms across the cluster: 17 Å, 18.9 Å, and 19.9 Å (Ling et al., 2010). This gives an average radius of 18.6 Å. The inner diameter is approximately 15 Å, and sodium ions and water molecules in this area are disordered on the time length of X-ray diffraction experiments. A further description of the structure of U₂₄P₁₂, as determined by preliminary single crystal neutron diffraction experiments, will be discussed in Chapter 10.

Figure 4.3 Ball and stick (a) and polyhedral (b) representation of U₂₄P₁₂ from crystallographic data, where red balls indicate oxygen atoms, purple balls/polyhedra indicate phosphorus atoms/polyhedra, and yellow balls/polyhedra indicate uranium atoms/polyhedral.
The SAXS curve for 65 g/L U$_{24}$Pp$_{12}$ in ultrapure water was modeled using the NIST “core-shell” form factor, which is shown in Figure 4.4. The derived equation for the core shell form factor is shown in Equation 4.1.

\[
P(q) = \frac{\text{scale}}{V_s} \left[ \frac{3V_{\text{core}}(\rho_{\text{core}} - \rho_{\text{shell}})j_1(qr_{\text{core}})}{qr_{\text{core}}} - \frac{3V_{\text{shell}}(\rho_{\text{shell}} - \rho_{\text{solvent}})j_1(qr_{\text{shell}})}{qr_{\text{shell}}} \right] + \text{bkg}
\]

Equation 4.1

where \( P(q) \) is the form factor, \( j_1 = (\sin q - \cos q)/q \), \( r_{\text{shell}} = r_{\text{core}} + t \), and \( V_i = \left( \frac{4\pi}{3} \right) r_i^3 \). It is important to note that the core-shell form factor does not include interparticle interactions in the calculation.
Figure 4.5 shows the scattering pattern and model for $U_{24}Pp_{12}$ at a concentration of 65 g/L obtained from the Advanced Photon Source Beamline 15-ID-D ChemMatCars at Argonne National Laboratory. The data were modeled using a core shell form factor with a mean size of 7.12 ± 0.26 Å and a shell density much greater than the density of the core and solvent, because uranium forms the very dense shell and scatters X-rays stronger than the core/solvent of water plus sodium ions. A hard spheres structure factor was used to model distance between two clusters (26 ± 2 Å) and the volume fraction, or percentage of surrounding clusters that interact with a particular cluster (12.2 ± 1.4%). The model is not a perfect fit for the data, with large mismatch at both high- and low-q, but it the best modeling tool currently available for our data.
Figure 4.5 USAXS Scattering pattern for an aqueous solution of 65 g/L U_{24}P_{12} (red circles) with the model (black line) obtained by USAXS where the high-q area data were modeled using a core-shell form factor with a mean size of 7.4 Å and a hard spheres structure factor with a radius of 25 Å and volume fraction of 11%. The low-q data were modeled using a single unified fit of the Porod/Power law slope of approximately 3, indicating a rough surface.

The Porod/Power Law slope (P) from the unified level can be determined by the fit of the scattering pattern at low-q. This slope gives information on the surface morphology of the species in solution, specifically the dimensionality of an object in solution and the smoothness of the surface. The relationship between Porod slope and the shape of objects is shown in Figure 4.6. For U_{24}P_{12} in aqueous solution, the Porod/Power Law slope is 2.71 ± 0.02, which is indicative of a species between a mass...
fractal and a surface fractal—a three dimensional network of cross-linking and branching particles in random orientation with a rough surface (in Figure 4.6).

Figure 4.6 Porod law behaviors for a variety of different shapes, where the solid black lines indicate the shape and the red circles indicate the region that the Porod slope describes. The Porod slope is the $n$ in $Q^n$ (from Hammouda, 2009).
4.4.1 The Guinier Approximation and the Radius of Gyration

The Guinier approximation (Equation 4.2) is used to determine the radius of gyration \( R_g \) from small-angle scattering profiles, where \( I(q) \) is the intensity a particular angular relationship \( q \) and \((\Delta n_e)^2\) to \( I(\theta) \) or the square of the total particle scattering length (Guinier, 1939). \( R_g \) is defined as the mean square distance from the center of gravity to the respective electrons, or the average distance from the core of a particle to each mass constituent. Except for cases of extreme anisometry, the Guinier region can be used to determine \( R_g \) for a species in solution (Glatter & Kratky, 1982).

\[
I_1(q) = (\Delta n_e)^2 e^{-q^2 R_g^2 / 3} \quad \text{Equation 4.2}
\]

Using the Guinier approximation, \( R_g \) is derived from the slope of the linear portion of the scattering plot of \( \ln(I(g)) \) against \( q^2 \), with the condition that \( q * R_g < 1.3 \).

By taking the natural log of Eq. 4.2, the equation of the scattering line is given in Eq. 4.3 (Feigin & Svergun, 1987). This gives a linear relationship where \( R_g \) is the square-root of the slope divided by three.

\[
\ln(I(q)) = \ln(I(0)) - \left( \frac{q^2 R_g^2}{3} \right) \quad \text{Equation 4.3}
\]

Figure 4.7 shows the Guinier approximation for the SAXS pattern of U_{24}P_{12}. From the slope of the linear region, \( R_g \) for U_{24}P_{12} was calculated to be 8.9 Å, which can be related to the crystallographic radius of a spherical shell (Eq. 4.4). Using the inner (7.4 Å) and outer (averaged, 9.3 Å) radii, both determined from the center of the cluster to the
center of inner or outer oxygen atoms, respectively, we find that \( R_g \) from the crystallographic data is slightly smaller (8.4 Å).

\[
R_g^2 = \frac{3 (R_{outer}^6 - R_{inner}^6)}{5 (R_{outer}^3 - R_{inner}^3)}
\]

Equation 4.4

Figure 4.7 Guinier approximation determined from small-angle scattering data of a solution of 65 g/L \( \text{U}_{24}\text{Pp}_{12} \) (shown in black). The linear region, satisfying the requirement of \((q \times R_g > 1.3)\), is indicated by a solid red line, from which the slope is used to find \( R_g \) for particles in solution.

4.4.2 Pair Distance Distribution Function

The pair distance distribution function (PDDF) relates to the morphology of a cluster. The function itself is the overall probability of finding electrons a particular distance, \( r \), from each other for all \( r \) in the system (Figure 4.8). Using SAXS data, the
PDDF can be determined using Equation 3.5, where the \((\Delta \rho)^2 V\) is a scaling factor called the contrast/volume of scatters. The PDDF is given as \(p(r)\), where \(r\) is the distance.

\[
I(Q) = (\Delta \rho)^2 V \int_0^B 4\pi r^2 dp(r) \frac{\sin(Qr)}{Qr} = (\Delta \rho)^2 V \sum_0^B 4\pi r^2 \Delta p(r) \frac{\sin(Qr)}{Qr}
\]

Equation 4.5
Figure 4.8 A Visual representation of the pair distance function, where the black rings represent a particular distance from the center of a particle and the red arrows represent the paired electrons at a particular pair distance, $r$, from each other. The sum of all these pair distances gives the overall pair distance function.
The function $p(r)$ describes the paired set of distances between electrons in a particle, and the maximum dimension is where the PDDF falls to zero (Feigen & Svergun, 1987). The PDDF for $U_{24}P_{12}$ is shown in Figure 4.9, with fit peak distributions (Table 4.1) determined using the OriginPro Multiple Peak Fit tool (OriginLab, Northampton, MA). The major Gaussian curve, centered at approximately 10 Å, is asymmetric (green and blue distributions), with a small shoulder centered around 5 Å (red distribution) and another shoulder centered around 20 Å (cyan distribution). Asymmetry toward large radial distances is characteristic of hollow spheres (Volkmer et al., 2000). This is consistent with $U_{24}P_{12}$, as a core shell, where the low-distance shoulder represents the difference between electrons in the shell corresponding to the thickness (red curve Figure 3.7).
Figure 4.9: The PDDF derived from SAXS data for a solution of 65 g/L $U_{24}P_{12}$ (black squares), fit with four distributions using Gauss fit (Table 4.1). The red distribution corresponds to the shell thickness, the green and blue distributions correspond to the cluster itself, and the cyan distribution corresponds to the cluster-Na ion interaction on the outside of the cluster. The magenta curve is the cumulative fit for the four distributions and correlates to the data with a $R^2$ of 0.99997.
## TABLE 4.1

**NONLINEAR CURVE FIT GAUSS DATA FOR THE PDDF FROM SAXS DATAT OF A 65 G/L SOLUTION OF U$_{24}$Pp$_{12}$**

<table>
<thead>
<tr>
<th>Distribution</th>
<th>Maximum (Å)</th>
<th>Area Under Curve (× 10$^{-13}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.86 ± 0.03</td>
<td>2.48 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>10.4 ± 0.03</td>
<td>10.9 ± 0.2</td>
</tr>
<tr>
<td>3</td>
<td>14.9 ± 0.05</td>
<td>3.29 ± 0.2</td>
</tr>
<tr>
<td>4</td>
<td>20.1 ± 0.04</td>
<td>0.69 ± 0.02</td>
</tr>
</tbody>
</table>

For U$_{24}$Pp$_{12}$, the thickness of the shell of the cluster is measured from the center of the uranyl oxygen inside the cluster (O$_{yl,\text{int}}$) to the center of pyrophosphate oxygen pointing out of the cluster (O$_{py,nb}$), approximately 5 Å. The geometry for this calculation is shown in Figure 3.8, where $x$ is the distance between the centers of O$_{yl,\text{int}}$ and O$_{py,nb}$. The thickness of the shell is given by $x+2.76$, where 2.72 Å is the diameter of an oxygen ion (Shannon, 1976). This thickness is calculated to be 7.2 Å.
Figure 4.10 Geometry to determine the thickness of the shell of $\text{U}_{24}\text{Pp}_{12}$, where a triangle was drawn using the centers of $\text{O}_{\text{yl,int}}$ and $\text{O}_{\text{py,free}}$ as two vertices and the third vertex ($z$) is the intersection of the $x$ and $y$ axis of these two atoms, respectively, with an angle of 54.7° for $\text{O}_{\text{py,free}}-\text{O}_{\text{y,int}}-z$. The tangent of this angle was used to find the leg labeled as $x$ to determine the thickness of the shell of $\text{U}_{24}\text{Pp}_{12}$.

The high-distance shoulder (cyan distribution, Figure 4.9) is attributed to interactions between the uranyl cluster and sodium counter ions on the outside of the cluster. Sodium has a hydrated radius of approximately 3.6 Å (Conway, 1981, Ionic Hydration in Chemistry and Biophysics), while the bare sodium ion has a radius of 1 Å (Shannon, 1976). If the sodium were interacting with the cluster as a hydrated ion, the maximum dimension of the PDDF would be about 28 Å. If the sodium were interacting with the cluster as a bare ion, the maximum dimension of the PDDF would be about 23 Å (From blue distribution, Fig 4.9). From the PDDF, the maximum dimension in solution is
about 24 Å, which suggests the interaction with the counter ion participates in an inner sphere interaction with the cluster.

4.5 Concentration Effect of Solutions of U_{24}P_{12}

To determine the effect of cluster concentration on the scattering behavior of U_{24}P_{12}, USAXS/SAXS data were collected for samples at five different concentrations of U_{24}P_{12} in ultrapure water: 10 g/L, 20 g/L, 30 g/L, 40 g/L, and 50 g/L. The solutions were made from dilutions of a 65 g/L solution verified by ICP-OES. The combined USAXS/SAXS scattering patterns for these concentrations are shown in Figure 4.11. All five concentrations have the characteristic scattering pattern for U_{24}P_{12} in the high-q region (0.1 to 1.2 Å^{-1}). The sample with a concentration of 10 g/L U_{24}P_{12} provides a weaker scattering pattern, so the high-q region is much less defined.
Figure 4.11 Comparison of USAXS/SAXS scattering profiles for aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ at 10 g/L (black squares), 20 g/L (red circles), 30 g/L (green up-triangles), 40 g/L (blue down-triangles), and 50 g/L (magenta left-triangles), which show a characteristic scattering pattern of aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ in the high-q region. Jumps in intensity are due to X-ray induced bubbles forming in the capillary, and are not a result of structural changes.

Weak interparticle interactions of $\text{U}_{24}\text{Pp}_{12}$ clusters are indicated by the well in the mid-q region (0.01 to 0.1 Å$^{-1}$) of the scattering pattern. Here, interactions do not include formation of chemical bonds, but rather are due to the electrostatic forces applied to a particle by a neighboring particle in solution. As the concentration increases, this intensity well deepens, and a structure factor must be added to the model to obtain a better fit to the experimental data. The structure factors used to model these data are hard
spheres, which are dependent on the volume fraction, or the percentage of nearest neighbors participating in interactions, and the correlation distance between mass centers of a particle and its nearest participating neighbor (Beaucage, 1995) and is based on the Percus-Yevich approximation for direct correlation between two particles (Percus & Yevich, 1957). These two parameters were extracted from the data via the model. The concentration effects on these two structure factor parameters are shown in Figure 4.12.
Figure 4.12 Change in structure factor parameters from models of data from USAXS experiments on aqueous solutions of U$_{24}$P$_{12}$, where the top graph is the correlation distance and the bottom graph is volume fraction for each solution at five cluster concentrations. The error bars were determined by uncertainty analyses of each parameter at each concentration by Irena macros.
Because the correlation distance is the distance from the center of one cluster to the center of another cluster, twice the average radius (approximately 20 Å) was subtracted from the model distance to indicate the distance between the clusters edge-to-edge. From this data, the distance between clusters decreases linearly as the concentration increases.

Similarly, the volume fraction involved in the interaction of clusters follows a linear trend. At low concentrations, the volume fraction involved in the interaction is low, corresponding to 9% of nearest neighbors participating in interactions. As the concentration increases, the volume fraction of nearest neighbors increases to 20% at 50 g/L.

The relationship between cluster concentration and distance may have an impact on the solubility of the cluster. It is thought that when the distance between clusters reaches a certain minimum distance, clusters begin to precipitate as a solid. This minimum distance can be calculated mathematically.

The maximum release of uranium from solubility experiments (Chapter 3) was 50,000 ppm (0.21 M U). Using this concentration of uranium and the crystallographic mass of the cluster, the number of individual $\text{U}_{24}\text{Pp}_{12}$ clusters in solution was calculated to be $5.5\times10^{20}$ clusters in one milliliter of water. Assuming maximum packing of spheres ($0.74\times10^{21}$ particles/nm$^3$), the distance between clusters from edge to edge was calculated to be 3.2 nm. This is shorter than extrapolation of structure factor USAXS modeling data to 69 g/L, giving distance between particles of 3.9 nm.

Plotting the pair distance distribution functions (Eq. 4.5) from the USAXS data at each of the five cluster concentrations of $\text{U}_{24}\text{Pp}_{12}$ shows an apparent impact of
concentration evident from SAXS data. The five PDDFs are shown in Figure 4.13. Each of the PDDFs was analyzed using the Multiple Peaks Fitting tool in OriginPro (OriginLab, Northampton, MA) to determine the four distributions that comprise the overall curve, as discussed earlier in this chapter. The distributions and the cumulative fit for each cluster concentration are given in Appendix C. The data from these fits is summarized in Table 4.2.
Figure 4.13 PDDFs derived from SAXS data for aqueous solutions of U$_{24}$Pp$_{12}$ at 10 g/L (black squares), 20 g/L (red circles), 30 g/L (green up-triangles), 40 g/L (blue down-triangles), and 50 g/L (magenta left-triangles). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros.
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Distribution Peak</th>
<th>Peak Maximum (Å)</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 g/L</td>
<td>1</td>
<td>5.93 ± 0.03</td>
<td>460 ± 13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.6 ± 0.1</td>
<td>1340 ± 27</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>17.1 ± 0.1</td>
<td>525 ± 19</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>22.4 ± 0.1</td>
<td>125 ± 4.0</td>
</tr>
<tr>
<td>R² = 0.9994</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 g/L</td>
<td>1</td>
<td>5.28 ± 0.07</td>
<td>954 ± 52</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.42 ± 0.07</td>
<td>1010 ± 190</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13.1 ± 0.2</td>
<td>3730 ± 220</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>23.3 ± 0.1</td>
<td>202 ± 54</td>
</tr>
<tr>
<td>R² = 0.9987</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 g/L</td>
<td>1</td>
<td>5.21 ± 0.04</td>
<td>1025 ± 32</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.7 ± 0.1</td>
<td>3630 ± 83</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.4 ± 0.1</td>
<td>1340 ± 62</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.4 ± 0.1</td>
<td>160 ± 5.6</td>
</tr>
<tr>
<td>R² = 0.9999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 g/L</td>
<td>1</td>
<td>5.13 ± 0.05</td>
<td>1670 ± 63</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.7 ± 0.1</td>
<td>6020 ± 180</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.4 ± 0.1</td>
<td>2310 ± 140</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.4 ± 0.1</td>
<td>257 ± 10</td>
</tr>
<tr>
<td>R² = 0.9999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 g/L</td>
<td>1</td>
<td>4.93 ± 0.03</td>
<td>1800 ± 51</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.4 ± 0.1</td>
<td>7100 ± 240</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.1 ± 0.1</td>
<td>3450 ± 200</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.5 ± 0.1</td>
<td>228 ± 11</td>
</tr>
<tr>
<td>R² = 0.9999</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As the concentration of U$_{24}$P$_{12}$ increases, the total area under the PDDF increases. The percentage of area that is attributed to the cation interaction distribution (Peak 4 in Table 4.2) decreases as the concentration increases. As the concentration increases, the distribution due to the cluster-sodium ion interaction becomes narrower (Figure 4.14), and there is a higher probability that the sodium ion is closer to the cluster.
This is likely due to a stronger ion pairing effect between the cluster and sodium counter ions at higher concentrations. Ion-cluster pairing has been noted for transition metal polyoxometalates, supporting the theory of cation-mediated aggregation for anionic polyoxometalates (Pigga et al., 2010).

Figure 4.14 Peak fit distributions for the $\text{U}_{24}\text{P}_{12}-\text{Na}$ interaction from the PDDF from SAXS data for aqueous solutions of $\text{U}_{24}\text{P}_{12}$ at 10 g/L (black solid line), 20 g/L (red dotted line), 30 g/L (green small dashed line), 40 g/L (blue large dashed line), and 50 g/L (magenta dot-dash line). As the concentration increases, the distribution width decreases and height increases, indicating a higher probability of the sodium ion being found closer to the cluster.
4.6 Stability of clusters and powders of U$_{24}$P$_{12}$

The solubility of U$_{24}$P$_{12}$ in concentrated aqueous solution has been studied using ICP-OES (Chap. 3), and it has been shown to persist at aqueous concentrations greater than 12 g/L for more than six months. The stability of crystals outside their mother solution, and the persistence of cluster material after grinding of crystals, have not previously been studied. Crystals of U$_{24}$P$_{12}$ do not appear to be stable in air, and they become opaque yellow and begin to crumble as exposure occurs (Figure 4.15). Crystals of U$_{24}$P$_{12}$ immediately after harvesting and after 30 days exposure in air were analyzed by thermogravimetric analysis. For the fresh crystals, 62 mol water were lost per mol U$_{24}$P$_{12}$. For the crystals exposed to air, 51 mol of water were lost per mol U$_{24}$P$_{12}$. Therefore, crystals of U$_{24}$P$_{12}$ dehydrate when exposed to air.
Figure 4.15 (a) A crystal of U$_{24}$Pp$_{12}$, 1 mm long, in oil immediately after harvesting. The crystal is a translucent yellow with well defined edges. (b) A crystal of U$_{24}$Pp$_{12}$, 2 mm long, three days after harvesting, dry, and exposed to air. The crystal is opaque and yellow, and has begun to crumble, evidenced by the shards surrounding the large crystal, due to dehydration.

Since the cluster crystal in air on a timescale of days is very fragile, single crystal X-ray diffraction cannot be used to verify that the material still contains U$_{24}$Pp$_{12}$. Powder X-ray diffraction was used to collect diffraction patterns for powders of these crystals, and the resulting diffractogram indicated an X-ray amorphous material, with no distinct diffraction peaks (Figure 4.16).
Figure 4.16 PXRD pattern for ground crystals of $U_{24}Pp_{12}$. Data were collected at ambient conditions over a 2θ range from 5-55°, and the stage with the slide was rotated at a speed of 15 rotations per minute. The resulting powder pattern indicates that the sample is amorphous to X-rays.

4.6.1 Electrospray Ionization Mass Spectrometry of $U_{24}Pp_{12}$ crystals and powders

Because the ground crystals of $U_{24}Pp_{12}$ produced a diffraction pattern that indicated an X-ray amorphous material, crystals of $U_{24}Pp_{12}$ and powder of $U_{24}Pp_{12}$ were dissolved after exposure to air for one hour and 24hrs and compared to that of crystals and powder dissolved immediately after harvesting to determine if the material still contained $U_{24}Pp_{12}$ signatures observable by electrospray ionization mass spectrometry (ESI-MS). The spectra are shown in Figure 4.17.
Figure 4.17 ESI-MS spectra for aqueous solutions of $U_{24}Pp_{12}$ made by dissolving (a) crystals and (b) powder immediately after harvesting or grinding (black), one hour exposure in air before dissolution (blue), and 24 hr of exposure in air before dissolution (red), indicating that cluster material remains after exposure to air.

In general the ESI spectra do not show much change over time. There is very little change between the crystals and the powder, and the spectra are consistent with aqueous solutions of $U_{24}Pp_{12}$. Because the ESI-MS spectra are similar over time, the solutions are qualitatively similar. This indicates that although the crystallinity is diminished over time exposed to or by grinding, clusters of $U_{24}Pp_{12}$ remain intact.

4.6.2 Raman Spectroscopy of $U_{24}Pp_{12}$ crystals and powder

Raman spectroscopy was used to further demonstrate the persistence of $U_{24}Pp_{12}$ upon exposure to air and as a powder. Figure 4.18 shows the Raman spectra for $U_{24}Pp_{12}$
as a single crystal immediately after harvesting and a powder exposed to air. The spectra are identical with peak positions for uranyl and pyrophosphate vibrational modes respectively (Amme et al., 2002; Rudolph, 2012), indicating that the two samples are composed of the same material.

Figure 4.18 Micro-Raman spectra for a single crystal of U_{24}Pp_{12} immediately after harvesting (black) and a powder of U_{24}Pp_{12} after one day of exposure to air (gray). The peaks attributed to the uranyl stretch, pyrophosphate stretch, and TEAH stretches are in the same locations, shown by dashed lines.
4.7 Discussion

$U_{24}Pp_{12}$ is an oblate uranyl nanocluster containing 24 uranyl hexagonal bipyramids arranged in four membered rings through a shared peroxide edge. Twelve bridging pyrophosphate groups further connect six such rings to form the overall structure of $Na_{30}[(UO_2)_{24}(HP_2O_7)_6(H_2P_2O_7)_6] \Box nH_2O$. In aqueous solution, the cluster formula is $[(UO_2)_{24}(HP_2O_7)_6(H_2P_2O_7)_6]^{30-}$ (Johnson et al., 2013).

The large charge on the uranyl portion of the cluster is balanced by sodium ions within and outside the cluster, as well as protonation of some of the pyrophosphate groups (Johnson et al., 2013). Modeling of USAXS/SAXS data are consistent with a core shell cluster with apparent counter-cations outside the cluster as shown via the pair distance distribution data. The interaction of ions with the cluster in solution is an important phenomenon, which will be further probed in Chapters 5, 6, 7 and 8.

The clusters behave as discrete ions in solution under ambient conditions, and over 2 months time, no detectable aggregation occurs. In order for aggregation to occur, the large negative charge between the clusters must be screened to allow clusters close enough to each other. In crystals of $U_{24}Pp_{12}$, the large charge balanced by sodium ions and protonation of the pyrophosphate. In the case of sodium, it is possible that there are either not enough ions in the crystals to effectively screen the large charge of the clusters enough for aggregation to occur or that the monovalent charge does not effectively screen the charge of the cluster. The ability to protonate pyrophosphate oxygen atoms may allow for aggregation at lower solution pH (especially pH < $pK_a = 6.7$), where the pyrophosphate group is more likely to be protonated.
As the concentration of $\text{U}_2\text{Pp}_{12}$ in solution is increased, the distance between particles must decrease and the volume fraction of clusters that are weakly interacting with each other increases. At a minimum distance, calculated to be approximately 4 nm, the solution contains the maximum concentration of $\text{U}_2\text{Pp}_{12}$ at room temperature. Experimental and mathematical model data indicate the maximum concentration in solution is approximately 69 g/L. From mathematical calculations, the distance between the clusters may be closer to 3 nm. It is possible that this distance is representative of twice the double layer of a single cluster of $\text{U}_2\text{Pp}_{12}$. As the double layers of individual clusters, composed of bond sodium and hydrated sodium ions, begin to impinge on one another, the clusters may precipitate out of solution as crystals of $\text{U}_2\text{Pp}_{12}$. This hypothesis can be further supported by computational modeling of the charge double layer around the clusters and comparison of interparticle distances between multiple cluster solutions at maximum concentration.

Clusters of $\text{U}_2\text{Pp}_{12}$ in crystals and powders are not affected by dehydration of the crystal. Although the crystallinity of the samples is compromised when the samples are exposed to air for extended periods of time, clusters within the material remain intact. This suggests that the waters of hydration that are essential to the crystal are not essential to the cluster structure. The stability of the cluster material is important for research of precipitates further explained in Chapters 5, 6, and 7.
CHAPTER 5:
CONCENTRATION AND TIME DEPENDENCE OF AGGREGATION OF U$_{24}$PP$_{12}$
WITH ADDED MONOVALENT CATIONS

5.1 Introduction

One potential application of uranyl nanoclusters is a new method for the separation of uranium from irradiated nuclear fuel (Wylie et al., 2014). Fission products are a byproduct of irradiation of nuclear fuel in a reactor and are formed by the splitting of an unstable nuclei into smaller fragments (Percebois, 2003). The distribution of fission products from fission of $^{235}$U is show in Figure 1.2. Because irradiated fuel is not composed solely of uranium, dissolution of the fuel matrix can also result in dissolution of fission products and other cations into the aqueous uranium phase and potentially interaction between the uranium clusters and these ions.

Although clusters have not been found outside of the laboratory, it is possible that uranyl clusters can form in the environment or in locations where uranium or irradiated fuel is in contact with water. In these cases, environmentally relevant cations, such as sodium and potassium, may also be available for interaction with the uranyl cluster. Uranium contaminated sites, such as the Hanford site in Washington state, also have co-contaminants, which can interact with uranyl clusters. Probing cluster-cation interactions allows for predicting how uranyl clusters will behave under certain solution conditions.
Previous studies of the interactions between uranyl clusters and cations in solution are limited (Wallace, 2013). In this chapter, solutions of aqueous $U_{24}P_{12}$ with added monovalent cations and the resulting precipitates of these solutions are studied using light scattering, X-ray scattering, X-ray diffraction, Raman spectroscopy, and X-ray fluorescence to probe a complex aqueous cluster solution. Because separation of uranium from simulated fuel is based on size (Wylie et al., 2014), understanding how the presence of additional monovalent cations impacts the size of the species in solution is important. The monovalent cations chosen in the experiments described herein are representative of potential environmental and contaminant ions to which uranyl clusters may be exposed in reprocessing of uranium using clusters or in the environment.

5.2 Experimental Procedure

Aggregation of $U_{24}P_{12}$ in water was examined following the addition of monovalent cations in their nitrate forms at multiple cation concentrations (M) with respect to the amount of monovalent cation in the concentrated aqueous nanocluster solution. The behavior was characterized using dynamic light scattering (DLS), synchrotron-based ultra small angle X-ray scattering (USAXS), and pinhole-based small angle X-ray scattering (SAXS). The cations added to aqueous cluster solution in this study are listed in Table 5.1.
TABLE 5.1
MONOVALENT CATIONS ADDED TO AQUEOUS CLUSTER SOLUTIONS OF
U$_{24}$P$_{12}$

<table>
<thead>
<tr>
<th>Cation Studied</th>
<th>Cation Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>0.5 M Li(NO$_3$)</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.5 M Na(NO$_3$)</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.5 M K(NO$_3$)</td>
</tr>
<tr>
<td>Rubidium</td>
<td>0.5 M Rb(NO$_3$)</td>
</tr>
<tr>
<td>Cesium</td>
<td>0.5 M Cs(NO$_3$)</td>
</tr>
<tr>
<td>Silver</td>
<td>0.5 M Ag(NO$_3$)</td>
</tr>
</tbody>
</table>

Crystals of U$_{24}$P$_{12}$ were synthesized as described in Chapter 3. Monodisperse solutions of the cluster were obtained by harvesting and dissolving the crystals in ultrapure water at a concentration of 60 mg U$_{24}$P$_{12}$ crystals per 1 mL of ultrapure water. For each trial, 500 μL of the cluster solution were prepared per aliquot. Three aliquots for each cation were inoculated with 12.5 μL, 25 μL, or 50 μL of 0.5M $M^+(NO_3)$ stock, where $M$ is the monovalent ion added to the system. Samples were then vortexed, centrifuged at 14000 relative centrifugal force for three minutes, and filtered through a 0.2μm polytetrafluoroethylene (PTFE) syringe filter to remove any large particulates or precipitates.

5.2.1 Dynamic Light Scattering

Approximately 250 μL of each of the prepared solutions was transferred into a clean cuvette for data analysis. Qualitative dynamic light scattering (DLS) studies were performed at the University of Notre Dame using a Malvern Zetasizer Nano DLS.
instrument. Due to the fixed 173° source-sample-detector angle, the aggregate size could not be extrapolated to a 0° scattering angle. As such, these analyses are useful for detecting aggregation based on the size of the predominate species in solution. A significant increase of the hydrodynamic radius (R_H) accompanies aggregation.

