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**Solution and Solid-State Studies of Alkali Metal Aggregate Assemblies**

**John Jacob Morris**

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## CHAPTER 1

### INTRODUCTION

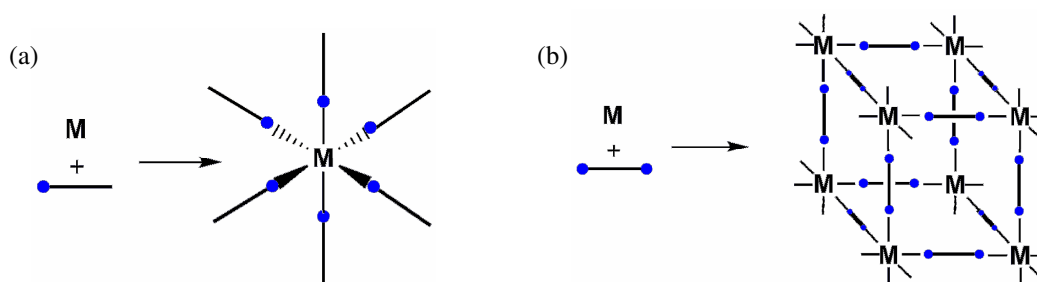
#### 1.1 Outline

The synthesis and characterization of extended network assemblies is an area of intense academic and industrial research.<sup>1</sup> Interest in these materials stems from their potential utility in numerous applications as well as the fundamental challenges associated with their design and synthesis.<sup>2</sup> The following sections will briefly summarize: (i) the components necessary to construct coordination networks, (ii) a selection of their potential applications as novel materials, (iii) the use of alkali metals in the synthesis of extended materials, and (iv) the previous work in our group using alkali metal aggregates as secondary-building units.

#### 1.2 The Design of Coordination Frameworks

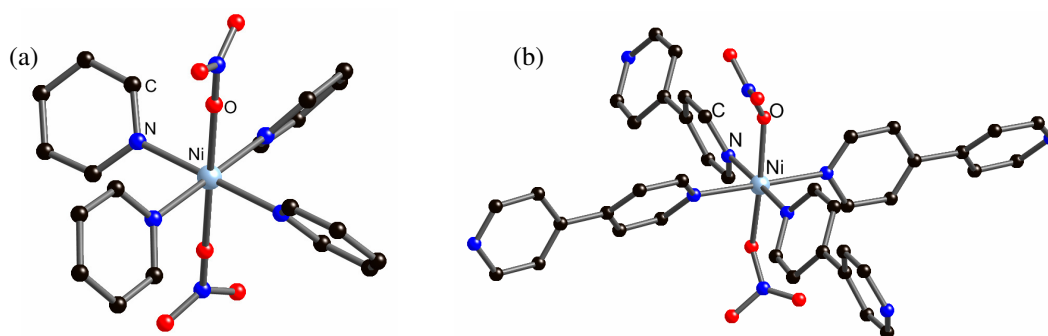
The node and linker approach for the synthesis of extended materials was pioneered in the early 1990s by Robson,<sup>3</sup> Desiraju,<sup>4</sup> Fujita,<sup>5</sup> Wuest,<sup>6</sup> and others.<sup>7</sup> This strategy uses the established principles of molecular chemistry to generate extended periodic networks. A successful method developed is the use of unsaturated metal centers in combination with divergent organic donor ligands to generate one-, two-, and three-

dimensional coordination networks or polymers.<sup>8</sup> In addition, a notable area of success has been the formation of covalently-linked frameworks using ditopic carboxylates,<sup>9</sup> sulfonates,<sup>10</sup> and phosphonates<sup>11</sup> with metal ions and clusters. Other types of interactions such as hydrogen bonding,<sup>12</sup>  $\pi$ - $\pi$  interactions,<sup>13</sup> ionic interactions,<sup>14</sup> lipophilic interactions,<sup>15</sup> metal-metal interactions,<sup>16</sup> and halogen bonding<sup>17</sup> have also been used to build network assemblies, and will be discussed more fully in Chapter 7. Whereas traditional coordination chemistry has focused on the synthesis of molecular species using convergent organic ligands, coordination frameworks are prepared using divergent ligands (Figure 1.1).