DLS measurements were taken at 25°C in sets of ten scans, with each scan lasting 30 seconds. These measurements were repeated four times to evaluate reproducibility and to ensure that the system was not rapidly changing. Each sample was analyzed immediately after cation addition and subsequent centrifugation to evaluate the rate of aggregation-inducing behavior of U_{24}P_{12}. The samples were monitored for a two-week period to assess changes in aggregation behavior. As needed, samples were centrifuged again to remove any suspended precipitate.

The R_H values for each sample are reported using the intensity distribution of size. Although the intensity distribution, based on Rayleigh scattering, is the more accurate measure of size at a given angle for this instrument, the intensity (I) is highly biased towards larger particles in solution, following I \propto d^6. As such, the volume distribution was used to identify the dominant particle size population. The volume distribution, unlike intensity, is not size-biased, but it is a less accurate measure of particle size because it requires mathematical manipulation of raw data. The volume distribution is used for the monovalent cations because of the small size of the species in solution, but intensity distribution can be used for aggregated solutions. For the purposes of this research, a sample is considered to have a monodisperse size of species in solution if only one distribution appears in the volume distribution, even if multiple distributions are present in the intensity distribution.
5.2.2 Ultra-Small and Small Angle X-ray Scattering

Ultra small angle X-ray scattering (USAXS) data were collected for aqueous solutions of U$_{24}$P$_{12}$ with added monovalent cations at Beamline 15-ID-D at the Advanced Photon Source (APS) at Argonne National Laboratory. Aqueous solutions of U$_{24}$P$_{12}$ were prepared as described in Section 5.1 and divided into 500 μL aliquots. Two samples of U$_{24}$P$_{12}$ without any added cations were reserved for analysis. The remaining aliquots contained differing initial concentrations of cation nitrates, summarized in Table 5.2. It is important to note that this does not represent the final concentration of cation in the system at the time of analysis or the concentration of metal ions incorporated into the aggregate due to precipitation over time. Each sample was first analyzed using DLS to determine the degree of aggregation and consistency with previous experiments. Samples were then loaded into doubly-contained Kapton capillaries and shipped to the APS at Argonne National Laboratory. Approximately one week passed from the initial addition of cations to the analyses at the APS, but only samples free from precipitates were chosen for USAXS analysis. Details of the experimental setup are outlined in Chapter 2. Scattering data were analyzed and modeled using the Nika and Irena packages for the Igor platform (Ilavsky & Jemian, 2009).

5.2.3 Powder Diffraction of Precipitates

Powder X-ray diffraction (PXRD) patterns were collected for ground crystals of U$_{24}$P$_{12}$ as well as the resulting precipitate from each experiment for aqueous solutions U$_{24}$P$_{12}$ with added monovalent cations. To accumulate enough precipitate, 0.5 M $M\text{NO}_3$
was added until an appreciable amount of precipitate was obtained. The total amount of \(\text{MNO}_3\) added may exceed the maximum amount used during the DLS experiments. Due to the limited amount of material for study, samples were prepared slightly differently than described in Chapter 2. After the precipitate was dried, it was ground without the addition of a solvent using a mortar and pestle and the powder was then pressed between two slides to give a flat, even surface. The top slide was then removed, leaving the pressed powder surface exposed.

X-ray diffraction data were collected using a Bruker D8 Advance DaVinci powder X-ray diffractometer. Data were collected over the 2\(\theta\) range of 5-55\(^\circ\) with a step size of 0.01-0.02\(^\circ\). The counting time per step was ten seconds, giving total run times between 8 and 12 hrs per sample. The sample was rotated at a rate of 15 rotations per second in the diffracting position.

5.2.4 X-ray Fluorescence of Precipitates

Powders used for PXRD were analyzed using X-ray fluorescence (XRF). A few milligrams of powder were loaded onto carbon tape and affixed to a glass slide for analysis using the EDAX Orbis Micro-XRF. The instrument was operated under vacuum to allow for analysis of lighter elements. Analysis of the sodium and lithium precipitates was not possible due to the limits of the technique, and no data were collected for untreated \(\text{U}_{24}\text{P}_{12}\) or precipitates from aqueous cluster solutions with added sodium or lithium. Data were collected for 200 live seconds at 50 KV and 300 \(\mu\)A. A 30 \(\mu\)m spot size was used for analysis.
5.2.5 Raman Spectroscopy of Precipitates

The powders analyzed using PXRD and XRF were also analyzed using solid-state Raman spectroscopy. The powders were loaded onto carbon tape on a glass slide. The precipitates were analyzed at a laser power of 100 mW over the spectral range of 80 to 3200 cm\(^{-1}\). Each measurement was integrated over 15 seconds with three coadditions and 45 seconds counting the background.

For comparison with the spectra of the precipitated materials, powdered U\(_{24}\)Pp\(_{12}\) and a single crystal of U\(_{24}\)Pp\(_{12}\) were analyzed. Particular attention was paid to the modes at approximately 815 cm\(^{-1}\) and 850 cm\(^{-1}\). These vibrations correspond to stretches due to the uranyl group and the pyrophosphate group, respectively (Amme et al., 2002; Rudolph, 2012).

5.3 Dynamic Light Scattering of Solutions of U\(_{24}\)Pp\(_{12}\) with Added Monovalent Cations

5.3.1 Concentration Dependence of Aggregation for U\(_{24}\)Pp\(_{12}\) with Added Monovalent Cations

Samples of 65 g/L U\(_{24}\)Pp\(_{12}\) in ultrapure water (500 μL each) were inoculated with 12.5, 25, and 50 μL of 0.5 M MNO\(_3\), where M is Li, N, K, Rb, Cs, or Ag. Following the addition of salt to the sample and centrifugation, initial DLS measurements were taken. Figure 5.1 shows the volume distribution data for salt samples with 12.5 μL of salt added to the aqueous U\(_{24}\)Pp\(_{12}\). With respect to the volume distribution of untreated U\(_{24}\)Pp\(_{12}\) (shown in black), the volume distribution of the cluster-ion solutions indicated the particle size in solution is only slightly larger than that of aqueous solutions of U\(_{24}\)Pp\(_{12}\).
without added cations. Because these sizes are close to the detection limit of the DLS instrument, these differences are likely not significant. Aqueous solutions of U$_{24}$P$_{12}$ did not aggregate immediately when monovalent cations were added to the cluster solution.

Figure 5.1 Volume distribution for DLS data for aqueous solutions of U$_{24}$P$_{12}$ after being inoculated with 12.5 μL of monovalent cations. Aqueous solution of U$_{24}$P$_{12}$ without added cations (untreated) is shown in black, with added lithium is shown in orange, sodium in blue, potassium in red, rubidium in magenta, cesium in green, and silver is shown in cyan. The distributions of all peaks at approximately the same size, indicating aggregation does not occur immediately after monovalent cations are added to aqueous cluster solutions.
After DLS analysis, the $R_h$ data at each concentration of monovalent cations from the intensity distribution were compared (Figure 5.2). Data for $U_{24}P_{12}$ with 50 μL of RbNO$_3$ was not measured because a gel-like material unsuitable for DLS analysis formed. From the data shown in Figure 5.2, aqueous cluster solutions with added cations (colored) and the untreated aqueous cluster solution (black) are approximately equivalent. For aqueous solutions of $U_{24}P_{12}$ with added monovalent cations, nothing occurs initially to the solutions even when larger amounts of cation are added. At most, dimers or trimers of $U_{24}P_{12}$ form in the initial solutions with added monovalent cations.
Figure 5.2 Initial hydrodynamic radii of species in aqueous solutions of $U_{24}P_{12}$ inoculated with increasing amounts of lithium (orange), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). For comparison, untreated $U_{24}P_{12}$ is shown in black, showing that no aggregation occurs initially as a result of the increasing the amount of monovalent cations added to cluster solution. Error bars are determined by multiple analyses of the same system.

5.3.2 Time Dependence of Aggregation of $U_{24}P_{12}$ with Added Monovalent Cations

The samples of aqueous solutions of $U_{24}P_{12}$ with added monovalent cations were monitored for approximately 15 days to evaluate the change in $R_h$ over time (Figure 5.3). For comparison, the size of untreated $U_{24}P_{12}$ is marked by a hashed black line in the figure. With the exception of the cluster solution with added Cs, the measured $R_h$ value of the cluster-cation solutions did not change significantly.
Figure 5.3 The change in hydrodynamic radii over time for species in solutions of $\text{U}_{24}\text{Pp}_{12}$ inoculated with 12.5 μL of lithium (orange), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). For comparison, the $R_H$ of untreated $\text{U}_{24}\text{Pp}_{12}$ is shown by the dashed black line. Aggregation is only present in aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added cesium, with a large increase in $R_H$ three days after cesium was added. The other solutions with added monovalent ions did not induce aggregation over a two-week period.

The behavior of $\text{U}_{24}\text{Pp}_{12}$ with added Cs (shown in green in Figure 5.3) is distinctly different from the systems with other added monovalent cations. After two days, the size of the species in solution increases greatly from less than 1 nm to approximately 57 nm by day 3. The size of the species in solution then increases slowly, ending with a hydrodynamic radius of approximately 95 nm by 14 days. Hypotheses as to
why aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added Cs show aggregation will be discussed in Section 5.8.

5.4 Ultra-Small Angle X-ray Scattering of Solutions of $\text{U}_{24}\text{Pp}_{12}$ with Added Monovalent Cations

5.4.1 Modeling of USAXS data for $\text{U}_{24}\text{Pp}_{12}$ with Added Monovalent Cations

For USAXS studies, aqueous samples of $\text{U}_{24}\text{Pp}_{12}$ were inoculated with the monovalent cations of interest as nitrate salts. The concentrations of the cations in solution immediately after inoculation are listed in Table 5.2. Samples were analyzed at the Advanced Photon Source at Argonne National Laboratory approximately one week after inoculation. The scattering patterns for aqueous $\text{U}_{24}\text{Pp}_{12}$ with the addition of the six monovalent cations studied here are shown in Figure 5.4. Modeling of the data was conducted using the Modeling II tool in the Irena macros (Ilavsky & Jemian, 2009). For more information about the Irena macros and Modeling II, see Chapter 2.
TABLE 5.2

CONCENTRATIONS OF CATIONS ADDED TO $\text{U}_{24}\text{Pp}_{12}$ FOR USAXS ANALYSIS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source of Cation</th>
<th>Concentration of Cation in Sample upon Spiking (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Li</td>
<td>LiNO$_3$</td>
<td>0.025</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Na</td>
<td>NaNO$_3$</td>
<td>0.035</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+K</td>
<td>KNO$_3$</td>
<td>0.030</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Rb</td>
<td>RbNO$_3$</td>
<td>0.025</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Cs</td>
<td>CsNO$_3$</td>
<td>0.025</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Ag</td>
<td>AgNO$_3$</td>
<td>0.030</td>
</tr>
</tbody>
</table>

For the purpose of modeling of the USAXS scattering patterns (Figure 5.4), three regions based on $q$ are considered. The first region, at high-$q$ ($q>10^{-1}$), is due to the size and shape of $\text{U}_{24}\text{Pp}_{12}$. This region, described by the form factor as a dilute system, is modeled first. The form factor used to model all the scattering herein was a core-shell species, described in detail in Chapter 4. The parameters of the form factor include the average size of the particle, thickness of the shell, density of the core ($\rho_{\text{core}}$), density of the shell ($\rho_{\text{shell}}$), and the density of the solvent ($\rho_{\text{solv}}$). Because the shell in this case is formed by coordinated uranyl ions and uranium scatters X-rays stronger than the other atoms involved, the shell thickness for each sample is modeled as a single atom. The scattering behavior of uranium also causes the density of the shell to be much greater than that of the solvent and core. These parameters are listed in Table 5.3.
Figure 5.4 USAXS scattering patterns for aqueous solutions of $U_{24}Pp_{12}$ inoculated with lithium (black), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). The characteristic scattering pattern for $U_{24}Pp_{12}$ in aqueous solution is present at high-q.

The second region of q considered, at moderate-q ($\sim 10^{-2} < q < 10^{-1}$), is modeled including a structure factor. Structure factors are added to the model to evaluate how the base clusters are arranged in solution. The form factor includes two more parameters—a distance and a volume fraction parameter. The distance is used to model the spacing between centers of two clusters. The volume fraction parameter is used to model the percent of space surrounding a cluster (in volume) that contains another cluster. With the
exception of Na (best modeled as a dilute system), the other data sets were modeled using the hard spheres structure factor and the associated parameters are listed in Table 5.3.

**TABLE 5.3**

USAXS MODELING PARAMETERS FOR U_{24}PP_{12} WITH MONOVALENT CATIONS

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Form Factor:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean Size (Å)</td>
<td>7.40 ± 0.17</td>
<td>7.00 ± 0.14</td>
<td>7.60 ± 0.18</td>
<td>7.20 ± 0.17</td>
<td>8.3 ± 0.0051</td>
<td>7.40 ± 0.15</td>
</tr>
<tr>
<td><strong>Core Shell Density</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core Shell Mobility</td>
<td>$P_{\text{shell}} &gt;&gt; P_{\text{solv}}$</td>
<td>$P_{\text{shell}} &gt;&gt; P_{\text{solv}}$</td>
<td>$P_{\text{shell}} &gt;&gt; P_{\text{solv}}$</td>
<td>$P_{\text{shell}} &gt;&gt; P_{\text{solv}}$</td>
<td>$P_{\text{shell}} &gt;&gt; P_{\text{solv}}$</td>
<td>$P_{\text{shell}} &gt;&gt; P_{\text{solv}}$</td>
</tr>
<tr>
<td>$\rho_{\text{core}} \approx \rho_{\text{solv}}$</td>
<td>$\rho_{\text{core}} \approx \rho_{\text{solv}}$</td>
<td>$\rho_{\text{core}} \approx \rho_{\text{solv}}$</td>
<td>$\rho_{\text{core}} \approx \rho_{\text{solv}}$</td>
<td>$\rho_{\text{core}} \approx \rho_{\text{solv}}$</td>
<td>$\rho_{\text{core}} \approx \rho_{\text{solv}}$</td>
<td></td>
</tr>
<tr>
<td><strong>Structure Factor:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distance Between Cluster Centers (Å)</td>
<td>24.6 ± 2.8</td>
<td>23.8 ± 1.9</td>
<td>30.2 ± 5.5</td>
<td>31.9 ± 5.4</td>
<td>17.5 ± 3.9</td>
<td></td>
</tr>
<tr>
<td><strong>Hard Spheres</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume Fraction (%)</td>
<td>9.7 ± 1.7</td>
<td>7.4 ± 1.5</td>
<td>7.0 ± 1.7</td>
<td>2.2 ± 1.6</td>
<td>2.9 ± 0.95</td>
<td></td>
</tr>
<tr>
<td><strong>Unified Fit</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porod Slope</td>
<td>2.47 ± 0.05</td>
<td>2.56 ± 0.03</td>
<td>1.33 ± 0.04</td>
<td>2.57 ± 0.03</td>
<td>*Unified Fit Used</td>
<td>2.64 ± 0.01</td>
</tr>
</tbody>
</table>
The first two regions of $q$ described above are both modeled in a single population using a size distribution model. However, the final region, at low-$q$ ($q < 10^{-2}$), is modeled as a single, separate population using a unified level model. Unified level is used to model the long-range Guinier and Porod/Power Law regions. The Modeling II tool only allows for modeling of one unified level (i.e. one $R_g$ and/or one power law slope). If two separate unified levels are present such as in the system with Cs, the unified fit tool in the Irena macros must be used.

With the exception of $U_{24}Pp_{12}$ with Cs, the aqueous cluster-monovalent cation solutions were sufficiently modeled with a single unified level using the Modeling II tool. For these samples, the unified level did not include an apparent Guinier sub-region, indicated by a rounding off (constantly changing slope) at lower-$q$ than the single-slope Porod/Power Law region, because the overall aggregate size is outside the instrumental bounds. To address this, the parameters to model the Guinier sub-region were set to $G=0$ and $R_g=1 \times 10^{10}$. Then, the Porod/Power Law region can be modeled using the parameters $B$, contrast and size, and $P$, a constant Power Law slope. The Power Law slopes are listed in Table 5.3. Fully modeled data for each sample can be found in Appendix B.

As stated previously, the scattering pattern for $U_{24}Pp_{12}$ with cesium contains two separate Unified Levels, with two Guinier regions and Porod/Power Law slopes, and so the Unified Fit tool must be used instead of Modeling II. The Unified fit tool allows for modeling of each region with its own $R_g$ and Power Law slope (Figure 5.5). The first unified level, with a Guinier sub-region at $q \approx 10^{-2}$, was found to have a radius of gyration of approximately 10 nm and a Power Law slope of 1. This information suggests
a rigid rod in solution (P=1) with a radius R and length L, as shown in Equation 5.1 for a specific $R_g=100$ Å.

$$R = \sqrt{23762 - \frac{L^2}{6}} \text{ Å}$$

Equation 5.1

Figure 5.5 Unified Fit model for $U_{24}P_{12}$ with Cs including fits for a higher-q unified level modeled best as a rod with an $R_g$ of 107 Å and a lower-q unified level that represents agglomeration of these rods into a mass fractal.
The second unified level occurs at lower q (Guinier sub-region \( \sim 10^{-3} \)). From the model, the \( R_g \) is approximately 2600 Å (260 nm). The Porod slope is approximately 2.5, which suggests a branched system or mass fractal, shown in Figure 4.6 in Chapter 4. It is more likely that this unified level is representative of an agglomeration of the particles modeled in the first unified level, as with transition metal polyoxometalates (Liu, 2003). Data for the unified fit analyses for aqueous solutions of \( U_{24}Pp_{12} \) with cesium are summarized in Table 5.4.

### TABLE 5.4

**UNIFIED FIT MODEL FROM USAXS DATA FOR \( U_{24}Pp_{12} \) WITH ADDED CS**

<table>
<thead>
<tr>
<th>Unified Level</th>
<th>( R_g ) (Å)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>106.5 ± 2.1</td>
<td>1</td>
</tr>
<tr>
<td>Level 2</td>
<td>2640 ± 4.4</td>
<td>2.288 ±0.003</td>
</tr>
</tbody>
</table>

Using the data from Table 5.3, comparisons between model values can give insight into how the addition of monovalent cations affects the size and shape of cluster species in solution. Figure 5.6 compares the structure factor parameters of distance between individual clusters and the percentage of nearest neighbors interacting with a particular cluster and the atomic number of the cation added to the solution. Sodium is omitted because a structure factor was not used to model \( U_{24}Pp_{12} \) with added sodium. There does not appear to be a statistically significant difference between the distances between clusters as the cation added changed, but there is a shift toward fewer neighbor interactions as the atomic number increases.
5.4.2 Guinier Approximation for aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with Added Monovalent Cations

The Guinier approximation (given in Chapter 3) is used to provide basic information about the size of the base particle in solutions containing $\text{U}_{24}\text{Pp}_{12}$. For these experiments, the base particle is $\text{U}_{24}\text{Pp}_{12}$, and should be unchanged unless the addition of cations causes a change in the cluster structure. To verify the presence of $\text{U}_{24}\text{Pp}_{12}$, scattering data were plotted as the square of q vs. the natural logarithm of the intensity.
Figure 5.7 Guinier Approximations for aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added (a) lithium, (b) sodium, (c) potassium, (d) rubidium, (e) cesium, and (f) silver. The data are shown in color for each figure, and the fit of the linear component, meeting the requirement \( qR_g < 1.3 \), is shown in black. The slope of the fit gives the \( R_g \), and for the solutions of \( \text{U}_{24}\text{Pp}_{12} \) with monovalent cations, the respective \( R_g \) is approximately 9 Å. This is consistent with \( \text{U}_{24}\text{Pp}_{12} \) as the base particle.
Based on the Guinier Approximation, the slope of the Guinier plot in the region where \( q*R_g > 1.3 \) is equivalent to the \((3*R_g)^2\). Figure 5.7 shows the scattering data (colored data points) and the fit for the approximation (black line). The fit of the approximation correlates well to the data for \( U_{24}P_{12} \) with all six cations studied as evidenced by the coefficient of determination for the cluster with each cation exceeding 0.999, listed in Table 5.5. Also listed in Table 5.5 are the slope of the approximation and the calculated radius of gyration for the base particle (\( U_{24}P_{12} \)).

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Slope</th>
<th>Coefficient of Determination</th>
<th>Radius of Gyration (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>-27.031</td>
<td>0.99925</td>
<td>9.01</td>
</tr>
<tr>
<td>Sodium</td>
<td>-24.164</td>
<td>0.99964</td>
<td>8.51</td>
</tr>
<tr>
<td>Potassium</td>
<td>-26.877</td>
<td>0.9995</td>
<td>8.98</td>
</tr>
<tr>
<td>Rubidium</td>
<td>-26.332</td>
<td>0.99961</td>
<td>8.89</td>
</tr>
<tr>
<td>Cesium</td>
<td>-26.959</td>
<td>0.99941</td>
<td>8.99</td>
</tr>
<tr>
<td>Silver</td>
<td>-27.056</td>
<td>0.99966</td>
<td>9.01</td>
</tr>
</tbody>
</table>

The expected radius of gyration for \( U_{24}P_{12} \) is approximately 9.01 Å, as shown in Chapter 3. The data for these experiments give values close 9 Å. This, supported by the high-q scattering pattern matching that of \( U_{24}P_{12} \), indicates that the cluster remains intact through the addition of salts. This is further supported by other instrumental techniques, such as electrospray ionization- mass spectrometry.
5.4.3 Pair Distance Functions for \( \text{U}_{24}\text{Pp}_{12} \) with Added Monovalent Cations

To evaluate the extent of interactions between the \( \text{U}_{24}\text{Pp}_{12} \) cluster and the added cations, the pair distance distribution function (PDDF) was modeled for the high-q data for each sample (Figure 5.8). The PDDF plots can be described as major asymmetric Gaussian curves with a side peak at distances greater than 18 Å. The asymmetric Gaussian is consistent with a spherical shell structure, or a core-shell species, and is as expected for \( \text{U}_{24}\text{Pp}_{12} \). There is a slight side peak at low distances (~5 Å), which is attributed to the thickness of the shell. This calculation for shell thickness is explained in detail in Chapter 4.
Figure 5.8 PDDFs derived from SAXS data for aqueous solutions of U$_{24}$P$_{12}$ with added lithium (black), sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros. The inset is a magnification of the cluster-cation region of the PDDF.
As with data for solutions of $\text{U}_{24}\text{Pp}_{12}$ at different concentration (Chap. 4), the PDDF for solutions of $\text{U}_{24}\text{Pp}_{12}$ with the addition of monovalent cations were fit using the Multiple Peaks Fit tool in Origin Pro (OriginLab, Northampton, MA). The fit for these solutions are given in Appendix C. The data from these fits is summarized in Table 5.6.

**TABLE 5.6**

**NONLINEAR CURVE FIT GAUSS DATA FOR THE PDDF FROM SAXS DATA FOR SOLUTIONS OF $\text{U}_{24}\text{Pp}_{12}$ WITH MONOVALENT CATIONS ADDED**

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Distribution Peak</th>
<th>Peak Maximum (Å)</th>
<th>Peak Width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>1</td>
<td>4.89 ± 0.05</td>
<td>3.80 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.7 ± 0.1</td>
<td>5.76 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5 ± 0.1</td>
<td>3.81 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.6 ± 0.1</td>
<td>2.25 ± 0.06</td>
</tr>
<tr>
<td>Sodium</td>
<td>1</td>
<td>4.97 ± 0.06</td>
<td>3.90 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.8 ± 0.05</td>
<td>5.52 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.6 ± 0.1</td>
<td>4.02 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.7 ± 0.03</td>
<td>2.31 ± 0.06</td>
</tr>
<tr>
<td>Potassium</td>
<td>1</td>
<td>4.98 ± 0.06</td>
<td>3.94 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.8 ± 0.05</td>
<td>5.71 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.7 ± 0.09</td>
<td>4.03 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.8 ± 0.03</td>
<td>2.37 ± 0.06</td>
</tr>
<tr>
<td>Rubidium</td>
<td>1</td>
<td>4.48 ± 0.05</td>
<td>3.61 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.7 ± 0.05</td>
<td>6.54 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5 ± 0.07</td>
<td>3.59 ± 0.22</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.4 ± 0.04</td>
<td>2.41 ± 0.11</td>
</tr>
<tr>
<td>Cesium</td>
<td>1</td>
<td>4.93 ± 0.06</td>
<td>3.88 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.9 ± 0.06</td>
<td>6.07 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.7 ± 0.09</td>
<td>4.01 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.7 ± 0.04</td>
<td>2.41 ± 0.07</td>
</tr>
<tr>
<td>Silver</td>
<td>1</td>
<td>4.73 ± 0.06</td>
<td>3.57 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.6 ± 0.07</td>
<td>6.45 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.0 ± 0.06</td>
<td>3.26 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>19.9 ± 0.06</td>
<td>2.03 ± 0.13</td>
</tr>
</tbody>
</table>
The distribution of the fit associated with the fourth peak for the aqueous solutions of $U_{24}Pp_{12}$ with added monovalent cations is based on the cation interaction with the cluster (Figure 5.9). In systems with added lithium, sodium, potassium, and cesium, the maximum dimension of the cluster is approximately 23 Å. Systems with added rubidium and silver have a shorter maximum dimension, which suggests that the cation is held closer to $U_{24}Pp_{12}$.

Figure 5.9 Peak fit distributions for the $U_{24}Pp_{12}$-cation interactions from the PDDF from SAXS data for aqueous solutions of $U_{24}Pp_{12}$ with added lithium (black solid line), sodium (blue dotted line), potassium (red short dashed line), rubidium (magenta medium dashed line), cesium (green dot dash line), and silver (cyan long dash line). Systems with added lithium, sodium, potassium, and cesium have a maximum dimension of approximately 23 Å, while systems with added rubidium and silver are shorter.
To calculate the proximity of the cluster and the associated cation, the following equation was used:

\[
R_{PDF(\text{ion})} = \frac{D_{PDF(\text{max})}}{2} \cdot \frac{D_{\text{crystal}(\text{max})}}{2}
\]

Equation 5.1

where \( R_{PDF(\text{ion})} \) indicates the radius of interaction associated with the ion from the PDDF, \( D_{PDF(\text{max})} \) is the maximum value for the PDF, and \( D_{\text{crystal}(\text{max})} \) is the crystallographic diameter for the cluster. These values, along with the ionic radii and hydrated radii for the cations studied are plotted in Figure 5.10.
Figure 5.10 Comparison of ionic radii (open circles), hydrated radii (open triangles), and of radii calculated from Eq. 5.1, using data from PDDF for USAXS data of solutions of $U_{24}P_{12}$ with added lithium, sodium, potassium, rubidium, silver, and cesium. Atomic number of the added cation is used to allow for comparison of all three radii associated with each added cation.

The radii of the cation portion of the cation-cluster interaction (filled squares) are more closely related to the ionic radii (open circles) for the cations than the hydrated radii (open triangles). This suggests that the interaction between the cation and the clusters is a direct, inner-sphere interaction. $R_{PDF(ion)}$ for Li, Na, K, and Cs are similar, which does not suggest whether or not the cation interaction sites on $U_{24}P_{12}$ are fully occupied by the inoculating cation, shared occupancy with the inoculating cations and the crystal cations (Na), or still fully occupied by crystal ions.
5.5 Powder X-ray Diffraction of Precipitates of $\text{U}_{24}\text{Pp}_{12}$ with Added Monovalent Cations

When the cation is added to the solutions of $\text{U}_{24}\text{Pp}_{12}$, a precipitate sometimes forms. The presence or absence of precipitation is noted in Table 5.7, where NP indicates no precipitation, P/M indicates a precipitate that goes away with mixing, SP indicates a slight precipitate, and P indicates a definite precipitate from the system. In the cases where no precipitate is present after the addition of salts for DLS experiments, excess salt was added until a significant amount of precipitate was present. The precipitates were removed from solution and dried. The same samples were used for powder X-ray diffraction (PXRD), X-ray fluorescence (XRF), and Raman spectroscopy. $\text{U}_{24}\text{Pp}_{12}$ with lithium was the only cluster-monovalent cation precipitate that was not studied because the precipitate formed from solutions of $\text{U}_{24}\text{Pp}_{12}$ with added lithium did not dry completely after three months.

**TABLE 5.7**

**PRESENCE OF PRECIPITATE UPON ADDITION OF MONOVALENT CATIONS TO SOLUTIONS OF $\text{U}_{24}\text{Pp}_{12}$**

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>12.5 μL 0.5 M $M(\text{NO}_3)$ Added</th>
<th>25 μL 0.5 M $M(\text{NO}_3)$ Added</th>
<th>50 μL 0.5 M $M(\text{NO}_3)$ Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>NP</td>
<td>NP</td>
<td>NP</td>
</tr>
<tr>
<td>Sodium</td>
<td>NP</td>
<td>NP</td>
<td>SP</td>
</tr>
<tr>
<td>Potassium</td>
<td>NP</td>
<td>NP</td>
<td>NP</td>
</tr>
<tr>
<td>Rubidium</td>
<td>P/M</td>
<td>P/M</td>
<td>P (gel)</td>
</tr>
<tr>
<td>Cesium</td>
<td>P/M</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Silver</td>
<td>P/M</td>
<td>P/M</td>
<td>P/M</td>
</tr>
</tbody>
</table>
As for the X-ray diffraction powder pattern obtained from untreated, ground crystals of $\text{U}_2\text{Pp}_{12}$ (described in detail in Chapter 3), the diffraction patterns of the precipitates of aqueous solutions of $\text{U}_2\text{Pp}_{12}$ with added monovalent ions indicate the materials is largely amorphous. Figure 5.11 compares the diffraction pattern for untreated, ground crystals of $\text{U}_2\text{Pp}_{12}$ and the precipitates that formed from aqueous solutions of $\text{U}_2\text{Pp}_{12}$ with added monovalent cations. All of the precipitates for the cations studied in this chapter gave diffraction patterns with a broad peak in the 2θ range from about 15 to 35°, as expected for an X-ray amorphous material.
Figure 5.11 PXRD patterns for precipitates formed from aqueous solutions of $U_{24}P_{12}$ with added sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan). For comparison, the PXRD pattern for untreated, ground crystals of $U_{24}P_{12}$ (black) is shown on the bottom of the figure.
Although there are some sharp peaks present in the diffraction patterns for precipitates formed upon addition of sodium, potassium, and silver, the phase could not be identified. The sharp peaks present in the diffraction patterns of the precipitates formed from the addition of monovalent cations are not consistent with the simulated diffraction pattern from the single crystal X-ray diffraction structure of U₂₄Pₚ₁₂ (Figure 5.12). The presence of the amorphous signature and the sharp peaks in the diffraction pattern indicates that the precipitates are not a single phase.

Figure 5.12 The simulated powder diffraction pattern for U₂₄Pₚ₁₂ from the structure of U₂₄Pₚ₁₂ determined using single crystal X-ray diffraction data. The simulated pattern was calculated using Mercury (Macrae et al., 2008).
5.6 X-ray Fluorescence of Precipitates of $\text{U}_{24}\text{Pp}_{12}$ with Added Monovalent Cations

To further study the precipitates that formed when monovalent cations were added to aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$, they were analyzed using X-ray fluorescence (XRF). Qualitative XRF analyses were used to determine the presence of uranium, phosphorus, and the added cation in the precipitates using characteristic fluorescence energies for the respective elements. The presence of these elements in the precipitates from the aqueous cluster solutions with added monovalent cations are summarized in Table 5.8. Samples of untreated $\text{U}_{24}\text{Pp}_{12}$ and precipitates formed from aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added lithium or sodium were not studied because sodium and lithium are outside the detection limits of the instrument.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U</th>
<th>P</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12} + \text{K}$</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12} + \text{Rb}$</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12} + \text{Cs}$</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12} + \text{Ag}$</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

5.7 Raman Spectroscopy of Precipitates of $\text{U}_{24}\text{Pp}_{12}$ with Monovalent Cations

The precipitates formed from solutions of $\text{U}_{24}\text{Pp}_{12}$ with added monovalent cations were analyzed using Raman spectroscopy. Raman spectra for each of the cluster-ion
solutions studied were compared to Raman spectra for untreated $U_{24}Pp_{12}$ as a single crystal and a bulk powder. Comparisons of these spectra are shown in Figure 5.13.

![Figure 5.13 Raman spectra for untreated crystals of $U_{24}Pp_{12}$ (black) and precipitates formed from aqueous solutions of $U_{24}Pp_{12}$ with added sodium (blue), potassium (red), rubidium (magenta), cesium (green), and silver (cyan) with line 1 through the uranyl mode and line 2 through the pyrophosphate mode for the crystal of $U_{24}Pp_{12}$.](image)

As the cation added to solution changes, the peak attributed to the uranyl ($U$-$O_y$) stretch (line 1 in Figure 5.13) for precipitates of solutions with added rubidium, cesium, and silver shift to smaller wavenumbers. This red shift (Table 5.9) is likely due to the interaction of the cation with the uranyl oxygen atom on the cluster causing strain or other structural changes. The shifts in the spectra with sodium and potassium are very small and contained within instrumental error.
TABLE 5.9
COMPARISON OF THE RAMAN REDSHIFT FOR AQUEOUS SOLUTIONS OF
\( \text{U}_{24}\text{PP}_{12} \) WITH ADDED MONOVALENT CATIONS

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Raman Peak Position (cm(^{-1}))</th>
<th>Redshift (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>815</td>
<td>---</td>
</tr>
<tr>
<td>Sodium</td>
<td>814</td>
<td>1</td>
</tr>
<tr>
<td>Potassium</td>
<td>813</td>
<td>2</td>
</tr>
<tr>
<td>Rubidium</td>
<td>810.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Cesium</td>
<td>809</td>
<td>6</td>
</tr>
<tr>
<td>Silver</td>
<td>792.5</td>
<td>22.5</td>
</tr>
</tbody>
</table>

To probe the cause of the observed shifts of the uranyl modes, the magnitude of the redshift was compared to the charge density of the added cation. The shift does not correlate with charge density or ionic radius of the added cation (Figure 5.14). If silver is neglected and the shifts for potassium and sodium are included, a weak trend may occur (Figure 5.14 line). The distinct behavior of silver, the only monovalent transition metal studied, may be due to d-orbital interaction with oxygen atoms on the cluster.
Figure 5.14 Comparison of the red shift in Raman spectroscopy of the uranyl stretch for precipitates formed from solutions of $\text{U}_{24}\text{Pp}_{12}$ with added monovalent cations. A weak trend may occur for Group I cations. Silver does not follow this trend.

5.8 Discussion

The studies of the solutions and the precipitates from systems where $\text{U}_{24}\text{Pp}_{12}$ in aqueous solution is inoculated with monovalent cations provide much insight into the complex cluster-ion system. From DLS data of concentrated solutions of $\text{U}_{24}\text{Pp}_{12}$ with added monovalent cations, aggregates were not observed to form over time, except in the case of cesium. This suggests that the monovalent ions that are added to aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ are ineffective at screening the large negative charge of the cluster. Therefore, the clusters do not get close enough to aggregate without precipitating immediately.
In addition to indication of aggregation over time for the system of $\text{U}_{24}\text{Pp}_{12}$ with added cesium, USAXS data for the system with added cesium was also unique. The modeling of the scattering data suggests that clusters of $\text{U}_{24}\text{Pp}_{12}$ aggregate into rods and then these rods agglomerate into a larger structure, with both present in solution. The explanation as to why the system responds differently when cesium is added is unclear. All the cations added to aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ in this chapter have the same charge. The ion size and charge density for cesium are similar to other monovalent cations studied in this chapter, so those have also been excluded as explanations for the observation of aggregation in aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added cesium.

In all cases, the pair distance distribution functions from USAXS data for solutions of $\text{U}_{24}\text{Pp}_{12}$ with added monovalent cations indicate a direct, inner-sphere interaction between the cluster and the added ion. The changes in the DLS data and the USAXS patterns indicate that there is a cation-cluster interaction, which suggests at least a partial substitution for the initial sodium ions. The solution data is summarized in Table 5.10, where C represents the base cluster (0.6 nm), C’ represents aggregation of the base cluster C into a large species in solutions ($R_H > 10C$), C-N represents assembly of the base cluster C into n-meric units (2 indicates dimer, 3 indicates trimer), and C’’ represents aggregation of the aggregated base cluster (aggregation of C’).
TABLE 5.10  
EXTENT OF AGGREGATION IN CONCENTRATED SOLUTIONS OF U$_{24}$PP$_{12}$  
WITH MONOVALENT CATIONS

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Extent of Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>C-2 or C-3</td>
</tr>
<tr>
<td>Sodium (excess)</td>
<td>C-2</td>
</tr>
<tr>
<td>Potassium</td>
<td>C or C-2</td>
</tr>
<tr>
<td>Rubidium</td>
<td>C-2 or C-3</td>
</tr>
<tr>
<td>Cesium</td>
<td>C’</td>
</tr>
<tr>
<td>Silver</td>
<td>C or C-2</td>
</tr>
</tbody>
</table>

The precipitates of aqueous solutions of U$_{24}$PP$_{12}$ with added monovalent cations also support interactions between the clusters and the added cations. Raman spectra for these precipitates were similar to the spectra for untreated U$_{24}$PP$_{12}$, indicating the presence of cluster material in the precipitate. XRF data show that the added cation is also incorporated in the precipitates from the aqueous cluster solution, and interactions between the added ion and the cluster are indicated by the shifts of stretching peaks in Raman spectra. Further analysis of the precipitates may give more insight into which specific phases are present in the precipitates. The precipitates from concentrated aqueous solutions of U$_{24}$PP$_{12}$ with added monovalent cations are not soluble in water, unlike crystals of U$_{24}$PP$_{12}$, which may suggest that cluster material is not composed entirely of intact clusters.

Altogether, the experiments herein demonstrate the need for further understanding the nature of uranyl peroxyde clusters in complex solutions. The clusters cannot be thought of as isolated species separate from other ions in solution. Understanding cluster-
ion interactions is essential to applications of clusters in solution and environmental impacts of these clusters. Future studies of cation-cluster interactions are necessary to determine the bonding locations of added cations on the cluster and the extent of sodium exchange with the added cation.
CHAPTER 6:
CONCENTRATION AND TIME DEPENDENCE OF AGGREGATION OF \( \text{U}_{24}\text{PP}_{12} \)
WITH DIVALENT CATIONS

6.1 Introduction

As detailed in Chapter 5, interactions between uranyl clusters in aqueous solution and other cations present are important for applications such as separation of uranium from irradiated nuclear fuel and understanding interactions between nanoclusters if released into the environment. The divalent ions chosen for analysis in this Chapter are representative of common environmental cations such as magnesium and calcium. Strontium, barium, and lead cations are representative of fission products and elements that are present in the radioactive decay of uranium. Copper was selected because it is a common contaminant.

As a continuation of the research presented in Chapter 5, solutions of aqueous \( \text{U}_{24}\text{Pp}_{12} \) with added divalent cations and the resulting precipitates of these solutions were studied using light scattering, X-ray scattering, X-ray diffraction, Raman spectroscopy, and X-ray fluorescence to probe the complex aqueous cluster solution in this chapter. These studies, along with Chapters 5 and 7, increase the understanding of cluster-cation interactions in aqueous solution. The systems also test the hypothesis that screening of the large negative cluster charge is necessary for aggregation.

136
6.2 Experimental Procedure

Aggregation of \( \text{U}_{24}\text{Pp}_{12} \) in water was examined following the addition of divalent cations in their nitrate forms at multiple cation concentrations (M) with respect to the amount of divalent cation in the concentrated aqueous nanocluster solution. The behavior was characterized using dynamic light scattering (DLS), synchrotron-based ultra small angle X-ray scattering (USAXS), and pinhole-based small angle X-ray scattering (SAXS). The cations added to aqueous cluster solution in this study are listed in Table 6.1.

<table>
<thead>
<tr>
<th>Cation Studied</th>
<th>Cation Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>0.5 M Mg(NO(_3))(_2)</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.5 M Ca(NO(_3))(_2)</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.5 M Sr(NO(_3))(_2)</td>
</tr>
<tr>
<td>Barium</td>
<td>0.5 M Ba(NO(_3))(_2)</td>
</tr>
<tr>
<td>Lead</td>
<td>0.5 M Pb(NO(_3))(_2)</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>0.5 M Cu(NO(_3))(_2)</td>
</tr>
</tbody>
</table>

Crystals of \( \text{U}_{24}\text{Pp}_{12} \) were synthesized as described in Chapter 3. Monodisperse solutions of the cluster were obtained by harvesting and dissolving the crystals in ultrapure water at a concentration of 60 mg \( \text{U}_{24}\text{Pp}_{12} \) crystals per 1 mL of ultrapure water. For each trial, 500 \( \mu \)L of the cluster solution were prepared. Three aliquots for each cation were inoculated with 12.5 \( \mu \)L, 25 \( \mu \)L, or 50 \( \mu \)L of 0.5M \( M^2+\)(NO\(_3\)) stock, where \( M \) is the divalent ion added to the system. Samples were then vortexed, centrifuged at 14000
relative centrifugal force for three minutes, and filtered through a 0.2μm polytetrafluoroethylene (PTFE) syringe filter to remove any large particulates or precipitates.

6.2.1 Dynamic Light Scattering

Sample preparation for dynamic light scattering (DLS) analysis of aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added divalent cations was identical to that for aqueous cluster solutions with added monovalent cations, and is presented in depth in Chapter 5. The radius of hydration, $R_H$, values for each sample are reported using the intensity distribution of size. The size bias of the intensity distribution is not as important for aqueous cluster solutions with added divalent cations due to the size of the species in solution.

6.2.2 Ultra-Small and Small Angle X-ray Scattering

Sample preparation for ultra small angle X-ray scattering analysis of aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added divalent cations was identical to that for aqueous cluster solutions with added monovalent cations, and is explained in depth in Chapter 5. The initial concentrations of divalent cation nitrate added to the aqueous cluster solution prior to any precipitation are summarized in Table 6.2. Samples were loaded into doubly-contained Kapton capillaries and shipped to the APS at Argonne National Laboratory. Approximately one week passed from the initial addition of cations to the analyses at the APS, but only samples free from precipitates were chosen for USAXS analysis. Details
of the experimental setup are outlined in Chapter 2. Scattering data were analyzed and modeled using the Nika and Irena packages for the Igor platform (Ilavsky & Jemian, 2009).

6.2.3 Powder Diffraction of Precipitates

Powder X-ray diffraction (PXRD) patterns were collected for ground crystals of U$_{24}$Pp$_{12}$ as well as the resulting precipitate from each experiment for aqueous solutions of U$_{24}$Pp$_{12}$ with added divalent cations using the same sample preparation as listed in Chapter 5. X-ray diffraction data were collected using a Bruker D8 Advance DaVinci powder X-ray diffractometer. Data were collected over the 2θ range of 5-55° with a step size of 0.01-0.02°. The counting time per step was ten seconds, giving total run times between 8 and 12 hrs per sample. The sample was rotated at a rate of 15 rotations per second in the diffracting position.

6.2.4 X-ray Fluorescence of Precipitates

Powders used for PXRD were analyzed using X-ray fluorescence (XRF). A few milligrams of powder were loaded onto carbon tape and affixed to a glass slide for analysis using the EDAX Orbis Micro-XRF. The instrument was operated under vacuum to allow for analysis of lighter elements. Analyses of untreated U$_{24}$Pp$_{12}$ were not possible due to the limitations of the technique. Data were collected for 200 live seconds at 50 kV and 300 μA. A 30 μm spot size was used for analysis.
6.2.5 Raman Spectroscopy of Precipitates

The powders analyzed using PXRD and XRF were also analyzed using solid-state Raman spectroscopy. The precipitates were analyzed at a laser power of 100 mW over the spectral range of 80 to 3200 cm\(^{-1}\). Each measurement was integrated over 15 seconds with three coadditions and 45 seconds counting the background.

For comparison with the spectra of the precipitated materials, powdered U\(_{24}\)P\(_{12}\) and a single crystal of U\(_{24}\)P\(_{12}\) were analyzed. Particular attention was paid to the modes at approximately 815 cm\(^{-1}\) and 850 cm\(^{-1}\). These vibrations correspond to stretches due to the uranyl group and the pyrophosphate group, respectively (Amme et al., 2002; Rudolph, 2012).

6.3 Dynamic Light Scattering of Solutions of U\(_{24}\)P\(_{12}\) with Added Divalent Cations

6.3.1 Concentration Dependence of Aggregation for U\(_{24}\)P\(_{12}\) with Added Divalent Cations

Samples of 65 g/L U\(_{24}\)P\(_{12}\) in ultrapure water (500 μL each) were inoculated with 12.5, 25, and 50 μL of 0.5 M \(M(\text{NO}_3)_2\), where \(M\) is Mg, Ca, Sr, Ba, Pb, or Cu. Following the addition of salt to the sample and centrifugation, initial DLS measurements were taken. Figure 6.1 shows the volume distribution data for salt samples with 12.5 μL of salt added to the aqueous U\(_{24}\)P\(_{12}\). With respect to the volume distribution of untreated U\(_{24}\)P\(_{12}\) (shown in black), the volume distribution of the aqueous cluster solutions with added divalent cations indicate the particle size in solution is much larger than that of aqueous solutions of U\(_{24}\)P\(_{12}\) without added cations. This indicates that aggregation
occurs when the divalent cations studied are added to concentrated aqueous solutions of $U_{24}Pp_{12}$.

![Volume distributions for DLS data for aqueous solutions of $U_{24}Pp_{12}$ after being inoculated with 12.5 μL of divalent cations. Aqueous solution of $U_{24}Pp_{12}$ without added cations (untreated) is shown by the solid black line, while the systems with added divalent cations are shown in color. The distributions of all systems with added divalent cations occur at a much larger size than for the untreated system, indicating aggregation occurs immediately after divalent cations are added to aqueous cluster solutions.](image-url)
After DLS analysis, the $R_h$ data for samples at each added concentration of divalent cations from the intensity distribution were compared (Figure 6.2). From this data, it is apparent that aqueous cluster solutions with added cations (colored) have a much larger $R_h$ than the untreated aqueous cluster solution (black). This is consistent with aggregation of $U_{24}P_{12}$ within concentrated aqueous solutions with added divalent cations. All the systems studied were monodisperse except the system with added copper, which had two distinct size distributions for systems with 25 μL and 50 μL of added copper(II) nitrate. The distributions at smaller sizes are likely due to aggregation of $U_{24}P_{12}$ in concentrated aqueous cluster solutions with added copper, while the larger size distribution is due to agglomeration of the smaller size distribution aggregates.
Figure 6.2 Initial hydrodynamic radii of species in aqueous solutions of U$_{24}$P$_{p12}$ inoculated with increasing amounts of added divalent cations. For comparison, untreated U$_{24}$P$_{p12}$ is shown in black, showing that aggregation occurs for all systems studied regardless of the concentration of divalent cations added to cluster solution. The copper system was polydisperse with two distinct size distributions. Error bars were determined by multiple analyses of the same system.

6.3.2 Time Dependence on Aggregation for U$_{24}$P$_{p12}$ with Added Divalent Cations

The samples of aqueous solutions of U$_{24}$P$_{p12}$ with added divalent cations were monitored for approximately 15 days to evaluate the change in $R_h$ over time (Figure 6.3). For comparison, the size of untreated U$_{24}$P$_{p12}$ is marked by a hashed black line in the figure. For the systems studied with added divalent cations except the system with added barium, the $R_h$ values were all much greater than for concentrated aqueous solutions of U$_{24}$P$_{p12}$ without any added cations. This indicates that concentrated aqueous solutions of
U$_{24}$Pp$_{12}$ aggregate upon the addition of divalent cations. For the system with added barium, aggregation occurred initially, but the R$_{H}$ of the species in solution dropped to approximately 0.7 nm eight days after aggregation and remained small for the last six days of the study. This suggests that the aggregate formed in the system with Barium is unstable.

Figure 6.3 The change in hydrodynamic radii over time for species in solutions of U$_{24}$Pp$_{12}$ inoculated with 12.5 μL of magnesium (orange), calcium (blue), strontium (red), barium (magenta), lead (green), and copper (cyan). For comparison, the R$_{H}$ of untreated U$_{24}$Pp$_{12}$ is shown by the dashed black line. Aggregation is for all systems for the duration of the experiment, except for the system with added barium.
6.4 Ultra-Small Angle X-ray Scattering of Solutions of $U_{24}P_{12}$ with Added Divalent Cations

6.4.1 Modeling of USAXS Data for $U_{24}P_{12}$ with Added Divalent Cations

For USAXS studies, aqueous samples of $U_{24}P_{12}$ were inoculated with magnesium, calcium, and strontium as nitrate salts. The concentrations of the cations in solution immediately after inoculation are listed in Table 6.2. Samples were analyzed at the Advanced Photon Source at Argonne National Laboratory approximately one week after inoculation. The scattering patterns for aqueous $U_{24}P_{12}$ with the addition of the three divalent cations studied here are shown in Figure 6.4. Modeling of the data was conducted using the Modeling II tool in the Irena macros (Ilavsky & Jemian, 2009). For more information about the Irena macros and Modeling II, see Chapter 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source of Cation</th>
<th>Concentration of Cation in Sample (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{24}P_{12}+Mg$</td>
<td>Mg(NO$_3$)$_2$</td>
<td>0.005</td>
</tr>
<tr>
<td>$U_{24}P_{12}+Ca$</td>
<td>Ca(NO$_3$)$_2$</td>
<td>0.005</td>
</tr>
<tr>
<td>$U_{24}P_{12}+Sr$</td>
<td>Sr(NO$_3$)$_2$</td>
<td>0.025</td>
</tr>
</tbody>
</table>

For the purpose of modeling of the USAXS scattering patterns (Figure 5.4), three regions based on q are considered. The first region, at high-q ($q>10^{-1}$), is due to the size and shape of $U_{24}P_{12}$. This region, described by the form factor as a dilute system, is modeled first. The form factor used to model all the scattering herein was a core-shell species, described in detail in Chapter 4. The parameters of the form factor include the
average size of the particle, thickness of the shell, density of the core \( (\rho_{\text{core}}) \), density of the shell \( (\rho_{\text{shell}}) \), and the density of the solvent \( (\rho_{\text{solv}}) \). Because the shell in this case is formed by coordinated uranyl ions and uranium scatters X-rays stronger than the other atoms involved, the shell thickness for each sample is modeled as a single atom. The scattering behavior of uranium also causes the density of the shell to be much greater than that of the solvent and core. These parameters are listed in Table 6.3.

![Figure 6.4 USAXS scattering patterns for aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) inoculated with magnesium (black), calcium (blue), and strontium (red). The characteristic scattering pattern for \( \text{U}_{24}\text{Pp}_{12} \) in aqueous solution is present at high-\( q \).]
The second region of q considered, at moderate-q ($10^{-2} < q < 10^{-1}$), is modeled including a structure factor. Structure factors are added to the model to evaluate how the base clusters are arranged in solution. The form factor includes two more parameters—a distance and a volume fraction parameter. The distance is used to model the spacing between centers of two clusters. The volume fraction parameter is used to model the percent of space surrounding a cluster (in volume) that contains another cluster. All the data sets were modeled using the hard spheres structure factor and the associated parameters are listed in Table 6.3.
TABLE 6.3
USAXS MODELING PARAMETERS FOR U$_{24}$PP$_{12}$ WITH DIVALENT CATIONS

<table>
<thead>
<tr>
<th>Form Factor:</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Size</td>
<td>4.98 ± 0.02</td>
<td>7.56 ± 0.46</td>
<td>7.26 ± 0.26</td>
</tr>
<tr>
<td>(Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core Shell</td>
<td>ρ$<em>{shell} &gt;&gt;$ ρ$</em>{core} \approx$ ρ$_{solv}$</td>
<td>ρ$<em>{shell} &gt;&gt;$ ρ$</em>{core} \approx$ ρ$_{solv}$</td>
<td>ρ$<em>{shell} &gt;&gt;$ ρ$</em>{core} \approx$ ρ$_{solv}$</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structure Factor:</td>
<td>Distance Between Cluster Centers (Å)</td>
<td>27.6 ± 5.9</td>
<td>24.8 ± 4.5</td>
</tr>
<tr>
<td>Hard Spheres</td>
<td>Volume Fraction (%)</td>
<td>3.43 ± 0.48</td>
<td>6.2 ± 1.9</td>
</tr>
<tr>
<td>Unified Fit</td>
<td>Porod Slope</td>
<td>1.8 ± 0.1</td>
<td>1.8 ± 0.1</td>
</tr>
</tbody>
</table>

The first two regions of q described above are both modeled in a single population using a size distribution model. However, the final region, at low-q (q < 10$^{-2}$), is modeled as a single, separate population using a unified level model. Unified level is used to model the long-range Guinier and Porod/Power Law regions. The Modeling II tool only allows for modeling of one unified level (i.e. one R$_{g}$ and/or one Power Law slope). If two separate unified levels are present such as in the system with Sr, the unified fit tool in the Irena macros must be used.
With the exception of $\text{U}_{24}\text{Pp}_{12}$ with Sr, the aqueous cluster-divalent cation solutions were sufficiently modeled with a single unified level using the Modeling II tool. For these samples, the unified level did not include an apparent Guinier sub-region, indicated by a rounding off (constantly changing slope) at lower-q than the single-slope Porod/Power Law region, because the overall aggregate size is outside the instrumental bounds. To address this, the parameters to model the Guinier sub-region were set to $G=0$ and $R_g=1 \times 10^{10}$. Then, the Porod/Power Law region can be modeled using the parameters $B$, contrast and size, and $P$, a constant Power Law slope. The Power Law slopes are listed in Table 6.3. Fully modeled data for each sample can be found in Appendix B.

As stated previously, the scattering pattern for $\text{U}_{24}\text{Pp}_{12}$ with strontium contains two separate unified levels, with two distinct Guinier regions and Porod/Power Law slopes, and so the unified fit tool must be used instead of Modeling II. The unified fit tool allows for modeling of each region with its own $R_g$ and Power Law slope (Figure 6.5). The first unified level, with a Guinier sub-region at $q \approx 10^{-3}$, was found to have a radius of gyration of approximately 40 nm and a Power Law slope of 2.5. This information suggests a mass fractal in solution.
Figure 6.5 Unified Fit model for $\text{U}_{24}\text{Pp}_{12}$ with Sr including fits for a higher-q unified level modeled best as a mass fractal with an $R_g$ of 340 Å and a lower-q unified level that represents agglomeration of these fractals into a larger mass fractal.

The second unified level occurs at lower q (Guinier sub-region $<10^{-3}$). From the model, the $R_g$ is approximately 13000 Å (1300 nm). The Porod slope is approximately 1.5, which suggests a branched system or mass fractal, shown in Figure 4.6. It is more likely that this unified level is representative of an agglomeration of the particles modeled in the first unified level, as with transition metal polyoxometalates (Liu, 2003). Data for the unified fit analyses for aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with strontium are summarized in Table 6.4.
TABLE 6.4

UNIFIED FIT MODEL FROM USAXS DATA FOR U$_{24}$PP$_{12}$ WITH ADDED SR

<table>
<thead>
<tr>
<th>Unified Level</th>
<th>$R_g$ (Å)</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>380 ± 11</td>
<td>2.47 ± 0.01</td>
</tr>
<tr>
<td>Level 2</td>
<td>1370 ± 18</td>
<td>1.68 ± 0.01</td>
</tr>
</tbody>
</table>

Using the data from Table 6.3, comparisons between model values can give insight into how the addition of divalent cations affects the size and shape of cluster species in solution. Figure 6.6 compares the structure factor parameters of distance between individual clusters and the percentage of nearest neighbors interacting with a particular cluster with the atomic number of the divalent cation added to the solution. There are no statistically significant differences between the distances amongst clusters or the percentage of neighboring interactions as the cation added is changed.
6.4.2 Guinier Approximation for $\text{U}_{24}\text{Pp}_{12}$ with Added Divalent Cations

The Guinier approximation (given in Chapter 3) is used to provide basic information about the size of the base particle in solutions containing $\text{U}_{24}\text{Pp}_{12}$. For these experiments, the base particle is $\text{U}_{24}\text{Pp}_{12}$, and should be unchanged unless the addition of cations causes a change in the cluster structure. To verify the presence of $\text{U}_{24}\text{Pp}_{12}$, scattering data were plotted as the square of $q$ vs. the natural logarithm of the intensity.
Figure 6.7 Guinier Approximations for aqueous solutions of $U_{24}Pp_{12}$ with added (a) magnesium, (b) calcium, and (c) strontium. The data are shown in color for each figure, and the fit of the linear component, meeting the requirements $q \times R_g < 1.3$, is shown in black. The slope of the fit gives the $R_g$, and for the solutions of $U_{24}Pp_{12}$ with monovalent cations, the respective $R_g$ is approximately 9 Å. This is consistent with $U_{24}Pp_{12}$ as the base particle.
Based on the Guinier Approximation, the slope of the Guinier plot in the region where \( q*R_g > 1.3 \) is equivalent to \((3*R_g)^2\). Figure 6.7 shows the scattering data (colored data points) and the fit for the approximation (black line). The fit of the approximation correlates well to the data for \( U_{24}Pp_{12} \) with all three cations studied as evidenced by the coefficient of determination for the cluster with each cation of approximately 0.999, listed in Table 6.5. Also listed in Table 6.5 are the slope of the approximation and the calculated radius of gyration for the base particle (\( U_{24}Pp_{12} \)).

**TABLE 6.5**

GUINIER APPROXIMATION DATA FOR \( U_{24}Pp_{12} \) WITH DIVALENT CATIONS

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Slope</th>
<th>Coefficient of Determination</th>
<th>Radius of Gyration (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>-27.188</td>
<td>0.99867</td>
<td>9.03</td>
</tr>
<tr>
<td>Calcium</td>
<td>-27.197</td>
<td>0.99873</td>
<td>9.03</td>
</tr>
<tr>
<td>Strontium</td>
<td>-27.133</td>
<td>0.99918</td>
<td>9.02</td>
</tr>
</tbody>
</table>

The expected radius of gyration for \( U_{24}Pp_{12} \) is approximately 9.01 Å, as shown in Chapter 3. The data for these experiments are in agreement with this radius. This, supported by the high-q scattering pattern matching that of \( U_{24}Pp_{12} \), indicates that the cluster remains intact through the addition of salts. This is further supported by other instrumental techniques, such as electrospray ionization- mass spectrometry.
6.4.3 Pair Distance Functions for U$_{24}$P$_{12}$ with Added Divalent Cations

To evaluate the extent of interactions between the U$_{24}$P$_{12}$ cluster and the added cations, the pair distance distribution function (PDDF) was modeled for the high-q data for each sample (Figure 6.8). The PDDF plots can be described as major asymmetric Gaussian curves with a side peak at distances greater than 18 Å. The asymmetric Gaussian is consistent with a spherical shell structure, or a core-shell species, and is as expected for U$_{24}$P$_{12}$. There is a slight side peak at low distances (~5 Å), which is attributed to the thickness of the shell. This calculation for shell thickness is explained in detail in Chapter 4.
Figure 6.8 PDDFs derived from SAXS data for aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added magnesium (orange), calcium (blue), and strontium (red). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros. The inset is a magnification of the cluster-cation region of the PDDF.