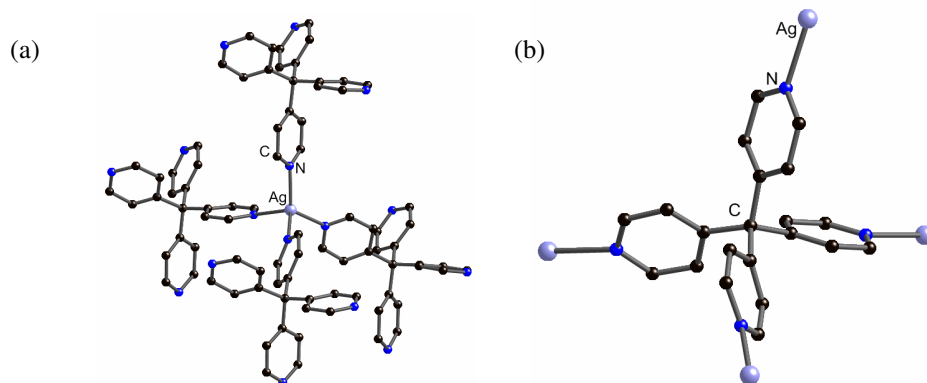
**Figure 1.1** Coordination of metals with (a) convergent organic ligands to form molecular complexes, and (b) divergent ligands to give polymeric complexes.

The choice of metal center often dictates the architecture of the resultant framework due to the differing coordination numbers and preferred geometries of the metal. An example is shown in Figure 1.2 in which a nickel center is equatorially coordinated by four pyridine molecules and axially coordinated by two nitrate anions.<sup>18</sup> Replacement of the terminal pyridyl groups with divergent 4,4'-bipyridine gives the same structural arrangement around the nickel.<sup>19</sup> However, the metal now acts as a square planar node, with the bipyridyl ligands bridging to four other nickel centers to give a two-dimensional  $4^4$ -net.



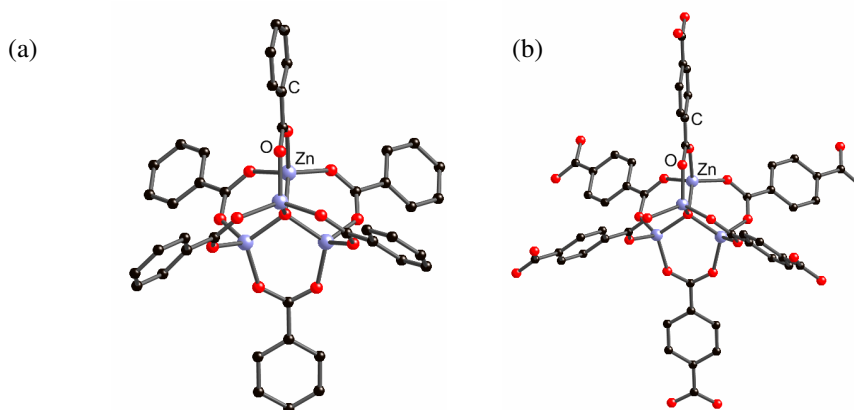
**Figure 1.2** (a) The molecular pyridine solvate of  $\text{Ni}^{\text{II}}(\text{NO}_3)_2$ . The pyridyl groups are in an equatorial position. (b) The bipyridyl solvate of  $\text{Ni}^{\text{II}}(\text{NO}_3)_2$ . The equatorial bipyridyl ligands bridge to other metals to give a square planar network.

In the above example, the bipyridine acts as a divergent linker between two metal sites. More complex networks can be designed by the combination of metal centers with multifunctional ligands. In these cases, the ligand contributes to the network topology and must also be described as a network node. Figure 1.3 shows an example from the combination of  $\text{Ag}(\text{I})$  centers with the tetrahedral organic linker TPM (TPM = tetra-(4-pyridyl)methane in the structure of  $[(\text{AgTPM})(\text{BF}_4)]_\infty$ .<sup>20</sup> The silver is considered a tetrahedral node and so is the TPM ligand. The extended structure has a three-dimensional diamondoid topology using two different nodes.