As with data for solutions of $\text{U}_{24}\text{Pp}_{12}$ at different concentrations (Chap. 4) and systems with added monovalent cations (Chap. 5), the PDDF for solutions of $\text{U}_{24}\text{Pp}_{12}$ with the addition of divalent cations were fit using the Multiple Peaks Fit tool in Origin Pro (OriginLab, Northampton, MA). The fit for these solutions are given in Appendix C. The data from these fits are summarized in Table 6.6.
TABLE 6.6
NONLINEAR CURVE FIT GAUSS DATA FOR THE PDDF FROM SAXS DATA
FOR SOLUTIONS OF U$_{24}$Pp$_{12}$ WITH DIVALENT CATIONS ADDED

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Distribution Peak</th>
<th>Peak Maximum (Å)</th>
<th>Peak Width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>1</td>
<td>4.89 ± 0.03</td>
<td>4.00 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.8 ± 0.1</td>
<td>5.69 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5 ± 0.1</td>
<td>3.82 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.8 ± 0.1</td>
<td>2.36 ± 0.04</td>
</tr>
<tr>
<td>$R^2 = 0.99998$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>1</td>
<td>4.92 ± 0.03</td>
<td>4.01 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.8 ± 0.1</td>
<td>5.60 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5 ± 0.1</td>
<td>3.84 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.8 ± 0.1</td>
<td>2.35 ± 0.04</td>
</tr>
<tr>
<td>$R^2 = 0.99998$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strontium</td>
<td>1</td>
<td>5.07 ± 0.03</td>
<td>3.99 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.8 ± 0.1</td>
<td>5.37 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5 ± 0.1</td>
<td>3.86 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.8 ± 0.1</td>
<td>2.28 ± 0.04</td>
</tr>
<tr>
<td>$R^2 = 0.99997$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The distribution of the fit associated with the fourth peak for the aqueous solutions of U$_{24}$Pp$_{12}$ with added cations is based on the cation interaction with the cluster (Figure 6.9). For the three systems studied, the distribution due to the cation-cluster interaction occur at the same distance, $R$, and have the same maximum dimension of approximately 23 Å. The major difference is the magnitude of $P(R)$ for each system, which represents the likelihood for electron density to occurring at particular radius. In the system with added strontium, the likelihood of electron density at a radius of 23 Å from the center of the cluster is the largest. This may indicate more cations surrounding the cluster in the system with added strontium than with added magnesium and calcium.
Figure 6.9 Peak fit distributions for the U$_{24}$Pp$_{12}$-cation interactions from the PDDF from SAXS data for aqueous solutions of U$_{24}$Pp$_{12}$ with added magnesium (orange solid line), calcium (blue dotted line), and strontium (red short dashed line). The peaks for all three systems are centered at the same radius, but the P(R) for the system with added strontium is larger, representing a larger probability of finding electron density at that distance from another site of density on the cluster.

6.5 Powder Diffraction of Precipitates of U$_{24}$Pp$_{12}$ with Added Divalent Cations

When divalent cations are added to the solutions of U$_{24}$Pp$_{12}$, a precipitate forms. These precipitates were removed from solution and dried. The same samples were used for powder X-ray diffraction (PXRD), X-ray fluorescence (XRF), and Raman spectroscopy. Precipitates for systems with added magnesium, calcium, strontium, barium, lead, and copper were studied.
As for the X-ray diffraction powder pattern obtained from untreated, ground crystals of $\text{U}_{24}\text{Pp}_{12}$ (described in detail in Chapter 3), the diffraction patterns of the precipitates of aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added monovalent ions indicate the materials are largely X-ray amorphous. Figure 6.10 compares the diffraction pattern for untreated, ground crystals of $\text{U}_{24}\text{Pp}_{12}$ and the precipitates that formed from aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added divalent cations. All of the precipitates for the cations studied in this chapter gave diffraction patterns with a broad peak in the 2θ range from about 15 to 35°, as expected for an X-ray amorphous material.

Unlike the systems with added monovalent cations (Chapter 5, Figure 5.11), no large, well-defined peaks are present in the PXRD patterns. Small, sharp peaks are present in the patterns for the systems of concentrated aqueous $\text{U}_{24}\text{Pp}_{12}$ with added magnesium, strontium, barium, and lead. These peaks are not consistent with the simulated diffraction pattern for crystalline $\text{U}_{24}\text{Pp}_{12}$, shown in Chapter 5 (Figure 5.12). The presence of the amorphous signature and sharp peaks in the PXRD pattern indicates the precipitates are not a single phase.
Figure 6.10 PXRD patterns for precipitates formed from aqueous solutions of $\text{U}_{24}\text{P}_{12}$ with added magnesium (orange), calcium (blue), strontium (red), barium (magenta), lead (green), and copper (cyan). For comparison, the PXRD pattern for untreated, ground crystals of $\text{U}_{24}\text{P}_{12}$ (black) is shown on the bottom of the figure.
6.6 X-ray Fluorescence of Precipitates of U$_{24}$P$_{p12}$ with Added Divalent Cations

To further study the precipitates that formed when divalent cations were added to aqueous solutions of U$_{24}$P$_{p12}$, they were analyzed using X-ray fluorescence (XRF). Qualitative XRF analyses were used to determine the presence of uranium, phosphorus, and the added cation in the precipitates using characteristic fluorescence energies for the respective elements. The presence of these elements in the precipitates from the aqueous cluster solutions with added divalent cations are summarized in Table 6.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>U</th>
<th>P</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$<em>{24}$P$</em>{p12}$ + Mg</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$<em>{24}$P$</em>{p12}$ + Ca</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$<em>{24}$P$</em>{p12}$ + Sr</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$<em>{24}$P$</em>{p12}$ + Ba</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$<em>{24}$P$</em>{p12}$ + Pb</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U$<em>{24}$P$</em>{p12}$ + Cu</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.7 Raman Spectroscopy of Precipitates of U$_{24}$P$_{p12}$ with Added Divalent Cations

The precipitates formed from solutions of U$_{24}$P$_{p12}$ with added divalent cations were analyzed using Raman spectroscopy. Raman spectra for each of the cluster-ion solutions studied were compared to Raman spectra for untreated U$_{24}$P$_{p12}$ as a single crystal and a bulk powder. Comparisons of these spectra are shown in Figure 6.11.
Figure 6.11 Raman spectra for untreated crystals of $U_{24}Pp_{12}$ (black) and precipitates formed from aqueous solutions of $U_{24}Pp_{12}$ with added magnesium (orange), calcium (blue), strontium (red), barium (magenta), and lead (green) with line 1 through the uranyl mode and line 2 through the pyrophosphate mode for the crystal of $U_{24}Pp_{12}$. 
Unlike what is seen with the Raman spectra for precipitates of aqueous solutions of $U_{24}P_{12}$ with added monovalent cations (Chap. 5, Figure 5.13), there are no significant shifts of the peak attributed to the uranyl ion (line 1 in Figure 6.11). Any apparent shifts are within instrumental error. This suggests that there is not as much interaction between the added divalent cations and the uranyl oxygen atoms of the cluster.

6.8 Discussion

The studies of the solutions and the precipitates from systems where $U_{24}P_{12}$ in aqueous solution is inoculated with divalent cations provide much insight into the complex cluster-ion system. From DLS data of concentrated solutions of $U_{24}P_{12}$ with added divalent cations, aggregates were observed to form over time for all the divalent cations studied. An aqueous solution of $U_{24}P_{12}$ with added strontium presented unique USAXS data that showed two distinct unified levels, associated with aggregates of two different sizes. One unified level likely corresponds to an aggregate of $U_{24}P_{12}$, while the other unified level corresponds to agglomeration of the aggregates in the previous level. The aggregate from USAXS data has a size of about 40 nm, which is in agreement with DLS data for the same system.

Evidence of aggregation in systems of $U_{24}P_{12}$ with added divalent cations support the hypothesis from the discussion of Chapter 5 regarding the importance of charge screening on aggregation of the clusters. Divalent cations, with a larger positive charge than monovalent cations, would be more effective in reducing the effective charge of the cluster in the solution species $Na_{n}M_{m}[U_{24}P_{12}]^{30-n-m}$. It would also require less divalent ions to effectively screen the charge.
In all cases, the pair distance distribution functions from USAXS data for solutions of $\text{U}_{24}\text{Pp}_{12}$ with added divalent cations indicate a direct, inner-sphere interaction between the cluster and the added ion. The changes in the DLS data and the USAXS patterns indicate that there is a cation-cluster interaction, which suggests at least a partial substitution for the initial sodium ions. Further experimentation is necessary to determine the extent of substitution with added divalent cations. The solution data is summarized in Table 6.8, where C represents the base cluster (0.6 nm), C’ represents aggregation of the base cluster C into a large species in solutions ($R_{41} > 10C$), C-N represents assembly of the base cluster C into n-meric units (2 indicates dimer, 3 indicates trimer), and C” represents aggregation of the aggregated base cluster (aggregation of C’).

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Extent of Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>C'/C’’</td>
</tr>
<tr>
<td>Calcium</td>
<td>C'/C’’</td>
</tr>
<tr>
<td>Strontium</td>
<td>C'/C’’</td>
</tr>
<tr>
<td>Barium</td>
<td>C’</td>
</tr>
<tr>
<td>Lead</td>
<td>C'/C’’</td>
</tr>
<tr>
<td>Copper</td>
<td>C'/C’’</td>
</tr>
</tbody>
</table>

The precipitates of aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added divalent cations also support the interaction between the cluster and the added cations. Raman spectra for these precipitates were similar to the spectra for untreated $\text{U}_{24}\text{Pp}_{12}$, indicating the presence of cluster material in the precipitate. XRF data show that the added cation is also
incorporated in the precipitates from the aqueous cluster solution. As with the precipitates in monovalent systems, the precipitates were not soluble in water. This suggests that the cluster material represents fragments of clusters, rather than whole clusters.

Together with data on aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added monovalent cations, the data from the experiments in this Chapter provide additional insight into cluster-cation interactions. From this research, it is clear that clusters of \( \text{U}_{24}\text{Pp}_{12} \) interact with other cations in solution. In cluster-based uranium reprocessing procedures, this may require an additional step after the filtration of the uranium, such as addition of a chelating agent or heating, to remove added cations present in the uranium solution phase.
CHAPTER 7:
CONCENTRATION AND TIME DEPENDENCE OF AGGREGATION OF U$_{24}$Pp$_{12}$
WITH TRIVALENT CATIONS

7.1 Introduction

As described in Chapters 5 and 6, interactions between uranyl clusters in aqueous solution and other cations present in aqueous uranium phase are important for applications such as separation of uranium from irradiated nuclear fuel and determining environmental cluster interactions. As a continuation of the research presented in Chapters 5 and 6, solutions of aqueous U$_{24}$Pp$_{12}$ with added trivalent cations and the resulting precipitates from these solutions are studied using light scattering, X-ray scattering, X-ray diffraction, Raman spectroscopy, and X-ray fluorescence to probe a complex aqueous cluster solution in this chapter. The trivalent cations chosen for study may represent potential fission products or contaminants that may be present in situations where uranyl clusters are also present. These studies, along with Chapters 5 and 6, increase the understanding of cluster-cation interactions in aqueous solution.

7.2 Experimental Procedure

Aggregation of U$_{24}$Pp$_{12}$ in water was examined following the addition of trivalent cations in their nitrate forms at multiple cation concentrations (M) with respect to the
amount of trivalent cation in the concentrated aqueous nanocluster solution. The behavior was characterized using dynamic light scattering (DLS), synchrotron-based ultra small angle X-ray scattering (USAXS), and pinhole-based small angle X-ray scattering (pin-SAXS). The cations added to aqueous cluster solutions in this study are listed in Table 7.1.

**TABLE 7.1**

**TRIVALENT CATIONS ADDED TO AQUEOUS CLUSTER SOLUTIONS OF U₂₄Pp₁₂**

<table>
<thead>
<tr>
<th>Cation Studied</th>
<th>Cation Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>0.5 M La(NO₃)₃</td>
</tr>
<tr>
<td>Cerium</td>
<td>0.5 M Ce(NO₃)₃</td>
</tr>
<tr>
<td>Neodymium</td>
<td>0.5 M Nd(NO₃)₃</td>
</tr>
<tr>
<td>Europium</td>
<td>0.5 M Eu(NO₃)₃</td>
</tr>
<tr>
<td>Holmium</td>
<td>0.5 M Ho(NO₃)₃</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.5 M Al(NO₃)₃</td>
</tr>
</tbody>
</table>

Crystals of U₂₄Pp₁₂ were synthesized as described in Chapter 3. Monodisperse solutions of the cluster were obtained by harvesting and dissolving the crystals in ultrapure water at a concentration of 60 mg U₂₄Pp₁₂ crystals per 1 mL of ultrapure water. For each trial, 500 μL of the cluster solution were prepared. Three aliquots for each cation were inoculated with 12.5 μL, 25 μL, or 50 μL of 0.5M M₃⁺(NO₃) stock, where M is the trivalent ion added to the system. Samples were then vortexed, centrifuged at 14000 relative centrifugal force for three minutes, and filtered through a 0.2μm
polytetrafluoroethylene (PTFE) syringe filter to remove any large particulates or precipitates.

7.2.1 Dynamic Light Scattering

Sample preparation for dynamic light scattering (DLS) analysis of aqueous solutions of $U_{24}P_{12}$ with added trivalent cations was identical to that for aqueous cluster solutions with added monovalent and divalent cations, and is explained in depth in Chapters 5 and 6. The radius of hydration, $R_H$, values for each sample are reported using the intensity distribution of size. The size bias of the intensity distribution is not as important for aqueous cluster solutions with added trivalent cations due to the size of the species in solution.

7.2.2 Ultra-Small and Small Angle X-ray Scattering

Sample preparation for ultra small angle X-ray scattering (USAXS) analysis of aqueous solutions of $U_{24}P_{12}$ with added trivalent cations was identical to that for aqueous cluster solutions with added monovalent and divalent cations, and is explained in depth in Chapter 5. The initial concentrations of trivalent cation nitrate added to the aqueous cluster solution prior to any precipitation are summarized in Table 7.2. Samples were loaded into doubly-contained Kapton capillaries and shipped to the APS at Argonne National Laboratory. Approximately one week passed from the initial addition of cations to the analyses at the APS, but only samples free from precipitates were chosen for USAXS analysis. Details of the experimental setup are outlined in Chapter 2. Scattering data were analyzed and modeled using the Nika and Irena packages for the Igor platform (Ilavsky & Jemian, 2009).
7.2.3 Powder Diffraction of Precipitates

Powder X-ray diffraction (PXRD) patterns were collected for ground crystals of $U_{24}Pp_{12}$ as well as the resulting precipitate from each experiment for aqueous solutions of $U_{24}Pp_{12}$ with added trivalent cations using the same sample preparation as listed in Chapter 5. X-ray diffraction data were collected using a Bruker D8 Advance Davinci powder X-ray diffractometer. Data were collected over the $2\theta$ range of 5-55° with a step size of 0.01-0.02°. The counting time per step was ten seconds, giving total run times between 8 and 12 hrs per sample. The sample was rotated at a rate of 15 rotations per second in the diffracting position.

7.2.4 X-ray Fluorescence of Precipitates

Powders used for PXRD were analyzed using X-ray fluorescence (XRF). A few milligrams of powder were loaded onto carbon tape and affixed to a glass slide for analysis using the EDAX Orbis Micro-XRF. The instrument was operated under vacuum to allow for analysis of lighter elements. Analysis of the sodium and lithium precipitates was not possible due to the limits of the technique, and no data were collected for untreated $U_{24}Pp_{12}$. Data were collected for 200 live seconds at 50 kV and 300 μA. A 30 μm spot size was used for analysis.

7.2.5 Raman Spectroscopy of Precipitates

The powders analyzed using PXRD and XRF were also analyzed using solid-state Raman spectroscopy. The precipitates were analyzed at a laser power of 100 mW over the spectral range of 80 to 3200 cm$^{-1}$. Each measurement was integrated over 15 seconds with three coadditions and 45 seconds counting the background.
For comparison with the spectra of the precipitated materials, powdered U$_{24}$P$_{12}$ and a single crystal of U$_{24}$P$_{12}$ were analyzed. Particular attention was paid to the modes at approximately 815 cm$^{-1}$ and 850 cm$^{-1}$. These vibrations correspond to stretches due to the uranyl group and the pyrophosphate group, respectively (Amme et al., 2002; Rudolph, 2012).

7.3 Dynamic Light Scattering of Solutions of U$_{24}$P$_{12}$ with Added Trivalent Cations

7.3.1 Concentration Dependence of Aggregation for U$_{24}$P$_{12}$ with Added Trivalent Cations

Samples of 65 g/L U$_{24}$P$_{12}$ in ultrapure water (500 μL each) were inoculated with 12.5, 25, and 50 μL of 0.5 M $M$(NO$_3$)$_2$, where $M$ is La, Ce, Nd, Eu, Ho, or Al. Following the addition of salt to the sample and centrifugation, initial DLS measurements were taken. Figure 7.1 shows the volume distribution data for salt samples with 12.5 μL of salt added to the aqueous U$_{24}$P$_{12}$. With respect to the volume distribution of untreated U$_{24}$P$_{12}$ (shown in black), the volume distribution of the aqueous cluster solutions with added trivalent cations indicated the particle size in solution is much larger than that of aqueous solutions of U$_{24}$P$_{12}$ without added cations. This indicates that aggregation occurs when the trivalent cations studied are added to concentrated aqueous solutions of U$_{24}$P$_{12}$.
Figure 7.1 Volume distributions for DLS data for aqueous solutions of U$_{24}$P$_{12}$ after being inoculated with 12.5 μL of trivalent cations. Aqueous solution of U$_{24}$P$_{12}$ without added cations (untreated) is shown by the solid black line, and systems with added trivalent cations are shown in color. The distributions of all systems with added trivalent cations occur at a much larger size than for the untreated system, indicating aggregation occurs immediately after trivalent cations are added to aqueous cluster solutions.
After DLS analysis, the $R_h$ data at each added concentration of trivalent cations from the intensity distribution were compared (Figure 7.2). From this data, aqueous cluster solutions with added cations (colored) have a much larger $R_h$ than the untreated aqueous cluster solution (black). This is consistent with aggregation of $U_{24}Pp_{12}$ within concentrated aqueous solutions with added trivalent cations. All the systems studied were monodisperse except the system with added cerium, which had two distinct size distributions for systems with 25 μL of added cerium nitrate. The size of the species in solution in the system with 50 μL of added holmium does not suggest aggregation, or the aggregate precipitated out before the DLS measurement.
7.2 Initial hydrodynamic radii of species in aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ inoculated with increasing amounts of added trivalent. For comparison, untreated $\text{U}_{24}\text{Pp}_{12}$ is shown in black, showing that aggregation occurs for all systems studied regardless of the concentration of trivalent cations added to cluster solution.

The copper system was polydisperse with two distinct size distributions. Error bars were determined by multiple analyses of the same system.

Figure 7.2 Initial hydrodynamic radii of species in aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ inoculated with increasing amounts of added trivalent. For comparison, untreated $\text{U}_{24}\text{Pp}_{12}$ is shown in black, showing that aggregation occurs for all systems studied regardless of the concentration of trivalent cations added to cluster solution.

The copper system was polydisperse with two distinct size distributions. Error bars were determined by multiple analyses of the same system.

7.3.2 Time Dependence on Aggregation for $\text{U}_{24}\text{Pp}_{12}$ with Added Trivalent Cations

The samples of aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added trivalent cations were monitored for approximately 15 days to evaluate the change in $R_h$ over time (Figure 7.3).

For comparison, the size of untreated $\text{U}_{24}\text{Pp}_{12}$ is marked by a hashed black line in the figure. For the systems studied with added trivalent cations the $R_h$ values were all much
greater than for concentrated aqueous solutions of U$_{24}$P$_{12}$ without any added cations initially. This indicates that concentrated aqueous solutions of U$_{24}$P$_{12}$ aggregate upon the addition of trivalent cations. However, some of the systems indicated a small species in solution over time, which suggests that the aggregates in systems with added cerium and neodymium may be unstable. The system with added cerium also is polydisperse for the majority of the experiment.

![Hydrodynamic Radii Over Time](image)

**Figure 7.3** The change in hydrodynamic radii over time for species in solutions of U24Pp12 inoculated with 12.5 μL of added trivalent cations. For comparison, the R$_H$ of untreated U24Pp12 is shown by the dashed black line. Aggregation is present for all systems for the duration of the experiment, except for the system with added cerium and neodymium.
7.4 Ultra-Small Angle X-ray Scattering of Solutions of $\text{U}_{24}\text{Pp}_{12}$ with Added Trivalent Cations

7.4.1 Modeling of USAXS Data for $\text{U}_{24}\text{Pp}_{12}$ with Added Trivalent Cations

For USAXS studies, aqueous samples of $\text{U}_{24}\text{Pp}_{12}$ were inoculated with lanthanum, europium, holmium, and aluminum as nitrate salts. The concentrations of the cations in solution immediately after inoculation are listed in Table 7.2. Samples were analyzed at the Advanced Photon Source at Argonne National Laboratory approximately one week after inoculation. The scattering patterns for aqueous $\text{U}_{24}\text{Pp}_{12}$ with the addition of the four trivalent cations studied here are shown in Figure 7.4. Modeling of the data was conducted using the Modeling II tool in the Irena macros (Ilavsky & Jemian, 2009). For more information about the Irena macros and Modeling II, see Chapter 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source of Cation</th>
<th>Concentration of Cation in Sample (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+La</td>
<td>La(NO$_3$)$_3$</td>
<td>0.005</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Eu</td>
<td>Eu(NO$_3$)$_3$</td>
<td>0.005</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Ho</td>
<td>Ho(NO$_3$)$_3$</td>
<td>0.005</td>
</tr>
<tr>
<td>$\text{U}<em>{24}\text{Pp}</em>{12}$+Al</td>
<td>Al(NO$_3$)$_3$</td>
<td>0.015</td>
</tr>
</tbody>
</table>

For the purpose of modeling of the USAXS scattering patterns (Figure 5.4), three regions based on q are considered. The first region, at high-q ($q>10^{-1}$), is due to the size and shape of $\text{U}_{24}\text{Pp}_{12}$. This region, described by the form factor as a dilute system, is
modeled first. The form factor used to model all the scattering herein was a core-shell species, described in detail in Chapter 4. The parameters of the form factor include the average size of the particle, thickness of the shell, density of the core ($\rho_{\text{core}}$), density of the shell ($\rho_{\text{shell}}$), and the density of the solvent ($\rho_{\text{solv}}$). Because the shell in this case is formed by coordinated uranyl ions and uranium scatters X-rays stronger than the other atoms involved, the shell thickness for each sample is modeled as a single atom. The scattering behavior of uranium also causes the density of the shell to be much greater than that of the solvent and core. These parameters are listed in Table 7.3.

![USAXS scattering patterns for aqueous solutions of U$_{24}$Pp$_{12}$ inoculated with lanthanum (orange), europium (green), holmium (cyan), and aluminum (gray). The characteristic scattering pattern for U$_{24}$Pp$_{12}$ in aqueous solution is present at high-q.](image.png)
The second region of $q$ considered, at moderate-$q$ ($10^{-2} < q < 10^{-1}$), is modeled including a structure factor. Structure factors are added to the model to evaluate how the base clusters are arranged in solution. The form factor includes two more parameters—a distance and a volume fraction parameter. The distance is used to model the spacing between centers of two clusters. The volume fraction parameter is used to model the percent of space surrounding a cluster (in volume) that contains another cluster. With the exception of Al (best modeled as a dilute system), the other data sets were modeled using the hard spheres structure factor and the associated parameters are listed in Table 7.3.
TABLE 7.3

USAXS MODELING PARAMETERS FOR U$_{24}$PP$_{12}$ WITH DIVALENT CATIONS

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Eu</th>
<th>Ho</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Form Factor:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean Size (Å)</td>
<td>7.38 ± 0.31</td>
<td>7.23 ± 0.05</td>
<td>7.25 ± 0.15</td>
<td>7.18 ± 0.29</td>
</tr>
<tr>
<td><strong>Core Shell Density</strong></td>
<td>$\rho_{\text{shell}} &gt;&gt; \rho_{\text{core}}$ ≈ $\rho_{\text{solv}}$</td>
<td>$\rho_{\text{shell}} &gt;&gt; \rho_{\text{core}}$ ≈ $\rho_{\text{solv}}$</td>
<td>$\rho_{\text{shell}} &gt;&gt; \rho_{\text{core}}$ ≈ $\rho_{\text{solv}}$</td>
<td>$\rho_{\text{shell}} &gt;&gt; \rho_{\text{core}}$ ≈ $\rho_{\text{solv}}$</td>
</tr>
<tr>
<td><strong>Structure Factor:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distance Between Cluster Centers (Å)</td>
<td>28.0 ± 4.6</td>
<td>26.0 ± 3.6</td>
<td>26.5 ± 3.2</td>
<td>Dilute System</td>
</tr>
<tr>
<td><strong>Hard Spheres</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Volume Fraction (%)</td>
<td>7.4 ± 1.7</td>
<td>7.2 ± 1.4</td>
<td>7.9 ± 1.4</td>
<td>Dilute System</td>
</tr>
<tr>
<td><strong>Unified Fit</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porod Slope</td>
<td>2.4 ± 0.1</td>
<td>2.5 ± 0.1</td>
<td>2.4 ± 0.1</td>
<td>*Unified Fit Used</td>
</tr>
</tbody>
</table>

The first two regions of q described above are both modeled in a single population using a size distribution model. However, the final region, at low-q (q < 10$^{-2}$), is modeled as a single, separate population using a unified level model. Unified level is used to model the long-range Guinier and Porod/Power Law regions. The Modeling II tool only allows for modeling of one unified level (i.e. one $R_g$ and/or one Power Law slope). If two separate unified levels are present such as in the system with aluminum, the unified fit tool in the Irena macros must be used.
With the exception of $\text{U}_{24}\text{Pp}_{12}$ with added aluminum, the aqueous cluster-
monovalent cation solutions were sufficiently modeled with a single unified level using
the Modeling II tool. For these samples, the unified level did not include an apparent
Guinier sub-region, indicated by a rounding off (constantly changing slope) at lower-$q$
than the single-slope Porod/Power Law region, because the overall aggregate size is
outside the instrumental bounds. To address this, the parameters to model the Guinier
sub-region were set to $G=0$ and $R_g=1 \times 10^{10}$. Then, the Porod/Power Law region can be
modeled using the parameters $B$, contrast and size, and $P$, a constant Power Law slope.
The Power Law slopes are listed in Table 7.3. Fully modeled data for each sample can be
found in Appendix B.

As stated previously, the scattering pattern for $\text{U}_{24}\text{Pp}_{12}$ with aluminum contains
two separate unified levels, with two distinct Guinier regions and Porod/Power Law
slopes, and so the unified fit tool must be used instead of Modeling II. The unified fit tool
allows for modeling of each region with its own $R_g$ and Power Law slope (Figure 7.5).
The first unified level, with a Guinier sub-region at $q \approx 0.002$, was found to have a radius
of gyration of approximately 20 nm and a Power Law slope of 2.2. This information
suggests a mass fractal in solution.
Figure 6.5 Unified Fit model for U$_{24}$P$_{12}$ with Al including fits for a higher-q unified level modeled best as a mass fractal with an R$_g$ of 210 Å and a lower-q unified level that represents agglomeration of these fractals into a larger mass fractal.

The second unified level occurs at lower q (Guinier sub-region <10$^{-3}$). From the model, the R$_g$ is approximately 13000 Å (1300 nm). The Porod slope is approximately 1.7, which suggests a branched system or mass fractal, shown in Figure 4.6 in Chapter 4. It is more likely that this unified level is representative of an agglomeration of the particles modeled in the first unified level, as with transition metal polyoxometalates (Liu, 2003). Data for the unified fit analyses for aqueous solutions of U$_{24}$P$_{12}$ with aluminum are summarized in Table 7.4.
TABLE 7.4

UNIFIED FIT MODEL FROM USAXS DATA FOR U$_{24}$PP$_{12}$ WITH ADDED AL

<table>
<thead>
<tr>
<th>Unified Level</th>
<th>$R_g$ (Å)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>210 ± 29</td>
<td>2.24 ± 0.22</td>
</tr>
<tr>
<td>Level 2</td>
<td>12000 ± 2200</td>
<td>1.65 ± 0.03</td>
</tr>
</tbody>
</table>

Using the data from Table 7.3, comparisons between model values can give insight into how the addition of trivalent cations affects the size and shape of cluster species in solutions. Figure 7.6 compares the structure factor parameters of distance between individual clusters and the percentage of nearest neighbors interacting with a particular cluster with the atomic number of the trivalent cation added to the solution for all the systems except the system with added aluminum. There do not appear to be statistically significant differences between the distances between clusters or the percentage of neighboring interactions as the cation added changed.
7.4.2 Guinier Approximation for $U_{24}Pp_{12}$ with Added Trivalent Cations

The Guinier approximation (given in Chapter 3) is used to provide basic information about the size of the base particle in solutions containing $U_{24}Pp_{12}$. For these experiments, the base particle is $U_{24}Pp_{12}$, and should be unchanged unless the addition of cations causes a change in the cluster structure. To verify the presence of $U_{24}Pp_{12}$, scattering data were plotted as the square of $q$ vs. the natural logarithm of the intensity.
Figure 7.7 Guinier Approximations for aqueous solutions of U$_{24}$P$_{12}$ with added (a) lanthanum, (b) europium, (c) holmium, and (d) aluminum. The data are shown in color for each figure, and the fit of the linear component, meeting the requirements q×R$_g$<1.3, is shown in black. The slope of the fit gives the R$_g$, and for the solutions of U$_{24}$P$_{12}$ with monovalent cations, the respective R$_g$ is approximately 9 Å. This is consistent with U$_{24}$P$_{12}$ as the base particle.
Based on the Guinier Approximation, the slope of the Guinier plot in the region where $q*R_g > 1.3$ is equivalent to $(3*R_g)^2$. Figure 7.7 shows the scattering data (colored data points) and the fit for the approximation (black line). The fit of the approximation correlates well to the data for $U_{24}P_{12}$ with all three cations studied as evidenced by the coefficient of determination for the cluster with each cation of approximately 0.999, listed in Table 7.5. Also listed in Table 7.5 are the slopes of the approximation and the calculated radius of gyration for the base particle ($U_{24}P_{12}$).

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Slope</th>
<th>Coefficient of Determination</th>
<th>Radius of Gyration (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>-26.925</td>
<td>0.99953</td>
<td>8.99</td>
</tr>
<tr>
<td>Europium</td>
<td>-26.348</td>
<td>0.99957</td>
<td>8.89</td>
</tr>
<tr>
<td>Holmium</td>
<td>-26.317</td>
<td>0.99979</td>
<td>8.89</td>
</tr>
<tr>
<td>Aluminum</td>
<td>-26.499</td>
<td>0.99867</td>
<td>8.91</td>
</tr>
</tbody>
</table>

The expected radius of gyration for $U_{24}P_{12}$ is approximately 9.01 Å, as shown in Chapter 3. The values from these experiments are slightly smaller, but still in agreement with this radius within experimental uncertainty. This, supported by the high-q scattering pattern matching that of $U_{24}P_{12}$, indicates that the cluster remains intact through the addition of salts. This is further supported by other instrumental techniques, such as electrospray ionization- mass spectrometry.
7.4.3 Pair Distance Functions for \( \text{U}_{24}\text{Pp}_{12} \) with Added Divalent Cations

To evaluate the extent of interactions between the \( \text{U}_{24}\text{Pp}_{12} \) cluster and the added cations, the pair distance distribution function (PDDF) was modeled for the high-q data for each sample (Figure 7.8). The PDDF plots can be described as major asymmetric Gaussian curves with a side peak at distances greater than 18 Å. The asymmetric Gaussian is consistent with a spherical shell structure, or a core-shell species, and is as expected for \( \text{U}_{24}\text{Pp}_{12} \). There is a slight side peak at low distances (~5 Å), which is attributed to the thickness of the shell. The calculation for shell thickness is explained in detail in Chapter 4.
Figure 7.8 PDDFs derived from SAXS data for aqueous solutions of $U_{24}Pp_{12}$ with added lanthanum (orange), europium (green), holmium (cyan), and aluminum (gray). Error bars were determined by the analysis within the Pair Distance Function tool, a part of the Irena macros. The PDDF for systems of $U_{24}Pp_{12}$ with added lanthanum, europium, and holmium are typical for the cluster interacting with one cation at a single distance. The PDDF for $U_{24}Pp_{12}$ with added aluminum has multiple cation peaks, suggesting that there are cations interacting with the cluster at distances further away from the cluster.
As with data for solutions of $\text{U}_{24}\text{Pp}_{12}$ at different concentrations (Chap. 4) and systems with added monovalent and divalent cations (Chap. 5 and 6), the PDDF for solutions of $\text{U}_{24}\text{Pp}_{12}$ with the addition of trivalent cations were fit using the Multiple Peaks Fit tool in Origin Pro (OriginLab, Northampton, MA). The fits for these solutions are given in Appendix C. The data from these fits are summarized in Table 7.6.

### TABLE 7.6
NONLINEAR CURVE FIT GAUSS DATA FOR THE PDDF FROM SAXS DATA
FOR SOLUTIONS OF $\text{U}_{24}\text{Pp}_{12}$ WITH TRIVALENT CATIONS ADDED

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Distribution Peak</th>
<th>Peak Maximum (Å)</th>
<th>Peak Width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>1</td>
<td>4.72 ± 0.05</td>
<td>3.73 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.6 ± 0.1</td>
<td>5.83 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.4 ± 0.1</td>
<td>3.84 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.4 ± 0.1</td>
<td>2.27 ± 0.07</td>
</tr>
<tr>
<td>R² = 0.99989</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europium</td>
<td>1</td>
<td>4.34 ± 0.07</td>
<td>3.58 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.6 ± 0.1</td>
<td>6.78 ± 0.33</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.5 ± 0.3</td>
<td>4.07 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.3 ± 0.1</td>
<td>2.62 ± 0.13</td>
</tr>
<tr>
<td>R² = 0.99984</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holmium</td>
<td>1</td>
<td>4.32 ± 0.07</td>
<td>3.54 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.5 ± 0.1</td>
<td>6.64 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15.3 ± 0.2</td>
<td>4.09 ± 0.45</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.2 ± 0.1</td>
<td>2.47 ± 0.12</td>
</tr>
<tr>
<td>R² = 0.99985</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>1</td>
<td>4.44 ± 0.1</td>
<td>3.42 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.0 ± 0.08</td>
<td>5.42 ± 0.26</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>14.7 ± 0.1</td>
<td>3.50 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>19.5 ± 0.1</td>
<td>5.08 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25.7 ± 0.4</td>
<td>5.22 ± 0.42</td>
</tr>
<tr>
<td>R² = 0.99962</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The distribution of the fit associated with the fourth peak for the aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added cations is based on the cation interaction with the cluster.
(Figure 7.9). For the four systems studied, the distribution due to the cation-cluster interaction represented by the fourth peak occurs at the same distance, $R$. For the systems with added lanthanum, europium, and holmium, the PDDF fourth peak indicates a maximum dimension of approximately 23 Å, similar to the studies of systems of divalent cations (Chap. 6).

![Graph](image)

**Figure 7.9** Peak fit distributions for the $U_{24}P_{12}$-cation interactions from the PDDF from SAXS data for aqueous solutions of $U_{24}P_{12}$ with added lanthanum (orange solid line), europium (green dotted line), holmium (cyan short dashed line), and aluminum (gray dash-dot line). The fourth peaks for all four systems are centered at the same radius. Aluminum was fit with an additional peak (labeled as 5), which suggests cations interact at multiple distances from the cluster, though more are interacting at closer distances than distances further away from the cluster.
The PDDF from SAXS data of U$_{24}$P$_{12}$ with added aluminum is different than the systems with added lanthanide elements and systems with added mono- and divalent cations. While the other systems were fit with a single distribution representing cation-cluster interactions, the system with added aluminum was best fit with two cation-cluster interaction peaks. This suggests that the cations are interacting with the cluster at two different maximum distances, one at about 4 Å and one about 13 Å. In this system, it is extremely unlikely that sodium ions are the only cations interacting with the sample. As such, the added aluminum cation must be interacting with the cluster.

7.5 Powder Diffraction of Precipitates of U$_{24}$P$_{12}$ with Added Trivalent Cations

When trivalent cations are added to the solutions of U$_{24}$P$_{12}$, a precipitate forms. These precipitates were removed from solution and dried. The same samples were used for powder X-ray diffraction (PXRD), X-ray fluorescence (XRF), and Raman spectroscopy. Precipitates for systems with added lanthanum, cerium, neodymium, and samarium were studied.

As for the X-ray diffraction powder pattern obtained from untreated, ground crystals of U$_{24}$P$_{12}$ (described in detail in Chapter 3), the diffraction patterns of the precipitates of aqueous solutions of U$_{24}$P$_{12}$ with added trivalent ions indicate the materials is largely amorphous. Figure 7.10 compares the diffraction pattern for untreated, ground crystals of U$_{24}$P$_{12}$ and the precipitates that formed from aqueous solutions of U$_{24}$P$_{12}$ with added trivalent cations. All of the precipitates for the cations
studied in this chapter gave diffraction patterns with a broad peak in the 2θ range from about 15 to 35°, as expected for an X-ray amorphous material.

Similar to the systems with added monovalent cations (Chapter 5, Figure 5.11), large, well-defined peaks are present in the PXRD patterns for systems with added samarium, neodymium, and lanthanum. These peaks are not consistent with the simulated diffraction pattern for crystalline $\text{U}_{24}\text{P}_{12}$, shown in Chapter 5 (Figure 5.12). The presence of the amorphous signature and sharp peaks in the PXRD pattern indicates the precipitates are not a single phase.
Figure 7.10 PXRD patterns for precipitates formed from aqueous solutions of U$_{24}$P$_{12}$ with added lanthanum (orange), cerium (blue), neodymium (red), and samarium (magenta). For comparison, the PXRD pattern for untreated, ground crystals of U$_{24}$P$_{12}$ (black) is shown on the bottom of the figure.
7.6 X-ray Fluorescence of Precipitates of $\text{U}_{24}\text{Pp}_{12}$ with Added Trivalent Cations

To further study the precipitates that formed when trivalent cations were added to aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$, they were analyzed using X-ray fluorescence (XRF). Qualitative XRF analyses were used to determine the presence of uranium, phosphorus, and the added cation in the precipitates using characteristic fluorescence energies for the respective elements. The presence of these elements in the precipitates from the aqueous cluster solutions with added trivalent cations are summarized in Table 7.7.

**TABLE 7.7**

| PRESENCE OF ELEMENTS IN XRF ANALYSES OF PRECIPITATES FORMED FROM SOLUTIONS OF $\text{U}_{24}\text{Pp}_{12}$ WITH ADDED TRIVALENT CATIONS |
|------------------|---|---|---|---|---|---|---|---|
| Sample           | U | P | La | Ce | Nd | Sm | Eu | Ho | Al |
| $\text{U}_{24}\text{Pp}_{12} + \text{La}$ | X | X | X |   |   |   |   |   |   |
| $\text{U}_{24}\text{Pp}_{12} + \text{Ce}$ | X | X | X |   |   |   |   |   |   |
| $\text{U}_{24}\text{Pp}_{12} + \text{Nd}$ | X | X | X |   |   |   |   |   |   |
| $\text{U}_{24}\text{Pp}_{12} + \text{Sm}$ | X | X | X |   |   |   |   |   |   |
| $\text{U}_{24}\text{Pp}_{12} + \text{Eu}$ | X | X | X |   |   |   |   |   |   |
| $\text{U}_{24}\text{Pp}_{12} + \text{Ho}$ | X | X | X |   |   |   |   |   |   |
| $\text{U}_{24}\text{Pp}_{12} + \text{Al}$ | X | X |   |   |   |   |   |   |   |

7.7 Raman Spectroscopy of Precipitates of $\text{U}_{24}\text{Pp}_{12}$ with Added Divalent Cations

The precipitates formed from solutions of $\text{U}_{24}\text{Pp}_{12}$ with added trivalent cations were analyzed using Raman spectroscopy. Raman spectra for each of the cluster-ion solutions studied were compared to Raman spectra for untreated $\text{U}_{24}\text{Pp}_{12}$ as a single crystal and a bulk powder. Comparisons of these spectra are shown in Figure 7.11.
Figure 7.11 Raman spectra for untreated crystals of $\text{U}_{24}\text{Pp}_{12}$ (black) and precipitates formed from aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added lanthanum (orange), cerium (blue), holmium (cyan), and aluminum (gray) with a dotted line through the uranyl mode at approximately 815 cm$^{-1}$ and the pyrophosphate mode at approximately 856 cm$^{-1}$ for the crystal of $\text{U}_{24}\text{Pp}_{12}$. In the spectra for the systems with added aluminum and holmium, the two modes of interest are shifted to higher wavenumbers, indicating interactions between the added cations and the uranyl oxygen atoms and pyrophosphate oxygen atoms on the cluster.
Similar to what was seen for systems with added monovalent cations (Chapter 5, Figure 5.13), the Raman spectra for systems of $\text{U}_{24}\text{Pp}_{12}$ with added holmium and aluminum display a shift of the uranyl mode, but to higher wavenumbers. A shift in these systems also occurs in the pyrophosphate mode. This indicates that the added cations are interacting with the uranyl oxygen atoms and pyrophosphate oxygen atoms on the cluster, causing a change in the vibrational mode. The spectra for systems with added cerium and lanthanum do not exhibit shifts of the modes of interest, which is similar to the behavior of systems with added divalent cations (Chapter 6, Figure 6.11).

7.8 Discussion

The studies of the solutions and the precipitates from systems where $\text{U}_{24}\text{Pp}_{12}$ in aqueous solution is inoculated with trivalent cations provide much insight into the complex cluster-ion system. From DLS data of concentrated solutions of $\text{U}_{24}\text{Pp}_{12}$ with added trivalent cations, aggregates were observed in solution for all the trivalent cations studied initially. Over time, the systems with added cerium and neodymium had a large decrease in the $R_H$, which suggests that aggregates in these systems are unstable. The decrease in $R_H$ coincided with precipitation events.

The aggregation studies in this Chapter further support the hypothesis that the charge of the added cations may be important for determining whether or not aggregation of $\text{U}_{24}\text{Pp}_{12}$ will occur. Because the trivalent cations have the highest positive charges of the cations added to aqueous systems of $\text{U}_{24}\text{Pp}_{12}$ with added cations (Chapters 5-7), they would be the most effective at screening the large negative charge of $\text{U}_{24}\text{Pp}_{12}$. Therefore it would require even fewer trivalent cations than divalent cations to induce aggregation.
Further experimentation may support this hypothesis by determining the extent of substitution of trivalent cations at sodium sites.

An aqueous solution of \( \text{U}_{24}\text{Pp}_{12} \) with added aluminum presented unique USAXS data that showed two distinct unified levels, associated with aggregates of two different sizes. One unified level likely corresponds to an aggregate of \( \text{U}_{24}\text{Pp}_{12} \), while the other unified level corresponds to agglomeration of the aggregates in the previous level. The aggregate from USAXS data has a size of about 20 nm, which is in agreement with DLS data for the same system two weeks after inoculation.

In all cases, the pair distance distribution functions from USAXS data for solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added trivalent cations indicate a direct, inner-sphere interaction between the cluster and the added ion. The changes in the DLS data and the USAXS patterns indicate that there is a cation-cluster interaction, which suggests at least a partial substitution for the initial sodium ions. The solution data is summarized in Table 6.8, where C represents the base cluster (0.6 nm), C’ represents aggregation of the base cluster C into a large species in solutions (\( R_H > 10C \)), and C’’ represents aggregation of the aggregated base cluster (aggregation of C’).
TABLE 7.8

EXTENT OF AGGREGATION IN CONCENTRATED SOLUTIONS OF U$_{24}$PP$_{12}$ WITH TRIVALENT CATIONS

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Extent of Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>C'</td>
</tr>
<tr>
<td>Cerium</td>
<td>C'/C”$\rightarrow$ C</td>
</tr>
<tr>
<td>Neodymium</td>
<td>C' $\rightarrow$ C $\rightarrow$ C'</td>
</tr>
<tr>
<td>Europium</td>
<td>C'/C”</td>
</tr>
<tr>
<td>Holmium</td>
<td>C'/C”</td>
</tr>
<tr>
<td>Aluminum</td>
<td>C’</td>
</tr>
</tbody>
</table>

The precipitates of aqueous solutions of U$_{24}$PP$_{12}$ with added trivalent cations also support the interaction between the cluster and the added cations. Raman spectra for these precipitates were similar to the spectra for untreated U$_{24}$PP$_{12}$, indicating the presence of cluster material in the precipitate. In addition, XRF data show that the added cation is also incorporated in the precipitates from the aqueous cluster solution, and interactions between the added ion and the cluster are indicated by the shifts of stretching peaks in the Raman spectra. As with the precipitates for mono- and divalent systems, the precipitates from trivalent systems of U$_{24}$PP$_{12}$ are not soluble in water. This suggests that the cluster material is not intact clusters, but rather fragments of clusters.

In combination with the data from Chapters 5 and 6, the experiments in this Chapter demonstrate the impact of additional cations on the aqueous behavior of U$_{24}$PP$_{12}$. The clusters cannot be thought of as isolated species separate from other ions in solution. In Chapters 5-7, systems with added cations representative of common environmentally relevant cations, fission products from irradiation of uranium, and co-contaminants have demonstrated changes in cluster solution behavior based on the cation added to the
system. Understanding cluster-ion interactions is essential to applications of clusters in solution and environmental impacts of these clusters.
CHAPTER 8:
AGGREGATION OF U$_{24}$PP$_{12}$ CLUSTERS WITH CATIONS IN DILUTE SOLUTIONS

8.1 Introduction

Although the behavior of concentrated aqueous solutions of U$_{24}$PP$_{12}$ with added cations (Chapters 5-7) is important knowledge for future applications of uranyl clusters, studies of dilute solutions of U$_{24}$PP$_{12}$ with added cations are important for comparisons between uranyl clusters, or polyoxometalates (POMs), and transition metal POMs (TM-POMs). TM-POMs are often only slightly soluble, so dilute solutions are frequently used. In addition dilute solutions reduce the amount of variables in a system because dilute systems are simpler and less likely to precipitate.

Preliminary comparisons of the uranyl POMs and TM-POMs have demonstrated some similarities between the two types of polyoxometalates (Nyman & Burns, 2012), and one particular uranyl POM has been shown to aggregate in dilute solutions (Li et al., 2014) as with TM-POMs (Liu, 2002, 2003, 2010; Pigga, Joseph A. Teprovich, Robert A. Flowers, & Antonio, 2010; Yin, Li, & Liu, 2011). In this chapter, dilute solutions of U$_{24}$PP$_{12}$ with added mono- and divalent cations are studied using dynamic and static light scattering to determine the size, shape, and approximate density of aggregates in solution.
8.2 Experimental Methods

8.2.1 Sample Preparation

Following the same procedures as detailed in Chapters 3 through 7, crystals of U$_{24}$P$_{12}$ were harvested from their mother solution and dissolved in ultrapure water. Whereas previous experiments used a concentration of 65 grams of cluster crystals per liter of ultrapure water (g/L), the concentration of aqueous solutions of U$_{24}$P$_{12}$ were lowered to 0.5 g/L for these experiments, similar to concentrations used in TM-POM aggregation research (Liu, 2003). Cation nitrate salt solutions (0.5 to 0.005 M) were added to the aqueous cluster solutions to reach the concentration of cation indicated in Table 8.1. The intent was to add enough salt to the aqueous solutions of U$_{24}$P$_{12}$ to induce aggregation, but not precipitation. Samples were prepared at the University of Notre Dame and shipped to the University of Akron for light scattering analyses.

\[\text{TABLE 8.1}\]

<table>
<thead>
<tr>
<th>Cation Added</th>
<th>Cation Source</th>
<th>Concentration of Cation in Solution (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>KNO$_3$</td>
<td>3</td>
</tr>
<tr>
<td>Cs</td>
<td>CsNO$_3$</td>
<td>6</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(NO$_3$)$_2$</td>
<td>0.4</td>
</tr>
</tbody>
</table>

8.2.2 Dynamic Light Scattering

Prior to analysis, approximately 6 mL of 0.5 g/L aqueous solution of U$_{24}$P$_{12}$ with added cations were transferred to a 20 mL scintillation vial that had previously been
cleaned by acetone vapor. The samples were inserted into the sample chamber of a Brookhaven Instruments BI200-SM commercial light scattering system at the University of Akron, Akron, OH. The same system was used for both dynamic and static light scattering experiments.

Samples of aqueous solutions of U_{24}P_{12} with added cations were analyzed at five source-sample-detector (S-S-D) angles using the Brookhaven DLS software—90°, 75°, 60°, 45°, and 30°. Measurements were repeated five times at each angle to evaluate instrumental reproducibility. The length of each scan was dependent on the total scattering intensity.

The data at each source-sample-detector angle were analyzed using the CONTIN program (Provencher, 1982) to find the linewidth for the scattering size distributions. The linewidth, Γ_i, correlates to the size of the major peak. Using the equations listed for DLS analysis in Chapter 2, the radius of hydration, R_h, was calculated for each analysis. The average R_h at each angle was used to extrapolate to a S-S-D of 0° via the Stokes-Einstein relationship. This relationship was used to calculate R_{h,0} for each system.

8.2.3 Static Light Scattering

Using the same Brookhaven instrument as for the multi-angle DLS experiments, data were collected in static light scattering (SLS) mode. SLS data were collected over an angular range of 20 to 90°, with a step size of 2°. The data were automatically processed by the Brookhaven SLS software to provide a partial Zimm plot with a linear fit. A Zimm plot corresponds to the reciprocal intensity surface as a function of S-S-D angle (Zimm,
1948). The partial Zimm plot was used to determine \( R_g \) by varying the S-S-D angle at a single aggregate concentration. More information on Zimm plots is given in Chapter 2.

After \( R_g \) was been calculated from the SLS data and \( R_h \) has been calculated from the DLS data for the same sample, the ratio \( (R_g/R_h) \) was calculated to provide information about the structure of the aggregate. The “blackberry” as defined in TM-POM chemistry is approximately spherical in nature. For a solid sphere, the ratio of \( R_g/R_h \) is 0.77. However, blackberries are hollow (Liu, 2009), and the \( R_g/R_h \) ratio is 1.

8.3 Dilute Aqueous Solutions of \( \text{U}_{24}\text{Pp}_{12} \) with Added Potassium

For this experiment, \( \text{KNO}_3 \) was used as the source of potassium. The samples were analyzed two weeks after addition of salt.

8.3.1 Dynamic Light Scattering for 0.5 g/L Aqueous Solutions of \( \text{U}_{24}\text{Pp}_{12} \) with Added Potassium

Figure 8.1 gives the average DLS size distribution data for S-S-D angles of 30°, 45°, 60°, 75°, and 90°. The size distributions indicate the presence of a large species in solution than an individual cluster of \( \text{U}_{24}\text{Pp}_{12} \) (<1 nm). This indicates that aggregates of \( \text{U}_{24}\text{Pp}_{12} \) form in dilute aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) after small amounts of potassium are added.
Figure 8.1 Average multi-angle DLS distribution data for all species in a 0.5 aqueous solution of U$_{24}$Py$_{12}$ with added potassium at 30°, 45°, 60°, 75°, and 90° showing the angular dependence on size for the system.

### TABLE 8.2

PEAK OF DLS DISTRIBUTION DATA FOR 0.5 G/L AQUEOUS SOLUTIONS OF U$_{24}$PP$_{12}$ WITH ADDED POTASSIUM

<table>
<thead>
<tr>
<th>S-S-D Angle (°)</th>
<th>R$_h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>77.53 ± 3.88</td>
</tr>
<tr>
<td>45</td>
<td>73.95 ± 3.70</td>
</tr>
<tr>
<td>60</td>
<td>69.67 ± 3.48</td>
</tr>
<tr>
<td>75</td>
<td>65.79 ± 3.29</td>
</tr>
<tr>
<td>90</td>
<td>64.85 ± 3.24</td>
</tr>
</tbody>
</table>
Figure 8.1 shows a single distribution for each angle indicating at all aggregates have the same size. The average peaks of these distributions for each angle are listed in Table 8.2. All available distribution data for five angles are in Appendix D. Figure 8.2 shows the Stokes-Einstein relationship for the average Rₜ values calculated from the DLS distribution data of dilute aqueous solutions of U₂₄P₉ with potassium. The Rₜ₀ for this system is 79 ± 4 nm.

![Stokes-Einstein relationship graph](image)

Figure 8.2 The Stokes-Einstein relationship from average Rₜ values determined from DLS distributions of aqueous solutions of U₂₄P₉ with added potassium at multiple angles. Error bars are determined from replicate DLS measurements. The linear fit of the data is used to calculate an Rₜ₀ for the system of 79 nm.
8.3.2 Static Light Scattering and Shape Analysis for \( \text{U}_{24}\text{Pp}_{12} \) with Potassium Added

A partial Zimm (\( R_g \)) analysis of SLS data for dilute aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added potassium is shown in Figure 8.3. From the linear fit (\( R^2 = 0.999 \)) of the partial Zimm plot, the \( R_g \) was calculated to be 82 ± 4 nm. The \( R_g/R_h,0 \) ratio is approximately one, so the species in solution when potassium is added to dilute aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) is likely a hollow sphere with a diameter of about 160 nm.

![Figure 8.3 Partial Zimm (\( R_g \)) analysis of SLS Data of 0.5 g/L aqueous solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added potassium. A linear fit was applied to the data, and gave \( R_g \) 82 nm.](image)

8.4 Dilute Aqueous Solutions of \( \text{U}_{24}\text{Pp}_{12} \) with Added Cesium

For this experiment, Cs(NO\(_3\)) was used as the source of cesium. The samples were analyzed two weeks after addition of salt.
8.4.1 Dynamic Light Scattering for 0.5 g/L Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Cesium

Figure 8.4 shows the average DLS size distribution data for S-S-D angles of 30°, 45°, 60°, 75°, and 90°. The size distributions indicate the presence of a species in solution that is larger than the size of an individual cluster of U$_{24}$Pp$_{12}$ (<1 nm). This indicates that aggregates of U$_{24}$Pp$_{12}$ form in dilute aqueous solutions of U$_{24}$Pp$_{12}$ after cesium has been added.

Figure 8.4 Average multi-angle DLS distribution data for all species in a 0.5 g/L aqueous solution of U$_{24}$Pp$_{12}$ with added cesium at 30°, 45°, 60°, 75°, and 90° showing the angular dependence on size for the system.
TABLE 8.3

PEAK OF DLS DISTRIBUTION DATA FOR 0.5 G/L AQUEOUS SOLUTIONS OF U_{24}P_{12} WITH ADDED CESIUM

<table>
<thead>
<tr>
<th>S-S-D Angle (°)</th>
<th>R_h (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>47.88 ± 2.39</td>
</tr>
<tr>
<td>45</td>
<td>46.10 ± 2.31</td>
</tr>
<tr>
<td>60</td>
<td>43.99 ± 2.20</td>
</tr>
<tr>
<td>75</td>
<td>43.24 ± 2.16</td>
</tr>
<tr>
<td>90</td>
<td>41.15 ± 2.06</td>
</tr>
</tbody>
</table>

Figure 8.4 shows a single distribution for each angle. The average peak of this distribution for each angle is listed in Table 8.3. Distribution data for all angles are in Appendix D. Figure 8.5 shows the Stokes-Einstein relationship for the average R_h values calculated from the DLS distributions of 0.5 g/L aqueous solutions of U_{24}P_{12} with added cesium. The R_{h,0} for this system is 49 ± 3 nm.
Figure 8.5 The Stokes-Einstein relationship from average R\textsubscript{h} values determined from DLS distributions of aqueous solutions of U\textsubscript{24}P\textsubscript{p12} with added cesium at multiple angles. Error bars are determined from replicate DLS measurements. The linear fit of the data is used to calculate an R\textsubscript{h,0} for the system of 49 nm.

8.4.2 Static Light Scattering and Shape Analysis for U\textsubscript{24}P\textsubscript{p12} with Cesium Added

A partial Zimm (R\textsubscript{g}) analysis of SLS data for U\textsubscript{24}P\textsubscript{p12} with cesium is shown in Figure 8.6, with the fit included. From the linear fit of the partial Zimm plot (R\textsuperscript{2} = 0.939), the R\textsubscript{g} was calculated to be 55 ± 3 nm. The R\textsubscript{g}/R\textsubscript{h,0} ratio is approximately one, indicating that the species in solution when cesium is added to 0.5 g/L aqueous solutions of U\textsubscript{24}P\textsubscript{p12} is a hollow sphere with a diameter of about 110 nm.
8.5 Dilute Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Copper

For this experiment, Cu(NO$_3$)$_2$ was used as the source of copper. The samples were analyzed after two weeks after addition of salt.

8.5.1 Dynamic Light Scattering for 0.5 g/L Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Copper

Figure 8.7 shows the average DLS size distribution data for S-S-D angles of 30°, 45°, 60°, 75°, and 90°. The size distributions indicate the presence of a species in solution.
that is larger than the size of an individual cluster of $\text{U}_{24}\text{Pp}_{12}$ ($<1$ nm). This indicates that aggregates of $\text{U}_{24}\text{Pp}_{12}$ form in 0.5 g/L aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ after copper has been added.

Figure 8.7 Average multi-angle DLS distribution data for all species in a dilute aqueous solution of $\text{U}_{24}\text{Pp}_{12}$ with added copper at 30°, 45°, 60°, 75°, and 90° showing the angular dependence on size for the system.
TABLE 8.4

PEAK OF DLS DISTRIBUTION DATA FOR 0.5 G/L AQUEOUS SOLUTIONS OF U$_{24}$P$_{12}$ WITH ADDED COPPER

<table>
<thead>
<tr>
<th>S-S-D Angle (°)</th>
<th>$R_h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>71.31 ± 5.77</td>
</tr>
<tr>
<td>45</td>
<td>69.09 ± 2.56</td>
</tr>
<tr>
<td>60</td>
<td>68.90 ± 0.92</td>
</tr>
<tr>
<td>75</td>
<td>67.24 ± 0.58</td>
</tr>
<tr>
<td>90</td>
<td>64.90 ± 1.21</td>
</tr>
</tbody>
</table>

Figure 8.7 shows a single distribution for each angle. The average peaks of the distributions for each angle are listed in Table 8.4. The distribution data for all angles are in Appendix D. Figure 8.8 shows the Stokes-Einstein relationship for the average $R_h$ values calculated from DLS distributions of dilute aqueous solutions of U$_{24}$P$_{12}$ with added copper. The $R_{h,0}$ for this system is 73 ± 4 nm.
Figure 8.8 The Stokes-Einstein relationship from average $R_h$ values determined from DLS distributions of aqueous solutions of $U_{24}Pp_{12}$ with added copper at multiple angles. Error bars were determined from replicate DLS measurements. The linear fit of the data is used to calculate an $R_{h,0}$ for the system of 73 nm.