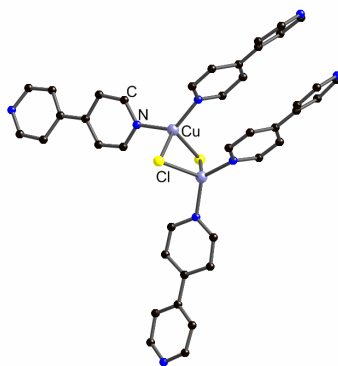
**Figure 1.3** The two different nodes in  $[(\text{AgTPM})(\text{BF}_4)]_\infty$  showing (a) the tetrahedral silver center coordinated by four TPM ligands, and (b) the tetrahedral TPM ligand coordinating to four different silver centers.

A related strategy has been to use metal clusters as nodes in directing network formation. Discrete binuclear,<sup>21</sup> trinuclear,<sup>22</sup> and tetranuclear<sup>23</sup> metal carboxylate clusters can be synthesized when monocarboxylates are employed. Yaghi and others have shown that these clusters can be used as secondary building units (SBUs) by replacing monocarboxylates with dicarboxylates to produce extended coordination networks.<sup>24</sup> An example is shown in Figure 1.4 in which a molecular  $[\text{Zn}_4\text{O}]^{6+}$  cluster is formed from the reaction of benzoic acid and zinc nitrate.<sup>23</sup> Replacement of the monocarboxylate with bifunctional 1,4-benzenedicarboxylate gives the same  $[\text{Zn}_4\text{O}]^{6+}$  cluster, but these are now linked through the aromatic group to give an extended coordination network with primitive cubic topology.<sup>25</sup>



**Figure 1.4** The  $[\text{Zn}_4\text{O}]^{6+}$  cluster with (a) benzene carboxylate as a terminal ligand, and (b) benzene dicarboxylate as a divergent linker.

Metal clusters can also be used as SBUs in combination with neutral divergent Lewis bases. Figure 1.5 shows a dimeric  $\text{Cu}_2\text{Cl}_2$  cluster tetracoordinated by 4,4'-bipyridine.<sup>26</sup> The dimer acts a tetrahedral SBU with connections to four other dimers through the neutral ligand to form a 3D diamondoid net.



**Figure 1.5** The dimeric  $\text{Cu}_2\text{Cl}_2$  aggregate tetrasolvated by divergent bipyridine.

### 1.3 Applications of Porous Frameworks

The interest in coordination frameworks stems from their potential use in a number of applications including catalysis,<sup>27</sup> optics,<sup>28</sup> electronics,<sup>29</sup> small molecule storage,<sup>30</sup> chemical separation,<sup>31</sup> ion exchange,<sup>32</sup> magnetism,<sup>33</sup> and nonlinear optics.<sup>34</sup> Selected highlights from four of these applications are briefly summarized below to illustrate the different interests in this field.

One of the highly publicized potential uses of coordination frameworks is for gas storage, most notably the onboard storage of  $\text{H}_2$  for automotive applications.<sup>35</sup> The U.S. Department of Energy has set  $\text{H}_2$  storage targets of 6.0 wt % gravimetric storage and 45 g  $\text{H}_2/\text{L}$  volumetric capacity at ambient temperature by 2010 for any material with industrial aspirations.<sup>36</sup> It should be noted that these values include the weight of the container as well as any other necessary components. The 2015 goal is even more challenging, with a storage target of 9.0 wt %. Since the storage of  $\text{H}_2$  is a complex challenge, the most successful strategy will include using materials that can be fine-tuned in a systematic way to achieve the correct properties to effectively store the gas. Coordination frameworks offer a promising approach to this challenge because of their porosity, high surface area,

and tunability.<sup>37</sup> Williams has reported a coordination framework with a copper “paddlewheel” node,  $[\text{Cu}_3(\text{BTC})_2]_\infty$  (BTC = 1,3,5-benzenetricarboxylate), that adsorbs 2.54 wt %  $\text{H}_2$  at 77 K and 1 bar.<sup>38</sup> Yaghi has reported a series of frameworks consisting of tetrahedral  $[\text{Zn}_4\text{O}]^{6+}$  units connected by di- and tricarboxylates that were found to store large amounts of hydrogen at low temperatures and pressures. For example,  $[\text{Zn}_4\text{O}(\text{BDC})_3]_\infty$  (BDC = 1,4-benzenedicarboxylate) can reversibly adsorb 5.2 wt %  $\text{H}_2$  at 77 K and 50 bar.<sup>39</sup> As a comparison, the highest wt % for a zeolite is reported for ZSM-5, which can only uptake 0.7 wt % at 77 K. Yaghi also reported that the compound  $[\text{Zn}_4\text{O}(\text{BTB})_2]_\infty$  (BTB = 1,3,5-benzenetribenzoate) uptakes 7.0 wt % at 77 K and 50 bar, which is the highest reported  $\text{H}_2$  uptake to date for a coordination network.<sup>40</sup> These values are significantly lower at room temperature and this remains a challenge in the area.