8.5.2 Static Light Scattering for $U_{24}Pp_{12}$ with Copper Added

A partial Zimm ($R_g$) analysis of SLS data for 0.5 g/L aqueous solutions of $U_{24}Pp_{12}$ with added copper is shown in Figure 8.9. From the linear fit of the partial Zimm plot, the $R_g$ was calculated to be $72 \pm 4$ nm. The $R_g/R_{h,0}$ ratio is approximately one, indicating that the species in solution when copper is added to 0.5 g/L aqueous solutions of $U_{24}Pp_{12}$ is a hollow sphere with a diameter of 144 nm.
Figure 8.9 Partial Zimm ($R_g$) analysis of SLS data of dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added copper. A linear fit was applied to the data, from which the $R_g$ was calculated to be approximately 72 nm.

8.6 Discussion

For the three cations studied in this chapter (K, Cs, and Cu), the addition of salt to dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ induced formation of hollow, spherical blackberries. The amount of salt added for the monovalent cations (potassium and cesium) was an order of magnitude larger than that for the divalent cation (copper) studied. This supports the hypothesis stated in Chapter 6 that fewer cations are required to screen the large negative charge of a cluster of $\text{U}_{24}\text{Pp}_{12}$ to induce aggregation as the cation charge increases. No data for the systems with added trivalent cation is available because all
solutions of $\text{U}_{24}\text{Pp}_{12}$ with added trivalent cations formed precipitates. The diameters of the blackberries formed in solution for each system are summarize in Table 8.5. Addition of different cations produced blackberries of different sizes, which suggests that it is possible to control the size of the aggregate in solution by selection of the added cation, similar to the control in size demonstrated by solvent changes in TM-POM blackberries (Liu, 2009).

It is not clear which cation characteristics cause different sized blackberries upon addition to dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ due to the limited data available, however cation size or charge density may play a role. In addition to the size of the cation, the number of cluster sites to which a single cation bonds may impact the distance between clusters and the cluster-cation-cluster angle, both of which can affect the size of the overall blackberry. Potential bonding sites for cations and single-site versus multiple site bonding will be discussed in Chapter 9.
TABLE 8.5
SUMMARY OF BLACKBERRY SIZES IN DILUTE SOLUTIONS OF U$_{24}$PP$_{12}$ WITH ADDED CATIONS FROM DLS AND SLS DATA

<table>
<thead>
<tr>
<th>Cation Added to Dilute U$<em>{24}$PP$</em>{12}$ Solutions</th>
<th>Blackberry Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>160</td>
</tr>
<tr>
<td>Cs</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>150</td>
</tr>
</tbody>
</table>

The DLS and SLS data for 0.5 g/L aqueous solutions of U$_{24}$PP$_{12}$ with added cations differs from that in 65 g/L aqueous solutions of the same cluster. Direct numerical comparisons are not possible because the concentrated cluster-cations systems were only analyzed at one angle on a different instrument (Chapter 5 for K and Cs, Chapter 6 for Cu). Concentrated aqueous solutions of U$_{24}$PP$_{12}$ with added potassium did not aggregate after two weeks. Concentrated solutions of U$_{24}$PP$_{12}$ with cesium and copper contained aggregates, but the R$_h$ values for the concentrated systems were much greater than that for the dilute solutions.

Differences between the aggregation behaviors of U$_{24}$PP$_{12}$ in concentrated and dilute cluster solutions may be due to the proximity between clusters. In more dilute solutions, the clusters have more void space in which to arrange into the optimal geometry to form blackberries, especially because of the hollow nature of blackberries. In a concentrated solution, it would require movement of more particles per volume to form the hollow void in a blackberry. This may be especially unfavorable in cases were the
charge screening is insufficient, such as systems of $U_{24}Pp_{12}$ with added monovalent cations.
CHAPTER 9:
ANALYSIS OF AGGREGATION OF AQUEOUS SOLUTIONS OF U$_{24}$P$_{12}$ BY THE ADDITION OF CATIONS

9.1 Introduction

U$_{24}$P$_{12}$ is an oblate cluster composed of 24 uranyl hexagonal bipyramids, each of which contains a linear uranyl ion coordinated by two bidentate peroxide groups and two oxygen atoms from a single pyrophosphate group (Ling et al., 2010). These uranyl bipyramids are linked through the sharing of peroxide groups into tetrameric rings, which are further connected into the cage structure by pyrophosphate groups. The pyrophosphate groups are bidentate to each of two uranyl ions from different tetrameric rings. The uranyl peroxide pyrophosphate portion of U$_{24}$P$_{12}$ has an overall charge of -30 in the crystal (Ling et al., 2010). The large negative charge associated with U$_{24}$P$_{12}$ is balanced by sodium atoms to give the crystallographic structure Na$_{30}$.[(UO$_2$)(O$_2$)(HP$_2$O$_7$)$_6$(H$_2$P$_2$O$_7$)$_6$] (Johnson, et al., 2013). Because of the high negative charge of the cluster, concentrated solutions of U$_{24}$P$_{12}$ do not aggregate (Chapter 4). However, in Chapters 5 through 8, aqueous solutions of U$_{24}$P$_{12}$ have aggregated when cations were added to the system. In this chapter, potential locations for interaction between the ions in solution and the cluster are investigated.
9.2 Locations of Cations Associated with $U_{24}P_{12}$

In aqueous solutions of $U_{24}P_{12}$, charge-balancing sodium ions are likely located both within and outside of the cluster. For crystals of $U_{24}P_{12}$, the exterior sodium ions are unable to be resolved using X-ray diffraction. Preliminary neutron diffraction studies of $U_{24}P_{12}$ have suggested positions of sodium ions on the outside the cluster, which will be discussed in Chapter 11. The sodium ions inside the cluster are well refined from X-ray data and are bonded to the $O_{\text{uranyl}}$ atoms of the tetrameric rings that extend toward the center of the cluster (Figure 9.1). From X-ray crystallography, the Na-$O_{\text{uranyl}}$ bond distances in $U_{24}P_{12}$ have been found to be approximately 2.5 Å. The Na-O bond distance of 2.5 Å is in agreement with Na-O bond lengths with several other uranyl structures, a few of which are summarized in Table 9.1.
**TABLE 9.1**

NA-O BOND LENGTHS IN SODIUM URANYL STRUCTURES

<table>
<thead>
<tr>
<th>Structural Formula</th>
<th>Average Na-O Bond Length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂[(UO₂)₃O₃(OH)₂]</td>
<td>2.522</td>
<td>Li &amp; Burns, 2001</td>
</tr>
<tr>
<td>KNa₃(UO₂)₂(Si₄O₁₀)₂(H₂O)₄</td>
<td>2.490</td>
<td>Li &amp; Burns, 2001</td>
</tr>
<tr>
<td>(K₀.₅₆-Na₀.₄₂)₀.₀₄₅<a href="H%E2%82%82O">(UO₂)(SiO₃OH)</a>₁.₅</td>
<td>2.559</td>
<td>Burns, 1998</td>
</tr>
<tr>
<td>CsNa₈[(UO₂)₆O₈Mo₅O₂₀]</td>
<td>2.544</td>
<td>Nazarchuk, et al., 2009</td>
</tr>
<tr>
<td>CsNa₃[(UO₂)₄O₄Mo₂O₈]</td>
<td>2.639</td>
<td>Nazarchuk, et al., 2009</td>
</tr>
</tbody>
</table>

Studies of cation dynamics for cations inside and outside uranyl clusters in solution have been studied by Alam, *et al.* In particular, the group probed the transport of lithium ions in the U₂₈ cluster. The study showed that the small lithium ions can move in and out of the cluster through pores in the shell, even at room temperature (Alam, *et al.*, 2014), while large ions tend to block the pores. Because sodium is also a small ion and the only ion in U₂₄Pp₁₂, it is reasonable to assume that the sodium ions would also be dynamic in solutions of U₂₄Pp₁₂.
9.3 Hypothesized Location of Exterior Cations

In the structure of the U$_{24}$P$_{12}$ cluster, the only sites available for interactions with cations are oxygen atoms. The oxygen atoms in U$_{24}$P$_{12}$ can be divided into three major categories based on their bonding with other elements in the cluster—peroxide oxygen atoms (O$_{\text{per}}$), uranyl oxygen atoms (O$_{\text{ur}}$), and pyrophosphate oxygen atoms (O$_{\text{py}}$). There are two types of O$_{\text{ur}}$ atoms in the structure of U$_{24}$P$_{12}$—those that are directed toward the interior of the cluster (O$_{\text{ur,in}}$), and those extending outward from the exterior surface of the cluster (O$_{\text{ur,ex}}$). There are three types of pyrophosphate oxygen atoms per pyrophosphate molecule in U$_{24}$P$_{12}$—four oxygen atoms are bonded to the cluster uranyl ions (O$_{\text{py,c}}$), one central oxygen atom linking the phosphate atoms (O$_{\text{py,bridge}}$), and two
non-bridging oxygen atoms attached to the pyrophosphates (O\textsubscript{py, nb}) that extend away from the cluster. The potential sites for cation interactions on the exterior of U\textsubscript{24}P\textsubscript{p12} include O\textsubscript{per}, O\textsubscript{ur, ex}, O\textsubscript{py, link}, and O\textsubscript{py, nb}. These will be discussed in depth in the following sections.

9.3.1 Possible Interactions Between Sodium Ions and Peroxide Oxygen Atoms in U\textsubscript{24}P\textsubscript{p12}

Possible bonding interactions between sodium ions and O\textsubscript{per} atoms are shown in Figure 9.2. The structure for U\textsubscript{24}P\textsubscript{p12} studied herein has two confirmations for the tetrameric uranyl rings: those with the concave rings facing toward the center of the cluster (concave-in), and those with the concave rings facing away from the center of the cluster toward the area outside of the cluster (concave-out). In each conformation, there are outer O\textsubscript{per} sites (1 and 4 in Figure 9.2) and inner O\textsubscript{per} sites (2 and 3 in Figure 9.2).
Figure 9.2 Potential sites for bonding between external sodium ions and O_{per} atoms on (a) concave-in rings and (b) concave-out rings on U_{24}Pp_{12}. Sites 1 and 4 are the peroxide oxygen atoms extending away from the center of tetrameric concave-in and concave-out rings, respectively (referred to as outer O_{per}). Sites 2 and 3 are the O_{per} atoms extending toward the center of the tetrameric concave-in and concave-out rings, respectively (referred to as inner O_{per}).

Due to spatial constraints, it is unlikely that site 3 would be available for interaction with external sodium ions. The maximum distance between inner O_{per} atoms in either ring is approximately 3.7 Å, which is across the diagonal of the topological square. With a Na-O bond length of 2.5 Å, the sodium atom would need to be over the center of the topological square formed by the tetramer and bonded to all four inner O_{per} atoms, which will be referred to as multiple-uranyl bonding. The sodium ion would be located 1.68 Å above plane formed by the inner O_{per} atoms. This height is nearly as long as the U-O_{ur} bond. For site 3, this configuration is not possible because the Na ion would...
be too close to the $O_{ur,ex}$ atoms in the concave-out ring. Sites 1, 2, and 4 are not limited in this way.

There is another concern regarding $O_{per}$ atoms as viable bonding sites for sodium ions. Computational studies have indicated a covalent character for the peroxide ligand (Vlaisavljevich, Gagliardi, & Burns, 2010). If the $O_{per}$ atoms are more covalent in character, it is less likely that these atoms would form ionic bonds with a sodium ion.

9.3.2 Possible Interactions Between Sodium Ions and Exterior Uranyl Oxygen Atoms in $U_{24}Pp_{12}$

Figure 9.3 shows the possible bonding locations for $O_{ur,ex}$ atoms for both ring conformations in $U_{24}Pp_{12}$. A sodium ion can interact with these oxygen atoms in one of two ways, hypothetically. In the first, a sodium ion could bond to two, three, or four $O_{ur,ex}$ atoms in a multiple-uranyl bond above the topological square. In the second, the Na ion forms a bond with a single $O_{ur,ex}$ atom.
Bond valence calculations were used to analyze the potential for Na ions to bond to a particular oxygen atom. Using the bond valence method (Brown, 1976 a; Brown, 1976 b), with parameters determined in O’Keeffe and Brese (Brese & O’Keeffe, 1991) and Burns (Burns, et al., 1997), bond valences were calculated to be 1.85 v.u. for the O$_{ur,ex}$ atoms in the crystal structure. The ideal bond valence for an oxygen atom is 2 v.u. (Burns, et al., 1997), but a slight over-bonding is possible. Using a bond length of 2.5 Å for Na-O, the calculated strength of the Na-O bond would be approximately 0.15 v.u.. Therefore, it is possible for Na ions to interact with the O$_{ur,ex}$ atoms based on bond valence arguments.
In addition to bond valence arguments, spatial restrictions must also be considered. On site 2 for the concave-out rings, the O_{ur,ex} atoms are arranged similarly to the internal environment of the concave-in ring, where Na ions interact with all of the O_{ur} atoms. Also, due to the O_{ur,ex} atoms pointing towards the center of the ring, it is most likely that the Na cation would bond to all four site 2 O_{ur} atoms.

The geometry of site 1 does not favor four Na-O_{ur} bonds. The O_{ur,ex} atoms are facing away from the center of the ring, and the maximum distance between O_{ur,ex} atoms in possible all possible site 1 locations is 8 Å, measured across the ring. This distance is too long for a O_{ur,ex}-Na-O_{ur,ex} bond, even if the bond angle is 180°. Therefore, any bonding interactions between sodium ions and O_{ur,ex} atoms in site 1 would only involve one O_{ur} atom. It is possible, however, that the cation could bond with two adjacent O_{ur} atoms as well.

9.3.3 Possible Interactions Between Sodium Ions and Pyrophosphate Oxygen Atoms in \textit{U}_{24}\textit{Pp}_{12}

Figure 9.4 shows the possible bonding locations for O_{py} for both ring conformations for \textit{U}_{24}\textit{Pp}_{12}. There are two possible sites for bonding, which will be referred to as O_{py,nb} (site 1) and O_{py,bridge} (site 2). Bonding to either of these sites would be a bond to a single O_{py} atom.
Bond valence calculations for the crystal structure of $U_{24}P_{12}$ were done for both $O_{py,nb}$ and $O_{py,bridge}$. There are three symmetrically distinct $O_{py,nb}$, with an average P-O bond valence of 1.37 v.u., which suggests that the atom would likely be protonated. A Na-O bond would add approximately 0.15 v.u., so it is possible for $O_{py,nb}$ atoms to interact with either one or two sodium ions at a single atom, possibly replacing hydrogen ions.

The bridging pyrophosphate oxygen atoms (site 2 in Figure 9.4) are not available for bonding interactions with sodium ions. The $O_{py,bridge}$ atoms have a bond valence of 2.
v.u. Acceptance of a sodium bond by $O_{py,bridge}$ would result in over-bonding at this site, which is unfavorable.

9.4 Effect of Cation Addition on Aggregation of Aqueous Solutions of $U_{24}Pp_{12}$

When cations are added to the aqueous cluster solutions containing $U_{24}Pp_{12}$, pair distance functions from small angle X-ray scattering and X-ray fluorescence spectroscopy (Chapters 5-7) suggest that at least some of the associated sodium ions are replaced by the added cations. The potential sodium ion locations listed in Section 9.3 are also potential locations for added cations to interact with the cluster. However, the presence of ions alone is not indicative of whether or not aggregation will occur in concentrated solutions. Concentrated (50-65 g/L) and dilute aqueous solutions (0.5 g/L) of $U_{24}Pp_{12}$ will be considered individually.

9.4.1 Effect of Cation Addition on Aggregation for Concentrated Aqueous Solutions of $U_{24}Pp_{12}$

Concentrated aqueous solutions of $U_{24}Pp_{12}$ with no added cations contain sodium ions to balance the charge. For this untreated system, there is no evidence of aggregation over the two-week duration of the experiment (Chapter 4) in dynamic light scattering (DLS) analyses. The untreated system has been examined for long as four months, and no aggregation is noted. This suggests the sodium ions are insufficient to screen the large negative charge of $U_{24}Pp_{12}$ and permit individual clusters to interact with neighboring clusters to form aggregates.

The addition of sodium to the system does not induce aggregation in solution, as confirmed by DLS. As the concentration of sodium ions in the solution increases, a
precipitate containing $\text{U}_{24}\text{Pp}_{12}$ forms. Raman analysis of this precipitate indicates the material is cluster material, thus the clusters may have immediately aggregated to a large enough size for precipitation. Intensity measurements in DLS are size-biased, so even a small amount of aggregation in the solution should have been detectable. In addition, as the precipitation occurs, the reaction (Reaction 8.1) should progress toward further aggregation, based on LeChatelier’s Principle. In the reaction, $C$ is the cluster and $C’$ is the aggregate.

$$nC + m\text{Na}^+ \rightarrow n(\text{Na}-C’)^+ (n-m)\text{Na}^+$$  \hspace{1cm} \text{Reaction 9.1}

It is unlikely that salt concentration in a concentrated aqueous cluster solution determines whether or not aggregation occurs. The charge of monovalent sodium may be important relative to the aggregation of $\text{U}_{24}\text{Pp}_{12}$. Aggregation induced by monovalent, divalent, and trivalent cations in aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ is examined in Chapters 5 to 7. These results are presented in Figure 9.5.
Figure 9.5 Aggregation summary for concentrated solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added cations (indicated by blue circles), where systems of untreated solutions are discrete molecules, systems with added monovalent cations generally show only a small increase in size (possible dimers or trimers), and systems with added divalent and trivalent cations induce aggregation into large assemblies.
With the exception of concentrated solutions of $\text{U}_{24}\text{Pp}_{12}$ with added cesium, monovalent cations do not trigger aggregation beyond dimerization or trimerization of the cluster. This suggests that, overall, the +1 charge does not screen the negative charge of the cluster enough to allow clusters to aggregate. For all the di- and trivalent cations studied, large assemblies were present during DLS analysis of concentrated aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added cations. Therefore, an increased charge (+2 or +3) screens the large negative charge of the cluster more effectively, leading to aggregation of concentrated solutions of $\text{U}_{24}\text{Pp}_{12}$.

9.4.2 Effect of Cation Addition on Aggregation of $\text{U}_{24}\text{Pp}_{12}$ in Dilute Aqueous Solutions with added cations

After one month, untreated dilute solutions of $\text{U}_{24}\text{Pp}_{12}$ did not aggregate. From dynamic light scattering experiments, the scattering intensity remained constant over two more weeks of analyses. Dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ begin to decompose after thirty days, causing a change in the electrospray ionization mass spectrometry (ESI-MS) fingerprint. ESI-MS data for 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ is shown in Figure 9.6.
Figure 9.6 ESI-MS of an aqueous solution of 0.5 g/L $U_{24}P_{p12}$ over 62 days showing the equilibration of the cluster in solution and the beginning of fragmentation of the cluster between measurements on Day 26 and Day 38. Fragmentation is demonstrated by the disappearance of the second marked distribution.
The three systems that produced blackberries when dilute solutions of $\text{U}_{24}\text{Pp}_{12}$ are inoculated with cations (K, Cs, and Cu) are described in detail in Chapter 8. In addition to dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added potassium, cesium, and copper, dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ with added lithium, magnesium, strontium, lanthanum, neodymium, and europium were also prepared. The lithium system did produce a detectable DLS signal indicating that the cluster did not aggregate. The other systems precipitated, so they were not studied.

Although the charge of the ion added to the solutions of $\text{U}_{24}\text{Pp}_{12}$ was important for predicting aggregation in concentrated solutions, the charge does not directly impact aggregation in dilute solutions of $\text{U}_{24}\text{Pp}_{12}$. In dilute solutions, the clusters are more dispersed, meaning greater distances separate them. Therefore, the charge screening in concentrated solutions may be less important for dilute solutions. The presence of blackberries in systems with added potassium and cesium in dilute aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$ demonstrates that monovalent ions can induce aggregation under specific conditions.

In dilute solutions, the concentration of added cations is important in determining aggregation behavior of $\text{U}_{24}\text{Pp}_{12}$. The concentration of cesium and potassium added to solutions of $\text{U}_{24}\text{Pp}_{12}$ was much greater than the amount of copper added to produce blackberries of $\text{U}_{24}\text{Pp}_{12}$. The monovalent ions had concentrations in solution approximately ten times greater than that of divalent copper. This suggests that whether dilute solutions of $\text{U}_{24}\text{Pp}_{12}$ aggregate with the addition of cations is dependent on a combination of the charge of the ion and the concentration of the cation.
9.5 Discussion

Based on the bond-valence calculations for $\text{U}_{24}\text{Pp}_{12}$ and the geometry of the cluster it is likely that cations interact with the cluster at the oxygen atoms of the pyrophosphate group or the external uranyl oxygen atoms of the concave-in rings. It is possible that the pyrophosphate groups are the preferred bonding location for cations. The pyrophosphate oxygen atoms extend furthest into the space between clusters, making the site available. In addition, the pyrophosphate groups in $\text{U}_{24}\text{Pp}_{12}$ can be protonated and deprotonated, which suggests that they could also accept cations. In an untreated aqueous solution of $\text{U}_{24}\text{Pp}_{12}$, the cations present in solution are sodium. When additional cations are added to solution, at least some of the sodium ions are displaced by the added cation, which can lead to aggregation.

The mechanism of aggregation is complicated and has not been thoroughly investigated, but the importance of cation charge and the concentration of the cation in solution are discussed for dilute and concentrated aqueous solutions of $\text{U}_{24}\text{Pp}_{12}$. In concentrated solutions of $\text{U}_{24}\text{Pp}_{12}$, the charge of the added cation is important for determining whether aggregation of the cluster occurs, with monovalent ions tending to trigger only the formation of dimers or trimmers of $\text{U}_{24}\text{Pp}_{12}$ in solution, but di- and trivalent cations cause the formation of large aggregates of $\text{U}_{24}\text{Pp}_{12}$. In dilute solutions of $\text{U}_{24}\text{Pp}_{12}$, the charge of the added cation is less essential to determining aggregation. Aggregation of dilute solutions of $\text{U}_{24}\text{Pp}_{12}$ appears to depend on both the charge and concentration of the added cation in the system—the lower the charge, the greater the concentration of cation that is necessary to induce blackberry formation.
As mentioned in Chapter 8, differences in aggregation behavior between dilute and concentrated cluster solutions may be related to the proximity between clusters. Studies of dilute solutions of $\text{U}_{24}\text{Pp}_{12}$ have indicated that the clusters aggregate into hollow spheres. The movement of clusters required to create blackberries in concentrated solutions may not be possible, especially for the systems with added monovalent cations where the charge of the cluster is not screened as efficiently. If the charge is not screened as effectively, the repulsion between clusters may be too great to allow for free movement to form aggregates.

Insight into what determines aggregation of clusters in solution is important for the nanoscale control of uranium in solution. In order to control blackberry size in solution, it is important to determine which experimental parameters are most essential to inducing aggregation. Additionally, this knowledge can be used to determine the parameter to control in cases where aggregation of the clusters is undesirable.
CHAPTER 10:
AGGREGATION OF URNAYL CLUSTERS IN MIXED-SOLVENT SYSTEMS

10.1 Introduction

Transition metal polyoxometalates (TM-POMs) have been found to aggregate in mixed-solvent systems, such as water-acetone and water-ethanol (Haso et al., 2013). In a mixed-solvent system, the dielectric constant is decreased in comparison to pure aqueous solutions. Previous studies have shown that the dielectric constant is important for the aggregation of POMs (Hunter, 2001). In addition, the alcohol component in alcohol-water mixed solvent systems is attracted to the POM and contributes to hydrogen bonding, resulting in the formation of POM aggregates. No studies of the impact of mixed-solvent systems with uranyl clusters have been reported. In this Chapter, the behaviors of two uranyl clusters, $U_{24}P_{12}$ and $U_{60}$, are analyzed in mixed-solvent systems containing methanol or ethanol and water. The size of the aggregates in solution was monitored using dynamic light scattering (DLS).

10.2 Experimental Methods

10.2.1 Sample Preparation

Crystals of $U_{24}P_{12}$ were synthesized using the procedure described in Chapter 3. Crystals of $Li_xK_y[UO_2(O_2)(OH)]_{60}$, $U_{60}$, were synthesized from mother solutions of 1
mL of aqueous 0.5 M UO₂(NO₃)₂·6H₂O (99+%), 0.25 mL of aqueous 0.4 M KCl (99%), and 1 mL of aqueous 30% hydrogen peroxide. Aqueous 3.4 M LiOH (98%) was added drop-wise until the solution turned translucent orange at approximately pH = 9, which requires about 0.70 mL of aqueous base. Mother solutions were allowed to evaporate under ambient conditions for 7 to 10 days until block-shaped crystals formed. Once crystallization started, the vials were capped and allowed to further crystalize. The total yield of crystals per vial was 15-30 mg of U₆₀.

Similar to previous DLS experiments, crystals of U₂₄P₄₆ and U₆₀ were harvested from their mother solutions and were dissolved in ultrapure water at three concentrations of 0.5, 5, and 50 g of cluster per liter of ultrapure water. Because the clusters are not directly soluble in solutions of methanol or ethanol, the clusters were dissolved in water, and alcohol was added to form the aqueous-alcohol mixed solution. Aliquots of either methanol or ethanol were added to 500 μL of aqueous cluster solutions in 2:1, 1:1, and 1:2 alcohol:aqueous solution mixtures. Table 9.1 lists the starting concentration of clusters in solution for each of the nine aqueous: alcohol solutions studied.

TABLE 10.1

FINAL CLUSTER CONCENTRATION IN MIXED-SOLVENT SYSTEMS BASED ON THE INITIAL CLUSTER CONCENTRATION (TOP ROW) AND THE MIXTURE RATIO (LEFT-MOST COLUMN)

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Start Conc. – 0.5 g/L</th>
<th>Start Conc. – 5 g/L</th>
<th>Start Conc. – 50 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H₂O: Alcohol</td>
<td>0.33 g/L</td>
<td>3.33 g/L</td>
<td>33.3 g/L</td>
</tr>
<tr>
<td>1:1 H₂O: Alcohol</td>
<td>0.25 g/L</td>
<td>2.5 g/L</td>
<td>25 g/L</td>
</tr>
<tr>
<td>1:2 H₂O: Alcohol</td>
<td>0.17 g/L</td>
<td>1.67 g/L</td>
<td>16.7 g/L</td>
</tr>
</tbody>
</table>
Each sample of clusters in each mixed-solvent system was mixed thoroughly and centrifuged for three minutes with a rotational speed of 14000 rotational centrifugal force. After centrifugation, the samples were filtered through 0.2 μm hydrophilic polytetrafluoroethylene filters to remove any suspended particulates and were then transferred into uvettes for DLS analysis. The uvettes were capped and sealed with parafilm to limit evaporation during the duration of the experiment, which was approximately two weeks.

10.2.2 Dynamic Light Scattering of Mixed-Solvent Cluster Solutions

Samples of U_{24}P_{12} and U_{60} in mixed alcohol-water systems were analyzed multiple times using a Malvern Instruments Zetasizer Nano at a single angle (~173°) over two weeks. At each time point, 4 measurements of ten scans (30 seconds per scan) were taken for each sample. The samples were kept at room temperature for the duration of the experiment, but each sample temperature was equilibrated with the DLS sample chamber temperature (maintained at 25 ± 0.5 °C) for each measurement. The refractive indices for the dispersants are listed in Table 2 for methanol and Table 3 for ethanol.
TABLE 10.2

REFRACTIVE INDEX OF WATER-METHANOL MIXTURES
(HERRAEZ & BELDA, 2006)

<table>
<thead>
<tr>
<th>Mixture Ratio (H₂O:EtOH)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1.3396</td>
</tr>
<tr>
<td>1:1</td>
<td>1.3389</td>
</tr>
<tr>
<td>1:2</td>
<td>1.3360</td>
</tr>
</tbody>
</table>

Samples of U₂₄P₁₂ and U₆₀ in mixed alcohol-water systems were monitored periodically over a two-week period, to determine changes in the size of the species in solution. From each measurement, the radius of hydration (Rₗ) was extracted from the intensity distribution data. The Rₗ over time was compared for each concentration, cluster, and solvent. Because the DLS measurements were taken at a single angle, the data are relative and qualitative, and are used to determine whether aggregation is occurring in solution. The numerical values assigned for each sample do not represent the exact size of the species in solution and are for comparative analysis amongst the samples.
TABLE 10.3

REFRACTIVE INDEX OF WATER-ETHANOL MIXTURES (SCOTT, 1946)

<table>
<thead>
<tr>
<th>Mixture Ratio (H₂O:EtOH)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1.355</td>
</tr>
<tr>
<td>1:1</td>
<td>1.362</td>
</tr>
<tr>
<td>1:2</td>
<td>1.366</td>
</tr>
</tbody>
</table>

10.3 Solutions of U₂₄Pp₁₂ in Mixed-Solvent Systems

10.3.1 Water-Methanol Solutions Containing U₂₄Pp₁₂

Three aliquots of methanol were added to each of three concentrations of aqueous solutions of U₂₄Pp₁₂ to give the starting cluster concentrations of U₂₄Pp₁₂ summarized in Table 10.1. When the methanol was added, a yellow precipitate formed in some of the systems. Precipitation from the systems is summarized in Table 10.4. The solutions from each system were separated from the precipitate and analyzed by DLS.

TABLE 10.4

PRECIPITATION OF SOLUTIONS WITH U₂₄PP₁₂ WITH METHANOL

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Start Conc. – 0.5 g/L</th>
<th>Start Conc. – 5 g/L</th>
<th>Start Conc. – 50 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H₂O: MeOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:1 H₂O: MeOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:2 H₂O: MeOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
</tbody>
</table>
According to previous DLS analyses of concentrated aqueous solutions of the U$_{24}$Pp$_{12}$, the base cluster size $R_H$ is approximately 0.6 nm (Chapter 4). Aggregation of U$_{24}$Pp$_{12}$ occurs in solutions where the $R_H$ is greater (>10x) than the base cluster size. The changes in $R_H$ over time for each water-methanol system containing U$_{24}$Pp$_{12}$, as monitored by DLS, are included in Appendix E. The results of aggregation in mixed-solvent water-methanol solutions of U$_{24}$Pp$_{12}$ with various cluster concentrations are summarized in Table 10.5. The sample labels in Table 10.5 will be used for in this section, as well as sections 10.3.2, 10.4.1, and 10.4.2. In it C represents the base cluster (U$_{24}$Pp$_{12}$ or U$_{60}$), C’ represents an aggregate of the base cluster C, and C” represents an agglomerate of aggregates C’. Any combination of these labels will be indicated by including both species present separated by a slash.

**TABLE 10.5**

**SUMMARY OF AGGREGATION IN MIXED-SOLVENT WATER-METHANOL SOLUTIONS WITH U$_{24}$PP$_{12}$**

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Low Cluster Concentration</th>
<th>Moderate Cluster Concentration</th>
<th>High Cluster Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H$_2$O: MeOH</td>
<td>C’/C”</td>
<td>C’/C”</td>
<td>C’</td>
</tr>
<tr>
<td>1:1 H$_2$O: MeOH</td>
<td>C’</td>
<td>C’/C”</td>
<td>C’/C”</td>
</tr>
<tr>
<td>1:2 H$_2$O: MeOH</td>
<td>C’</td>
<td>C’/C”</td>
<td>C’/C”</td>
</tr>
</tbody>
</table>

For all the water-methanol mixed solvent systems studied containing U$_{24}$Pp$_{12}$, large species were present in the solution. The addition of methanol to each of three concentrations of aqueous solutions of U$_{24}$Pp$_{12}$ induced aggregation of the cluster. Of the
three concentrations of $U_{24}Pp_{12}$ with each water-methanol mixed-solvent ratio, the lowest concentrations of $U_{24}Pp_{12}$ resulted in aggregates that were the most stable for the 1:1 and 1:2 systems, as the $R_H$ remained relatively constant. The aggregate size of the 33.3 g/L $U_{24}Pp_{12}$ in the 2:1 water-methanol mixed solvent system was also stable over the two-week period. The other systems exhibited changes in $R_H$ that suggest agglomeration ($R_H$ increasing) and/or deagglomeration ($R_H$ decreasing) of the aggregates of $U_{24}Pp_{12}$.

10.3.2 Water-Ethanol Solutions Containing $U_{24}Pp_{12}$

Three aliquots of ethanol were added to three concentrations of aqueous solutions of $U_{24}Pp_{12}$ to give the starting cluster concentrations of $U_{24}Pp_{12}$ summarized in Table 10.1. When the ethanol was added, a yellow precipitate formed in some of the systems. Precipitation from the systems is summarized in Table 10.6. The solutions from each system were separated from the precipitate and analyzed by DLS. The changes in $R_H$ over time for each water-ethanol system containing $U_{24}Pp_{12}$, as monitored by DLS, are included in Appendix E.
TABLE 10.6

PRECIPITATION OF SOLUTIONS WITH U$_{24}$PP$_{12}$ WITH ETHANOL

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Start Conc. – 0.5 g/L</th>
<th>Start Conc. – 5 g/L</th>
<th>Start Conc. – 50 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H$_2$O: EtOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
</tr>
<tr>
<td>1:1 H$_2$O: EtOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:2 H$_2$O: EtOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
</tbody>
</table>

Aggregation of U$_{24}$PP$_{12}$ occurs in solutions with an R$_H$ exceeding approximately 10 nm. For all the water-ethanol systems studied, U$_{24}$PP$_{12}$ aggregated upon addition of ethanol to the system. The results of aggregation in mixed-solvent water-methanol solutions of U$_{24}$PP$_{12}$ with various cluster concentrations are summarized in Table 10.7. The labeling for Table 10.7 is explained in Section 10.3.1.

TABLE 10.7

SUMMARY OF AGGREGATION IN MIXED-SOLVENT WATER-ETHANOL SOLUTIONS WITH U$_{24}$PP$_{12}$

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Low Cluster Concentration</th>
<th>Moderate Cluster Concentration</th>
<th>High Cluster Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H$_2$O: EtOH</td>
<td>C'/C''</td>
<td>C'</td>
<td>C'</td>
</tr>
<tr>
<td>1:1 H$_2$O: EtOH</td>
<td>C'/C''</td>
<td>C'</td>
<td>C'/C''</td>
</tr>
<tr>
<td>1:2 H$_2$O: EtOH</td>
<td>C'/C''</td>
<td>C'</td>
<td>C'</td>
</tr>
</tbody>
</table>

For all the water-ethanol mixed solvent systems studied with U$_{24}$PP$_{12}$, large species were present in solution. The addition of ethanol to U$_{24}$PP$_{12}$ induced aggregation. Of the three concentrations of U$_{24}$PP$_{12}$ with each water-ethanol mixed-solvent ratio, the
moderate concentrations of $U_{24}P_{12}$ contain aggregates with the most stable sizes, indicated by a relatively constant $R_H$ for the duration of the experiment. The size of the aggregate in the 3.33 g/L $U_{24}P_{12}$ in 2:1 water-ethanol system, 2.5 g/L $U_{24}P_{12}$ in 1:1 water-ethanol system, and 1.67 g/L $U_{24}P_{12}$ in 1:2 water-ethanol system remains approximately constant over the two-week period. In the other water-ethanol systems, the $R_H$ fluctuated over time, which indicates agglomeration ($R_H$ increasing) and/or deagglomeration ($R_H$ decreasing).

10.4 Solutions of $U_{24}P_{12}$ in Mixed-Solvent Systems

10.4.1 Water-Methanol Solutions Containing $U_{60}$

Three aliquots of methanol were added to three concentrations of aqueous solutions of $U_{60}$ to give the starting cluster concentrations of $U_{60}$ summarized in Table 10.1. When the methanol was added, a yellow precipitate formed in some of the systems. Precipitation from the systems is summarized in Table 10.8. The solutions from each system were separated from the precipitate and analyzed by DLS. The changes in $R_H$ over time for each water-methanol system containing $U_{60}$, as monitored by DLS, are included in Appendix E.
TABLE 10.8

PRECIPITATION OF SOLUTIONS WITH U_{60} WITH METHANOL

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Start Conc. – 0.5 g/L</th>
<th>Start Conc. – 5 g/L</th>
<th>Start Conc. – 50 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H_{2}O: MeOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:1 H_{2}O: MeOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:2 H_{2}O: MeOH</td>
<td>No Precipitate</td>
<td>Precipitate</td>
<td>Precipitate</td>
</tr>
</tbody>
</table>

According to previous DLS analyses of concentrated aqueous solutions of U_{60}, the base cluster size in has an R_{H} of approximately 1 nm (Wallace, 2013). Aggregation of U_{60} occurs in solutions where the R_{H} is greater (>10x) than the base cluster size. The results of aggregation in mixed-solvent water-methanol solutions of U_{60} with various cluster concentrations are summarized in Table 10.9. The labeling for Table 10.9 is explained in Section 10.3.1.

TABLE 10.9

SUMMARY OF AGGREGATION IN MIXED-SOLVENT WATER-METHANOL SOLUTIONS WITH U_{60}

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Low Cluster Concentration</th>
<th>Moderate Cluster Concentration</th>
<th>High Cluster Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H_{2}O: EtOH</td>
<td>C’</td>
<td>C’/C”</td>
<td>C’</td>
</tr>
<tr>
<td>1:1 H_{2}O: EtOH</td>
<td>C’/C”</td>
<td>C’</td>
<td>C’</td>
</tr>
<tr>
<td>1:2 H_{2}O: EtOH</td>
<td>C’/C”</td>
<td>C’</td>
<td>C’/C”</td>
</tr>
</tbody>
</table>

For all the water-methanol mixed solvent systems studied with U_{60}, large species were present in the solution, which means the addition of methanol to U_{60} induced
aggregation. Of the three concentrations of U$_{60}$ with each water-methanol mixed-solvent ratios, the moderate concentrations of U$_{60}$ show the most stable aggregates, in terms of size, for the 1:1 and 1:2 water-methanol mixed solvent systems, indicated by a relatively unchanging R$_{H}$ for the duration of the experiment. The higher concentrations of U$_{60}$ were showed the least variability in size for the 2:1 and 1:1 water-methanol mixed-solvent systems. The size of the species in solution in the 0.33 g/L and 33.3 g/L concentrations of U$_{60}$ in 2:1 water-methanol system, 2.5 g/L and 25 g/L concentrations of U$_{60}$ in 1:1 water-methanol system, and 1.67 g/L concentration of U$_{60}$ in 1:2 water-methanol system remains approximately constant over the two-week period. Agglomeration of aggregates likely occurred in the other systems, indicated by R$_{H}$ increasing over the two-week period.

10.4.2 Water-Ethanol Solutions Containing U$_{60}$

Three aliquots of ethanol were added to three concentrations of aqueous solutions of U$_{60}$ to give the starting cluster concentrations of U$_{60}$ summarized in Table 10.1. When the ethanol was added, a yellow precipitate formed in some of the systems. Precipitation from the systems is summarized in Table 10.10. The solutions from each system were separated from the precipitate and analyzed by DLS. The changes in R$_{H}$ over time for each water-methanol system containing U$_{60}$, as monitored by DLS, are included in Appendix E.
TABLE 10.10
PRECIPITATION OF SOLUTIONS WITH U₆₀ WITH ETHANOL

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Start Conc. – 0.5 g/L</th>
<th>Start Conc. – 5 g/L</th>
<th>Start Conc. – 50 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H₂O: EtOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:1 H₂O: EtOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
<tr>
<td>1:2 H₂O: EtOH</td>
<td>No Precipitate</td>
<td>No Precipitate</td>
<td>Precipitate</td>
</tr>
</tbody>
</table>

Aggregation of U₆₀ occurs in solutions with an Rₕ exceeding approximately 10 nm. For all the water-ethanol mixed solvent systems studied with U₆₀, large species were present in the solution, which means the addition of ethanol to U₆₀ induced aggregation. The results of aggregation in mixed-solvent water-methanol solutions of U₂₄Pp₁₂ with various cluster concentrations are summarized in Table 10.11. The labeling for Table 10.7 is explained in Section 10.3.1.

TABLE 10.11
SUMMARY OF AGGREGATION IN MIXED-SOLVENT WATER-ETHANOL SOLUTIONS WITH U₆₀

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Low Cluster Concentration</th>
<th>Moderate Cluster Concentration</th>
<th>High Cluster Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 H₂O: EtOH</td>
<td>C’/C”</td>
<td>C’</td>
<td>C’</td>
</tr>
<tr>
<td>1:1 H₂O: EtOH</td>
<td>C’/C”</td>
<td>C’</td>
<td>C’</td>
</tr>
<tr>
<td>1:2 H₂O: EtOH</td>
<td>C’/C”</td>
<td>C’/C”</td>
<td>C’</td>
</tr>
</tbody>
</table>

Of the three concentrations of U₆₀ with each water-methanol mixed-solvent ratios, the moderate concentrations of U₆₀ are the most stable for the 2:1 and 1:1 water-ethanol
mixed solvent systems. The higher concentrations of U$_{60}$ produced aggregates with the most consistent sizes for all three water-methanol mixed-solvent systems studied. The size of the species in solution in the 3.33 g/L and 33.3 g/L concentrations of U$_{60}$ in 2:1 water-ethanol system, 2.5 g/L and 25 g/L concentrations of U$_{60}$ in 1:1 water-ethanol system, and 16.7 g/L concentration of U$_{60}$ in 1:2 water-ethanol system remains approximately constant over the two-week period. Agglomeration of aggregates likely occurred for all three mixed solvent systems studied at low cluster concentration, and well as for the moderate concentration of U$_{60}$ in 1:2 water-ethanol mixed solvent system.

10.5 Discussion

From the experiments in this Chapter, it is apparent that the addition of a polar solvent to an aqueous cluster solution of U$_{24}$P$_{12}$ or U$_{60}$ induced aggregation of the base cluster in solution. The presence of aggregates in solution was not dependent on the amount of methanol or ethanol added to each system or the concentration of cluster in solution. This aggregation is likely caused by a decrease in the dielectric constant for the solution when the alcohol is added, in comparison to the aqueous cluster solution, as well as hydrogen bonding between the respective cluster and the alcohol molecule.

The dielectric constant for a particular solution describes the solution’s polarity. As the dielectric constant decreases, so does the polarity of the solvent. This results in a decrease of the effective charge of a particle in the solvent. As stated in previous chapters on aggregation of U$_{24}$P$_{12}$, screening or decreasing the effective charge of the uranyl clusters increases the probability that aggregation of clusters will occur. Because aggregation occurs as the polarity of the solvent decreases for solutions of U$_{24}$P$_{12}$ and
U₆₀, it is also likely that increasing the temperature of solution may be another way to induce aggregation, as temperature increases result in a decrease of the dielectric constant of water.

For systems containing U₂₄Pp₁₂, the most stable aggregates formed in solutions with low and moderate cluster concentrations. Higher cluster concentrations tended to display fluctuations in the aggregate sizes. For U₆₀, the most stable aggregates formed in solutions with moderate to high cluster concentrations, with fluctuation in aggregate sizes observed at low concentrations. The differences in the formation of stable aggregates at varying cluster concentrations may be related to the bridging ligands available for hydrogen bonding. In the case of U₂₄Pp₁₂, the bridging ligand is the pyrophosphate group, which can protonate or deprotonate. In U₆₀, the bridging ligand is the hydroxyl group. The pyrophosphate group extends further into the space between clusters, which may enable the formation of multiple hydrogen bonds, resulting in larger aggregates or increased agglomeration, both of which may result in precipitation of the species or instability. Uranyl oxygen atoms are also possible sites for hydrogen bonding, but they are not considered here as computational studies have shown that these atoms are very poor hydrogen bond acceptors (Watson & Hay, 2011). However the uranyl oxygen atoms in U₆₀ may preferentially accept hydrogen bonds at these sites because the uranyl oxygen atoms extend furthest into the space between clusters.

Uranyl POMs, such as U₆₀ and U₂₄Pp₁₂, are very new in polyoxometalate chemistry, relative to the centuries old TM-POMs. As such, comparisons between uranyl POMs and TM-POMs provide valuable information, including how the use of actinides in the shell of the cluster can impact solution behavior (Nyman & Burns, 2012). The
behaviors of \( \text{U}_{24}\text{P}_{12} \) and \( \text{U}_{60} \) in mixed solvent alcohol-water systems are consistent with the behavior of transition metal polyanion metalates in similar systems. Studies have shown that clusters of \( \text{K}_{56}\text{Li}_{74}\text{H}_{22}[\text{Mn}_{40}\text{P}_{32}\text{W}_{224}\text{VIO}_{888}]^{152-} \) aggregate into hollow, spherical assemblies, blackberries, in methanol-water solutions due to the non-directional hydrogen bonding between the clusters and the alcohol molecules (Haso, et al., 2013). Aggregation of POMs is an important phenomenon because it expands the application of POMs from nanometer-sized structures into micron-sized applications in a variety of fields, including energy and optics (Long, et al., 2010).
CHAPTER 11:
PRELIMINARY NEUTRON DIFRACTION STUDIES OF U$_{24}$P$_{12}$

11.1 Introduction

Single crystal X-ray diffraction has been used extensively to determine the structures of uranyl peroxide clusters. The X-ray diffraction patterns are heavily dominated by scattering from uranium, and the data has been sufficient to resolve the locations of the U and O atoms constituting the cage of uranyl polyhedra. The data also have allowed for location of a variety of heavier counter ions. X-ray diffraction structures are limited, however, due to the inability to locate hydrogen atoms or light alkali counter ions that are present in the structure of the clusters. This is because the scattering efficiencies of these ions are much lower than uranium, and potentially disordered in some cases.

While X-rays diffract due to interactions with the electrons of an atom, neutrons diffract due to interactions with a nucleus of an atom. Neutron scattering factors are not dependent on the number of electrons. Thus, neutron diffraction can potentially be used to resolve the location of hydrogen and other light atoms within the structure of uranyl nanoclusters. This Chapter presents preliminary results from a proof-of-concept experiment conducted at the Spallation Neutron Source at Oak Ridge National Laboratory for the single-crystal neutron diffraction of U$_{24}$P$_{12}$. This experiment was conducted at beamline 12 on the TOPAZ single-crystal diffractometer.
11.2 Experimental Procedures

11.2.1 Synthesis of Millimeter-Sized Crystals of U\textsubscript{24}Pp\textsubscript{12}

Single-crystal neutron diffraction requires large, millimeter-sized crystals. The general synthesis of crystals of U\textsubscript{24}Pp\textsubscript{12} as described in depth in Chapter 3, results in crystals that are approximately 200 to 400 μm, which are unsuitable for neutron analysis. To synthesize crystals of millimeter size, mother solutions contained in vials were covered with Parafilm to slow nucleation and crystal growth, and yielded the growth of crystals in excess of one millimeter.

11.2.2 Mounting of Crystals of U\textsubscript{24}Pp\textsubscript{12}

Because this experiment was proof-of-concept and the materials were new to Oak Ridge National Laboratory’s Spallation Neutron Source (SNS), special consideration was given to the shipping and containment of the samples. Samples were mounted at the University of Notre Dame and shipped to the SNS prior to analysis. In Chapter 3, the stability of crystals of U\textsubscript{24}Pp\textsubscript{12} in air was probed. Upon exposure to air, crystallinity is diminished. To decrease the exposure of crystals to air, they were mounted using silicone-based vacuum grease.

Once the crystal was coated by the grease, the large crystal was gently placed in a 1.5 millimeter outer diameter Kapton tube that was heat sealed at one end. The crystal was positioned in the tubing no more than 0.5 mm from the heat-sealed edge, as shown in Figure 11.1. Extra grease was placed in the tubing and the tube was then epoxied to a magnetic Hampton base with stainless steel pin. The total height of the assembly, per the
specifications of the beamline scientists, was 21 mm. The entire assembly was covered with a protective cap, and shipped to the SNS.

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Figure 11.1 A magnified image of a crystal of U$_{24}$P$_{12}$ in grease sealed within a Kapton tube that is heat-sealed on the left end. For clarity, the approximate crystal dimensions have been outlined in green. The scale bar indicates 1 mm.

11.2.3 Preparation for Neutron Diffraction of U$_{24}$P$_{12}$

Upon arrival at the SNS, mounted samples were inspected at the TOPAZ hutch area under an optical microscope to ensure that the crystals were still intact and not damaged in the shipping process. A mounted sample was selected based on size and lack of apparent defects and placed on the goniometer. Figure 11.2 shows the sample mounted on the goniometer with the goniometer removed from the detector area. The goniometer arm was then lowered into the detector arrangement, and the hutch secured.
Figure 11.2 Sample mounting arrangement for the TOPAZ single-crystal diffractometer. The arrow points to the sample mounted in Kapton tube on a Hampton base affixed magnetically to the goniometer head. Below the mounted area is the detector array and the cold stream.

The detector array at TOPAZ is shown in Figure 11.3. The instrument has a total of 13 detectors arranged spherically around the sample, when the sample is lowered into position. These 13 detectors account for angular coverage of 1.2 steradians. The sample-to-detector distance ranges between 39 and 45 cm, and the source-sample-
detector distance is 18 m. The source is a neutron beam with a 2.5 mm diameter (Hoffman & Wang, 2013).
Figure 11.3 An example of the detector array for TOPAZ. Each dark brown square represents a detector, which is a two-dimensional energy dispersive Anger camera detector. Currently there are thirteen detectors around the instrument. The blue circle represents the placement of the sample in relation to the detectors, and blue lines from this circle represent diffraction to a particular detector (Hoffman & Wang, 2013).
11.2.4 Structure Solution of $U_{24}Pp_{12}$

Structure solution for both single-crystal X-ray diffraction and single-crystal neutron diffraction are explained in more detail in Chapter 2. The outline for structure solution for X-ray diffraction is summarized in Table 2.2, and the summary for neutron diffraction is given in Table 2.3. After the absorption correction, the procedures for the two radiation types are identical except for the selection of scattering curves during refinement.

For neutron diffraction, the neutron structure is added to a structure that was first solved using X-ray diffraction. The SHELX software is designed in a manner where $q$-peaks correspond to electron density, which means that an element with a larger electron density like uranium would produce a larger $q$-peak than a lighter element like oxygen. Because neutron diffraction is based on interactions with the nucleus of an element, the $q$-peaks in the SHELX software do not work in the same way. An “FMAP -2” command in the list file allows the program to generate positive and negative $q$-peaks to relate to the scattering length of neutrons. Some isotopes of elements, such as H, produce a negative $q$-peak to indicate a negative scattering length, which makes it much easier to refine such elements. For neutrons, the scattering length can be negative or positive based on the phase shift as the neutron is ejected from the nucleus. Positive $q$-peaks do not have the same character as $q$-peaks in X-ray scattering and can be very similar for different elements. Thus it is easier to start a neutron structure solution with a structure solved by X-ray diffraction.
11.3 X-ray Diffraction of U$_{24}$Pp$_{12}$

The structure of one conformation (crystal orientation) of a crystal of U$_{24}$Pp$_{12}$ solved by X-ray diffraction has been published previously (Ling et al., 2010). However, the published solved structure is from a different synthesis of U$_{24}$Pp$_{12}$ and is a different conformation. Using a razor blade, a small segment of a crystal U$_{24}$Pp$_{12}$ was placed in oil and mounted on a cryoloop. The crystal structure was analyzed using a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized MoKα radiation at a temperature of 100K. The Bruker SHELXL suite of programs was used to solve and refine the crystal structure. CrystalMaker v8.7.2 was used to develop crystal structure diagrams. Figure 11.1 illustrates the cage cluster.

![Figure 11.1](image1.png)

**Figure 11.1** Crystal structure of U$_{24}$Pp$_{12}$ from single-crystal X-ray diffraction structure solution. The orientation of the crystal in the x,y direction is shown in (a) and the orientation in the x,z direction is shown in (b), where the yellow polyhedra are uranyl polyhedra and the purple polyhedra are pyrophosphate groups. The two orientations demonstrate the oblate nature of the cluster, with four of the six uranyl tetramers with concavity towards the center of the cluster (central tetramer in a), the remaining two uranyl tetramers having opposite concavity (central tetramer in b).
In addition to the cage of the cluster, the structure solution from single-crystal X-ray diffraction gave positions of two sodium atoms located inside the cage cluster. Both of the sodium atoms were located below the uranyl tetramers of the concave-in rings, where they bond with all four uranyl oxygen atoms of a tetramer. The bonding environment is shown in Figure 9.1 in Chapter 9.

11.4 Preliminary Neutron Diffraction of $\text{U}_{24}\text{Pp}_{12}$

As this experiment is a proof-of-concept experiment, the desired finding is that a crystal of $\text{U}_{24}\text{Pp}_{12}$ diffracts in the neutron beam and the resulting data gives additional information beyond that which can be obtained using X-ray diffraction. Both crystals that were analyzed diffracted, and a full data collection was conducted on one of these samples. It required five days to generate a complete data set with optimal redundancy. Although data were obtained from this experiment, the background was high due to the use of regular vacuum grease instead of fluorinated grease and the use of the Kapton tubing.

Within the limitations of the data due to the high background, the data provided some additional information about the structure of $\text{U}_{24}\text{Pp}_{12}$. Once the neutron data was collected, the X-ray structure solution was used to further resolve additional atoms. The cage of the cluster remains unchanged in this process. The neutron data only gave additional information regarding the hydrogen atoms and sodium atoms within and outside the cluster. However, the $R$ value for the cluster is still very high (approximately 23%), so the data must be improved.
From the preliminary neutron diffraction data, sodium ions outside the cluster were located and refined. The sodium polyhedra are shown in blue in Figure 11.2. The sodium ions appear to group around the cluster in the vicinity of the pyrophosphate groups. The locations of some hydrogen atoms were also determined from the data, but due to the quality of the data, not all the locations are certain. A list of selected bond distances is given in Table 11.1.

Figure 11.5 Crystal structure of U$_{24}$P$_{12}$ from single-crystal neutron diffraction data without hydrogen atoms shown. The orientation of the crystal in the x,y direction is shown in (a) and the orientation in the x,z direction is shown in (b), where the yellow polyhedra are uranyl, the purple are pyrophosphate, and the blue are sodium.
### TABLE 11.1

SELECTED BOND DISTANCES IN THE STRUCTURE SOLUTION OF U$_{24}$PP$_{12}$ FROM NEUTRON DIFFRACTION DATA

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Distance (Å)</th>
<th>Bond</th>
<th>Bond Distance (Å)</th>
<th>Bond</th>
<th>Bond Distance (Å)</th>
</tr>
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<tr>
<td>U1—O17</td>
<td>1.78 (2)</td>
<td>U7—O8</td>
<td>1.776 (15)</td>
<td>Na1—O44</td>
<td>2.28 (3)</td>
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<td>U7—O37</td>
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<td>Na1—O3</td>
<td>2.35 (2)</td>
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<td>2.360 (17)</td>
<td>U7—O22</td>
<td>2.363 (17)</td>
<td>Na1—O71</td>
<td>2.42 (3)</td>
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<td>2.360 (17)</td>
<td>U7—O28</td>
<td>2.383 (16)</td>
<td>Na1—O49</td>
<td>2.47 (2)</td>
</tr>
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<td>2.364 (17)</td>
<td>U7—O59</td>
<td>2.392 (16)</td>
<td>Na1—O25</td>
<td>2.46 (2)</td>
</tr>
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<td>U1—O26</td>
<td>2.364 (17)</td>
<td>U7—O13</td>
<td>2.383 (17)</td>
<td>Na1—O53</td>
<td>2.48 (3)</td>
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<td>U7—O6</td>
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<td>2.38 (5)</td>
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<td>U7—O48</td>
<td>2.45 (2)</td>
<td>Na2—O77</td>
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<td>P1—O5</td>
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<td>P1—O1</td>
<td>1.53 (2)</td>
<td>Na4—O73</td>
<td>2.47 (4)</td>
</tr>
<tr>
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<td>P1—O31</td>
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<td>Na4—O64</td>
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<td>3.40 (3)</td>
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<td>P1—Na3</td>
<td>3.41 (3)</td>
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<tr>
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<td>P2—O13</td>
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</table>
11.5 Discussion

In so far as it was a proof-of-concept experiment, the single crystal neutron diffraction study of U$_{24}$P$_{12}$ was a success. The crystal selected for analysis diffracted and data was obtained that contributed to further solution of the structure of the cluster. However, due to the high background, the data did not result in a publishable structure solution. Further work was scheduled for October 2014, but due to target and chopper problems at the SNS, the beamtime was postponed until April 2015. In order to address the background issues, fluorinated grease will be used to coat pre-mounted crystals at the
University of Notre Dame prior to shipment to the SNS. In addition, unmounted crystals will be sent in their mother solution and mounted on a cryoloop directly at the SNS, which will likely result in better data with lower background diffraction.
12.1 Importance of Conducted Research

The research examined in this dissertation expands the knowledge of the behavior of uranyl peroxide nanoclusters, primarily $\text{U}_{24}\text{Pp}_{12}$, in the crystalline and aqueous states. Uranyl peroxide nanoclusters are novel materials with potential applications in an advanced nuclear fuel cycle. One such application includes the use of nanoclusters in reprocessing and recovering uranium from irradiated fuel (Wylie, et al. 2014). For uranyl clusters to be used most efficiently and effectively, more information must be available regarding their structure and solution behavior, especially in proposed aqueous reprocessing conditions. Additionally, information on solution behavior of uranyl clusters allows for comparisons between uranyl clusters and well-established transition metal polyoxometalates.

12.2 Solubility and Characterization of $\text{U}_{24}\text{Pp}_{12}$

The Burns group has synthesized a large family of uranyl peroxide cage clusters inspired by the mineral studtite. One of these cage clusters is $\text{U}_{24}\text{Pp}_{12}$, a uranyl peroxide pyrophosphate cluster with six uranyl tetreriaers linked through twelve pyrophosphate ligands. Each pyrophosphate ligand is bidentate to two uranyl tetreriaers. Previous bulk
characterization of this cluster has not been possible due to low yield and impure syntheses.

After optimization and scaling of the U$_{24}$Pp$_{12}$ synthesis, solubility and characterization of the cluster became possible. Solubility experiments have indicated that crystals of U$_{24}$Pp$_{12}$ release approximately 50,000 ppm of uranium into solution, yielding a maximum solution concentration of 69 g/L U$_{24}$Pp$_{12}$ in ultrapure water. Relative to uranyl phosphate minerals, the solubility of U$_{24}$Pp$_{12}$ crystals is approximately six orders of magnitude greater. From ultra small angle X-ray scattering experiments of aqueous solutions of U$_{24}$Pp$_{12}$ at multiple concentrations, the distance between clusters in solution was determined to be approximately 4 nm from center to center of neighboring clusters at 69 g/L. This is the minimum distance between clusters in a stable solution and is supported by mathematical calculations for minimum distance.

In addition to the solubility of U$_{24}$Pp$_{12}$ crystals, the stability of crystals of U$_{24}$Pp$_{12}$ was probed using electrospray-ionization mass spectrometry, Raman spectroscopy, thermogravimetric analysis, and powder X-ray diffraction. Crystals of U$_{24}$Pp$_{12}$ dehydrate in air, resulting in diminished crystallinity. The cluster material, however, remains intact. The decrease in crystallinity corresponds with the loss of water in the solid, suggesting that remaining waters are mostly essential to the persistence of individual clusters of U$_{24}$Pp$_{12}$.

Data from ultra small angle X-ray scattering experiments of aqueous solutions of U$_{24}$Pp$_{12}$ have shown that the radius of gyration of the cluster is approximately 9 Å. U$_{24}$Pp$_{12}$ is modeled as a core-shell species, with a shell density greater than the core and solvent densities. The pair distance functions calculated from these experiments support a
core-shell species and indicate interactions between the uranyl pyrophosphate cluster and sodium ions, which crystallize with the cluster. The interactions between the cluster and sodium ions in solution become more prominent as the concentration of cluster in solution increases, and the ions are more likely to be found closer to $U_{24}Pp_{12}$.

Dynamic light scattering analyses of concentrated aqueous solutions of $U_{24}Pp_{12}$ show that the clusters remain as discrete particles for over two months after crystals of the cluster are dissolved in water. The radius of hydration remains less than one nanometer for the duration of the experiment. Unlike what is expected from comparison to transition metal polyoxometalates, $U_{24}Pp_{12}$ did not aggregate in aqueous solution under ambient conditions after two months in either concentrated (65 g/L) or dilute (0.5 g/L) cluster concentrations.

12.3 Cation Mediated Aggregation of $U_{24}Pp_{12}$

Because aqueous solutions of $U_{24}Pp_{12}$ do not aggregate spontaneously in a reasonable timeframe, two methods of inducing aggregation in solution were investigated in this dissertation. The first method probed was cation-mediated aggregation by the addition of nitrate salts to aqueous cluster solutions. Conditions in which clusters and other ions are present simultaneously are representative of reprocessing conditions, where fission products can also leach from the irradiated fuel matrix, and environmental contamination, where clusters can interact with environmentally relevant cations or co-contaminants. To better understand the behavior of clusters in these situations, it is important to probe cluster-ion interactions.
When nitrate salts are added to concentrated aqueous solutions of $\text{U}_2\text{Pp}_12$ at 65 g/L, cation-mediated aggregation is dependent on the charge of the added cation. The addition of monovalent cations does not induce aggregation immediately, and, with the exception of systems with added cesium, the clusters do not aggregate over time. However, systems of $\text{U}_2\text{Pp}_12$ with added divalent and trivalent cations do induce aggregation immediately. Ultra small-angle X-ray scattering data also show changes in the cluster-cation interactions after cations are added to aqueous cluster solutions.

The resulting precipitates from concentrated aqueous solutions of $\text{U}_2\text{Pp}_12$ with added cations were characterized using powder X-ray diffraction, Raman spectroscopy, and X-ray fluorescence spectrometry. Analyses of these powders indicated that the precipitates contained all of uranium, phosphorus, and the respective added cation. Raman spectroscopy verified the presence of cluster material in the precipitates by the presence of the the uranyl and pyrophosphate vibrational modes. Shifting of the position (wavenumber) of uranyl and pyrophosphate modes in the precipitates resulted from interactions between the cation and the uranyl and pyrophosphate oxygen atoms respectively. The cations bonding at these sites is supported by bond valence calculations for $\text{U}_2\text{Pp}_12$.

For dilute solutions of $\text{U}_2\text{Pp}_12$, cation-mediated aggregation is not dependent only on the charge of the cation. Aqueous systems of $\text{U}_2\text{Pp}_12$ systems (0.5 g/L) were probed after the addition of monovalent (K and Cs) and divalent (Cu) cations. The combination of multi-angle dynamic light scattering experiments and static light scattering experiments verified that the clusters assembled into hollow, spherical aggregates in solution, in agreement with the blackberries reported in transition metal polyoxometalate
aggregation studies. The addition of different cations produced monodisperse solutions of aggregates with differing diameters, suggesting that blackberry size can be controlled by the cation added to the system. In these systems, cation-mediated aggregation was dependent on a combination of the charge of the cation and the amount of cation added to the dilute cluster solutions, with systems with added monovalent cations requiring much larger concentration of salt than required for systems with added divalent cations to induce aggregation.

12.4 Aggregation of Uranyl Peroxide Nanocluster in Mixed Solvent Systems

The second method of inducing aggregation was the use of mixed solvent systems. Aggregation of clusters of $U_{60}$ and $U_{24}Pp_{12}$ were studied in water-ethanol and water-methanol systems. For both clusters at all cluster concentrations and water-alcohol ratios, large species formed in solution, indicating aggregation. When polar organic solvents are added to the aqueous cluster solution, the dielectric constant decreases, allowing for increased interactions between clusters. This results in aggregation of $U_{24}Pp_{12}$ and $U_{60}$, similar to what has been reported for transition metal polyoxometalates in mixed solvent systems.

12.5 Neutron Diffraction of $U_{24}Pp_{12}$

Preliminary studies of single-crystal neutron diffraction of $U_{24}Pp_{12}$ were conducted to demonstrate proof-of-concept. Previously, structures of uranyl peroxide nanoclusters have been solved using single-crystal X-ray diffraction. These structure solutions are, in some cases, incomplete because X-ray diffraction is heavily biased
toward elements with larger electron densities, making it difficult to locate the positions of light elements such as hydrogen and lithium. Neutron diffraction is not biased in this way, and single crystal neutron diffraction can be used to provide a more complete crystal structure for uranyl clusters.

Single crystal neutron diffraction of $\text{U}_{24}\text{Pp}_{12}$ allowed for location of more sodium ion and hydrogen positions outside the cluster. However, the quality of the data was limited by the high background, attributed to the use of non-fluorinated vacuum grease and encapsulation of the crystal in Kapton tubing. Due to the high background, hydrogen positions were not all certain.

Further experimentation is necessary and was originally scheduled for October 2014, but the beamtime has been postponed until Spring 2015 due to issues at the Spallation Neutron Source (SNS). To improve the data, crystals will be mounted directly from mother solution at the SNS, eliminating the background due to the Kapton tubing. In addition, fluorinated vacuum grease, or Krytox, will be used to preserve the crystal. Both of these efforts should result in a decreased background and better neutron data, allowing for determination of more certain hydrogen and sodium positions.
APPENDIX A:

PUBLICATIONS AND CONFERENCE PRESENTATIONS

A.1 Publications


A.2 Publications in Preparation

Pellegrini, Kristi L.; Balboni, Enrica; Simms, Zoë N., Bell, Cassidi M.; Ilavsky, Jan; Szymanoski, Jennifer E.S.; Burns, Peter C. Analyzing high solubilities of uranyl cage cluster by probing the effect of cluster concentration.

Pellegrini, Kristi L.; Simms, Zoë N.; Evans, Isaac; Liu, Tianbo; Burns, Peter C. Cation-Mediated Aggregation in Concentrated Solutions of a Uranyl Pyrophosphate Polyoxometate Containing 24 Uranyl Polyhedra

A.3 Conference Presentations

Pellegrini, Kristi L.; Simms, Zoë N.; Bell, Cassidi M.; Szymanowski, Jennifer E.S.; Liu, Tianbo; Burns, Peter C. The Behavior of U$_{24}$P$_{12}$ Upon Addition of Salt to Aqueous Solutions. Energy Frontier Research Center Materials Science of Actinides All Hands Meeting, University of Notre Dame, Notre Dame, IN, November 2014

Pellegrini, Kristi L.; Martinez, Nicholas; Burns, Peter C. Induced Aggregation of U$_{24}$Py$_{12}$ by Adjustment of pH and the Addition of Metal Cations”. American Chemical Society Fall Meeting, Indianapolis, IN. September 2013

Pellegrini, Kristi L.; Martinez, Nicholas; Jouffret, Laurent; Burns, Peter C. Dissolution Studies of Autunite Minerals. Geological Association of Canada/Mineralogical Association of Canada Spring Meeting, Winnipeg, Manitoba, Canada. May 2013
Pellegrini, Kristi L.; Martinez, Nicholas; Burns, Peter C. Synthetic Growth of Uranyl Phosphate Minerals and in situ Raman Dissolution Studies. Geological Society of America Fall Meeting, Charlotte, NC. November 2012

Pellegrini, Kristi L.; Pianowski, Laura; Burns, Peter C. Induced aggregation of $\text{U}_2\text{P}$, a uranyl peroxide pyrophosphate nanoscale cage cluster, by alkali nitrates. Energy Frontier Research Center Materials Science of Actinides All Hands Meeting, University of Minnesota, Minneapolis, MN, September 2012


Pellegrini, Kristi L.; Martinez, Nicholas; Burns, Peter C. The Behavior of Uranyl Peroxide Pyrophosphate Nanoscale Cage Clusters in Aqueous Solution. American Vacuum Society Fall Meeting, Nashville, TN. November 2011

Pellegrini, Kristi L.; Martinez, Nicholas; Burns, Peter C. The Behavior of Uranyl Peroxide Pyrophosphate Nanoscale Cage Clusters in Aqueous Solution. Energy Frontier Research Center Materials Science of Actinides All Hands Meeting, University of Notre Dame, Notre Dame, IN, September 2011
APPENDIX B:

MODELED ULTRA SMALL ANGLE X-RAY SCATTERING PATTERNS

Ultra small angle X-ray scattering experiments were conducted at the beam line 15-ID-D ChemMatCars at the Advanced Photon Source at Argonne National Laboratory. The scattering patterns from these experiments were modeled using the Modeling II tool for the Irena Macros for the Igor Platform.

B.1 $U_{24}Pp_{12}$ with added Lithium

![Graph showing USAXS data and model](image)

Figure B.1 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of $65 \text{ g/L} U_{24}Pp_{12}$ with added lithium
B.2 $U_{24}Pp_{12}$ with added Sodium

Figure B.2 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $U_{24}Pp_{12}$ with added sodium.
B.3 $\text{U}_{24}\text{Pp}_{12}$ with added Potassium

Figure B.3 The model (black solid line) for the data from USAXS experiments (red data points) with concentrated $\text{U}_{24}\text{Pp}_{12}$ with added potassium.
B.4 $\text{U}_{24}\text{Pp}_{12}$ with added Rubidium

Figure B.4 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of $65 \text{ g/L}$ $\text{U}_{24}\text{Pp}_{12}$ with added rubidium.
B.5 \( \text{U}_2\text{P}_{12} \) with added Cesium

Figure B.5 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L \( \text{U}_2\text{P}_{12} \) with added cesium.
B.6 $\text{U}_{24}\text{Pp}_{12}$ with added Silver

Figure B.6 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added silver.
B.7 U$_{24}$P$_{12}$ with added Magnesium

Figure B.7 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L U$_{24}$P$_{12}$ with added magnesium.
B.8 $\text{U}_2\text{Pp}_{12}$ with added Calcium

![Graph showing the model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_2\text{Pp}_{12}$ with added calcium.](image)

Figure B.8 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_2\text{Pp}_{12}$ with added calcium.
Figure B.9 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added strontium.
B.10 $\text{U}_{24}\text{Pp}_{12}$ with added Lanthanum

Figure B.10 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added lanthanum.
B.11 U$_{24}$P$_{12}$ with added Europium

Figure B.11 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L U$_{24}$P$_{12}$ with added europium.
B.12 $\text{U}_{24}\text{Pp}_{12}$ with added Holmium

Figure B.12 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added holmium.
B.13 $\text{U}_{24}\text{Pp}_{12}$ with added Aluminum

Figure B.13 The model (black solid line) for the data from USAXS experiments (red data points) with aqueous solutions of 65 g/L $\text{U}_{24}\text{Pp}_{12}$ with added aluminum.
APPENDIX C:

PEAK FITTING FOR THE PAIR DISTANCE DISTRIBUTION FUNCTIONS FROM ULTRA SMALL ANGLE X-RAY SCATTERING DATA

Ultra small angle X-ray scattering experiments were conducted at the beam line 15-ID-D ChemMatCars at the Advanced Photon Source at Argonne National Laboratory. The pair distance distribution functions (PDDFS) from these experiments were calculated using the Pair Distance Function tool for the Irena Macros for the Igor Platform. The PDDF for each system was analyzed using the peak fitting tool for Origin Pro Software to determine the distributions within each PDDF.
C.1 PDDF Peak Fitting for Aqueous Solutions of 10 g/L U$_{24}$P$_{12}$

Figure C.1 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 10 g/L U$_{24}$P$_{12}$. Distributions 1, 2, and 3 correspond to cage of U$_{24}$P$_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.2 PDDF Peak fitting for Aqueous Solutions of 20 g/L $U_{24}P_{12}$

![Graph showing peak fitting of PDDF distributions for a solution of 20 g/L $U_{24}P_{12}$](image)

Figure C.2 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 20 g/L $U_{24}P_{12}$. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.3 PDDF Peak Fitting for Aqueous Solutions of 20 g/L $U_{24}P_{12}$

Figure C.3 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 30 g/L $U_{24}P_{12}$. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.4 PDDF Peak Fitting for Aqueous Solutions of 40 g/L U$_{24}$P$_{12}$

Figure C.4 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 40 g/L U$_{24}$P$_{12}$. Distributions 1, 2, and 3 correspond to cage of U$_{24}$P$_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.5 PDDF Peak Fitting for Aqueous Solutions of 50 g/L $U_{24}P_{12}$

Figure C.5 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 50 g/L $U_{24}P_{12}$. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.6 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$P$_{12}$ with Added Lithium

Figure C.6 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L U$_{24}$P$_{12}$ with added lithium. Distributions 1, 2, and 3 correspond to cage of U$_{24}$P$_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.7 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$P$_{12}$ with Added Sodium

Figure C.7 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L U$_{24}$P$_{12}$ with added sodium. Distributions 1, 2, and 3 correspond to cage of U$_{24}$P$_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.8 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$Pp$_{12}$ with Added Potassium

Figure C.8 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L U$_{24}$Pp$_{12}$ with added potassium. Distributions 1, 2, and 3 correspond to cage of U$_{24}$Pp$_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
Figure C.9 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L \( \text{U}_{24}\text{Pp}_{12} \) with added rubidium. Distributions 1, 2, and 3 correspond to cage of \( \text{U}_{24}\text{Pp}_{12} \), a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.10 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$P$_{12}$ with Added Cesium

Figure C.10 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L U$_{24}$P$_{12}$ with added cesium. Distributions 1, 2, and 3 correspond to cage of U$_{24}$P$_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.11 PDDF Peak Fitting for Concentrated Aqueous Solutions of $U_{24}P_{12}$ with Added Silver

Figure C.11 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added silver. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.12 PDDF Peak Fitting for Concentrated Aqueous Solutions of $U_{24}P_{12}$ with Added Calcium

Figure C.12 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added calcium. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.13 PDDF Peak Fitting for Concentrated Aqueous Solutions of $U_{24}P_{12}$ with Added Magnesium

![Figure C.13 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added magnesium. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.](image)

Figure C.13 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added magnesium. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
Figure C.14 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added strontium. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.15 PDDF Peak Fitting for Concentrated Aqueous Solutions of $U_{24}P_{12}$ with Added Lanthanum

Figure C.15 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added lanthanum. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.16 PDDF Peak Fitting for Concentrated Aqueous Solutions of $U_{24}P_{12}$ with Added Europium

Figure C.16 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added europium. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.17 PDDF Peak Fitting for Concentrated Aqueous Solutions of $U_{24}P_{12}$ with Added Holmium

Figure C.17 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L $U_{24}P_{12}$ with added holmium. Distributions 1, 2, and 3 correspond to cage of $U_{24}P_{12}$, a core shell species. Distribution 4 corresponds to the interaction between the sodium ion and the cluster.
C.18 PDDF Peak Fitting for Concentrated Aqueous Solutions of U$_{24}$P$_{12}$ with Added Aluminum

Figure C.18 Peak fitting of the distributions for the PDDF (black) from USAXS data for an aqueous solution of 65 g/L U$_{24}$P$_{12}$ with added aluminum. Distributions 1, 2, and 3 correspond to cage of U$_{24}$P$_{12}$, a core shell species. Distributions 4 and 5 correspond to the interaction between the sodium ion and the cluster.
APPENDIX D:

MULTI-ANGLE DYNAMIC LIGHT SCATTERING FOR DILUTE SOLUTIONS OF

\( \text{U}_{24}\text{Pp}_{12} \) WITH ADDED CATIIONS

D.1 Multi-angle Dynamic Light Scattering Data for 0.5 g/L solutions of \( \text{U}_{24}\text{Pp}_{12} \) with added Potassium

D.1.1 \( \text{U}_{24}\text{Pp}_{12} \) with added Potassium at source-sample-detector-distance of 30°

Figure D.1 Four DLS measurements of 0.5 g/L \( \text{U}_{24}\text{Pp}_{12} \) with added potassium at a source-sample-detector angle of 30°.
D.1.2 $\text{U}_{24}\text{Pp}_{12}$ with added Potassium at source-sample-detector-distance of 45°

Figure D.2 Five DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added potassium at a source-sample-detector angle of 45°.
D.1.3 $\text{U}_{24}\text{Pp}_{12}$ with added Potassium at source-sample-detector-distance of 60°

Figure D.3 Five DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added potassium at a source-sample-detector angle of 60°.
D.1.4 $U_{24}P_{12}$ with added Potassium at source-sample-detector-distance of 75°

Figure D.4 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added potassium at a source-sample-detector angle of 75°.
D.1.5 $\text{U}_{24}\text{Pp}_{12}$ with added Potassium at source-sample-detector-distance of 90°

Figure D.5 Four DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added potassium at a source-sample-detector angle of 75°.
D.2 Multi-angle Dynamic Light Scattering Data for 0.5 g/L solutions of U_{24}P_{12} with added Cesium

D.2.1 U_{24}P_{12} with added Cesium at source-sample-detector-distance of 30°

Figure D.6 Five DLS measurements of 0.5 g/L U_{24}P_{12} with added cesium at a source-sample-detector angle of 30°.
D.2.2 $\text{U}_{24}\text{Pp}_{12}$ with added Cesium at source-sample-detector-distance of 45°

Figure D.7 Five DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added cesium at a source-sample-detector angle of 45°.
D.2.3 $\text{U}_{24}\text{Pp}_{12}$ with added Cesium at source-sample-detector-distance of 60°

Figure D.8 Five DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added cesium at a source-sample-detector angle of 60°.
D.2.4 \( \text{U}_{24}\text{Pp}_{12} \) with added Cesium at source-sample-detector-distance of 75°.

Figure D.9 Five DLS measurements of 0.5 g/L \( \text{U}_{24}\text{Pp}_{12} \) with added cesium at a source-sample-detector angle of 75°.
D.2.5 $U_{24}P_{12}$ with added Cesium at source-sample-detector-distance of 90°

Figure D.10 Five DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added cesium at a source-sample-detector angle of 90°.
D.3 Multi-angle Dynamic Light Scattering Data for 0.5 g/L solutions of U24Pp12 with added Copper

D.3.1 U\textsubscript{24}Pp\textsubscript{12} with added Copper at source-sample-detector-distance of 30°

![Graph showing DLS measurements](image)

Figure D.11 Six DLS measurements of 0.5 g/L U\textsubscript{24}Pp\textsubscript{12} with added copper at a source-sample-detector angle of 30°.
D.3.2 \( \text{U}^{24}\text{Pp}_{12} \) with added Copper at source-sample-detector-distance of 45°

Figure D.12 Six DLS measurements of 0.5 g/L \( \text{U}^{24}\text{Pp}_{12} \) with added copper at a source-sample-detector angle of 45°.
D.3.3 $\text{U}_{24}\text{Pp}_{12}$ with added Copper at source-sample-detector-distance of $60^\circ$

Figure D.13 Five DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added copper at a source-sample-detector angle of $60^\circ$. 
D.3.4 $\text{U}_{24}\text{Pp}_{12}$ with added Copper at source-sample-detector-distance of $75^\circ$

Figure D.14 Five DLS measurements of 0.5 g/L $\text{U}_{24}\text{Pp}_{12}$ with added copper at a source-sample-detector angle of $75^\circ$. 

Trial 1
Trial 2
Trial 3
Trial 4
Trial 5
D.3.5 $U_{24}P_{12}$ with added Copper at source-sample-detector-distance of 90°

![Graph showing DLS measurements](image)

Figure D.15 Six DLS measurements of 0.5 g/L $U_{24}P_{12}$ with added copper at a source-sample-detector angle of 90°.
APPENDIX E:

SINGLE ANGLE DYNAMIC LIGHT SCATTERING DATA OF URANYL CAGE

CLUSTERS IN MIXED SOLVENT SYSTEMS

E.1 DLS Studies of Clusters of U$_{24}$P$_{p12}$ in Water-Methanol Solutions

Three aliquots of methanol were added to each of three concentrations of aqueous solutions of U$_{24}$P$_{p12}$ to form the mixed-solvent cluster system. The systems were analyzed over a two-week period to monitor aggregation of U$_{24}$P$_{p12}$. The R$_H$ for solutions of U$_{24}$P$_{p12}$ that has not aggregated is less than 1 nm.
Figure E.1 $R_H$ data for three concentrations of U$_{24}$Pp$_{12}$ in 2:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U$_{24}$Pp$_{12}$ of 0.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of U$_{24}$Pp$_{12}$ of 3.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The red triangles show data for the highest starting concentration of U$_{24}$Pp$_{12}$ of 33.3 g of cluster crystal per liter of 2:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
Figure E.2 $R_H$ data for three concentrations of $\text{U}_{24}\text{Pp}_{12}$ in 1:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $\text{U}_{24}\text{Pp}_{12}$ of 0.25 g of cluster crystal per liter of 1:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of $\text{U}_{24}\text{Pp}_{12}$ of 2.5 g of cluster crystal per liter of 1:1 water-methanol mixture. The red triangles show data for the highest starting concentration of $\text{U}_{24}\text{Pp}_{12}$ of 25 g of cluster crystal per liter of 1:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
Figure E.3 $R_H$ data for three concentrations of $U_{24}Pp_{12}$ in 1:2 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{24}Pp_{12}$ of 0.17 g of cluster crystal per liter of 1:2 water-methanol mixture. The blue squares show data for the moderate starting concentration of $U_{24}Pp_{12}$ of 1.67 g of cluster crystal per liter of 1:2 water-methanol mixture. The red triangles show data for the highest starting concentration of $U_{24}Pp_{12}$ of 16.7 g of cluster crystal per liter of 1:2 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
E.2 DLS Studies of Clusters of U$_{24}$P$_{12}$ in Ethanol-Water Solutions

Three aliquots of ethanol were added to each of three concentrations of aqueous solutions of U$_{24}$P$_{12}$ to form the mixed-solvent cluster system. The systems were analyzed over a two-week period to monitor aggregation of U$_{24}$P$_{12}$. The R$_{H}$ for solutions of U$_{24}$P$_{12}$ that has not aggregated is less than 1 nm.
Figure E.4 $R_H$ data for three concentrations of $U_{24P_{12}}$ in 2:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{24P_{12}}$ of 0.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of $U_{24P_{12}}$ of 3.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of $U_{24P_{12}}$ of 33.3 g of cluster crystal per liter of 2:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
Figure E.5 RH data for three concentrations of U₂₄P₅₂ in 1:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U₂₄P₅₂ of 0.25 g of cluster crystal per liter of 1:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of U₂₄P₅₂ of 2.5 g of cluster crystal per liter of 1:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of U₂₄P₅₂ of 25 g of cluster crystal per liter of 1:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
E.2.3 $\text{U}_{24}\text{Pp}_{12}$ in 1:2 Water-Ethanol Solutions

Figure E.6 $R_H$ data for three concentrations of $\text{U}_{24}\text{Pp}_{12}$ in 1:2 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $\text{U}_{24}\text{Pp}_{12}$ of 0.17 g of cluster crystal per liter of 1:2 water-ethanol mixture. The blue squares show data for the moderate starting concentration of $\text{U}_{24}\text{Pp}_{12}$ of 1.67 g of cluster crystal per liter of 1:2 water-ethanol mixture. The red triangles show data for the highest starting concentration of $\text{U}_{24}\text{Pp}_{12}$ of 16.7 g of cluster crystal per liter of 1:2 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
E.3 DLS Studies of Clusters of $U_{60}$ in Methanol-Water Solutions

Three aliquots of methanol were added to each of three concentrations of aqueous solutions of $U_{60}$ to form the mixed-solvent cluster system. The systems were analyzed over a two-week period to monitor aggregation of $U_{60}$. The $R_H$ for solutions of $U_{60}$ that has not aggregated is approximately 1 nm.
Figure E.7 $R_H$ data for three concentrations of $U_{60}$ in 2:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{60}$ of 0.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of $U_{60}$ of 3.33 g of cluster crystal per liter of 2:1 water-methanol mixture. The red triangles show data for the highest starting concentration of $U_{60}$ of 33.3 g of cluster crystal per liter of 2:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.

E.3.1 $U_{60}$ in 2:1 Water-Methanol Solutions
Figure E.8 $R_H$ data for three concentrations of $U_{60}$ in 1:1 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{60}$ of 0.25 g of cluster crystal per liter of 1:1 water-methanol mixture. The blue squares show data for the moderate starting concentration of $U_{24}P_{p_{12}}$ of 2.5 g of cluster crystal per liter of 1:1 water-methanol mixture. The red triangles show data for the highest starting concentration of $U_{60}$ of 25 g of cluster crystal per liter of 1:1 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
E.3.3 U$_{60}$ in 1:2 Water-Methanol Solutions

![Graph showing $R_H$ for three concentrations of U$_{60}$ over a two-week period.]

Figure E.9 $R_H$ data for three concentrations of U$_{60}$ in 1:2 mixed-solvent water-methanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of U$_{60}$ of 0.17 g of cluster crystal per liter of 1:2 water-methanol mixture. The blue squares show data for the moderate starting concentration of U$_{60}$ of 1.67 g of cluster crystal per liter of 1:2 water-methanol mixture. The red triangles show data for the highest starting concentration of U$_{60}$ of 16.7 g of cluster crystal per liter of 1:2 water-methanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
E.4 DLS Studies of Clusters of U$_{60}$ in Ethanol-Water Solutions

Three aliquots of methanol were added to each of three concentrations of aqueous solutions of U$_{60}$ to form the mixed-solvent cluster system. The systems were analyzed over a two-week period to monitor aggregation of U$_{60}$. The R$_H$ for solutions of U$_{60}$ that has not aggregated is approximately 1 nm.
E.4.1 $U_{60}$ in 2:1 Water-Methanol Solutions

Figure E.10 $R_H$ data for three concentrations of $U_{60}$ in 2:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{60}$ of 0.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of $U_{60}$ of 3.33 g of cluster crystal per liter of 2:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of $U_{60}$ of 33.3 g of cluster crystal per liter of 2:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
Figure E.11 $R_H$ data for three concentrations of $U_{60}$ in 1:1 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{60}$ of 0.25 g of cluster crystal per liter of 1:1 water-ethanol mixture. The blue squares show data for the moderate starting concentration of $U_{24Pp_{12}}$ of 2.5 g of cluster crystal per liter of 1:1 water-ethanol mixture. The red triangles show data for the highest starting concentration of $U_{60}$ of 25 g of cluster crystal per liter of 1:1 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
E.5 $U_{60}$ in 1:2 Water-Methanol Solutions

Figure E.12 $R_H$ data for three concentrations of $U_{60}$ in 1:2 mixed-solvent water-ethanol systems obtained from single-angle DLS analysis over a two-week period. The black diamonds show data for the lowest starting concentration of $U_{60}$ of 0.17 g of cluster crystal per liter of 1:2 water-ethanol mixture. The blue squares show data for the moderate starting concentration of $U_{60}$ of 1.67 g of cluster crystal per liter of 1:2 water-ethanol mixture. The red triangles show data for the highest starting concentration of $U_{60}$ of 16.7 g of cluster crystal per liter of 1:2 water-ethanol mixture. Error bars were determined from the standard deviation of multiple measurements of the same sample.
APPENDIX F:
CONCENTRATIONS OF URANIUM FROM ICP-OES ANALYSIS

F.1 Bulk Experiment of Dissolution of Crystals of U$_2$P$_{12}$

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Measurement 1 (ppm)</th>
<th>Measurement 2 (ppm)</th>
<th>Average (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>60.58</td>
<td>0</td>
<td>60.58</td>
</tr>
<tr>
<td>0.25</td>
<td>12327</td>
<td>14141</td>
<td>13238</td>
</tr>
<tr>
<td>1.25</td>
<td>11626</td>
<td>10472</td>
<td>11049</td>
</tr>
<tr>
<td>2.33</td>
<td>12222</td>
<td>9627</td>
<td>10924</td>
</tr>
<tr>
<td>9.83</td>
<td>12972</td>
<td>14265</td>
<td>13619</td>
</tr>
<tr>
<td>25.08</td>
<td>18375</td>
<td>16710</td>
<td>17543</td>
</tr>
<tr>
<td>47.92</td>
<td>17660</td>
<td>17079</td>
<td>17369</td>
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<td>120.13</td>
<td>34767</td>
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<td>34113</td>
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<td>144.75</td>
<td>24340</td>
<td>21871</td>
<td>23105</td>
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<tr>
<td>215.95</td>
<td>43088</td>
<td>44801</td>
<td>43944</td>
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<tr>
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<td>39574</td>
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<tr>
<td>551.08</td>
<td>45024</td>
<td>49922</td>
<td>47473</td>
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<tr>
<td>719.08</td>
<td>31171</td>
<td>38884</td>
<td>35027</td>
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</table>
F.2 Maximum Concentrations from Small Batch Dissolution of U$_{24}$P$_{12}$

**TABLE F.2**

**URANIUM CONCENTRATIONS FOR SMALL BATCH DISSOLUTION EXPERIMENTS AS MEASURED BY ICP-OES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measurement 1 (ppm)</th>
<th>Measurement 2 (ppm)</th>
<th>Measurement 3 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37189</td>
<td>40460</td>
<td>48118</td>
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<td>34497</td>
<td>41655</td>
<td>39860</td>
</tr>
</tbody>
</table>


338


Wallace, C. M. (2013). *Solution and aggregation behavior of the U60 nanocluster and post-detonation nuclear forensic analysis of trinitite*. (Ph.D.), University of Notre Dame, Notre Dame, IN.