Coordination frameworks can be used to uptake other small molecules with a good degree of selectivity.<sup>41</sup> Kitagawa reported the synthesis of  $[\text{Zn}_2(\text{ip})_2(\text{bpy})_2]_\infty$  (ip = isophthalate, bpy = 4,4'-bipyridine) which selectively adsorbs methanol and ethanol over benzene.<sup>42</sup> Kim reported that manganese formate,  $[\text{Mn}(\text{HCO}_2)_2]_\infty$ , could selectively uptake  $\text{H}_2$  (0.9 wt %) over  $\text{N}_2$  and argon at 78 K, and  $\text{CO}_2$  (20 wt %) over  $\text{N}_2$  and  $\text{CH}_4$  at 195 K.<sup>43</sup> The selectivity was attributed to the small aperture of the channel, which can discriminate between gases with small differences in diameters. Chen reported a similar result with the framework  $[\text{Cu}(\text{FMA})(4,4'\text{-Bpe})0.5]_\infty$  (FMA = fumarate, 4,4'-Bpe = trans-bis(4-pyridyl)ethylene) framework.<sup>44</sup> Fujita reported the favorable guest exchange of cyclohexane, anthracene, or perylene for enclathrated nitrobenzene in  $[(\text{ZnI}_2)_3(\text{TPT})_2]_\infty$  (TPT = 2,4,6-tris(4-pyridyl)triazine).<sup>45</sup>

Spin crossover (SCO) is a type of molecular magnetism that is the result of electronic instability caused by external stimuli. These external stimuli, which are commonly temperature and pressure, induce structural changes at the molecular level. The phenomenon is most characteristic of first-row transition metal complexes, which change between high- and low-spin forms. Spin crossover has been investigated for a number of coordination frameworks, and found to have a dependency on included guest molecules.<sup>46</sup> The formation of a host framework that interacts with exchangeable guest molecules in a switchable fashion has electronic applications in the field of molecular sensing. Real reported that the bimetallic framework  $[\text{Fe}^{\text{II}}(\text{pmd})(\text{OH}_2) \cdot \{\text{Ag}^{\text{I}}(\text{CN})_2\} \cdot 2\text{H}_2\text{O}]_{\infty}$  (pmd = pyrimidine) displays reversible uptake of guest molecules and contains electronic switching centers which are sensitive to the nature of the sorbed guests.<sup>47</sup> The framework structure displays flexibility with guest uptake and release, causing substantial changes in the local geometry of the iron(II) centers but without destroying the network connectivity. These structural changes result in shifting the SCO transition to a lower temperature.

Chiral coordination frameworks can be synthesized using terminal or divergent chiral ligands.<sup>48</sup> These frameworks can then be used to catalyze enantioselective reactions.<sup>49</sup> Lin reported the chiral framework,  $[\text{Cd}_3\text{Cl}_6\text{L}_3]$  ( $\text{L} = (R)$ -6,6'-dichloro-2,2'-dihydroxy-1,1'-binaphthyl-4,4'-bipyridine). This material can chemisorb titanium isopropoxide, and subsequently be used to catalyze the enantioselective addition of  $\text{ZnEt}_2$  to aromatic aldehydes.<sup>48a</sup> Kim reported that the chiral framework  $[\text{Zn}_2(\text{BDC})(\text{L-lac})(\text{dmf})]$  ( $\text{BDC} = 1,4$ -benzenedicarboxylate and  $\text{L-lac} = \text{lactate}$ ) could catalyze the enantioselective oxidation of thioethers to sulfoxides in the presence of urea



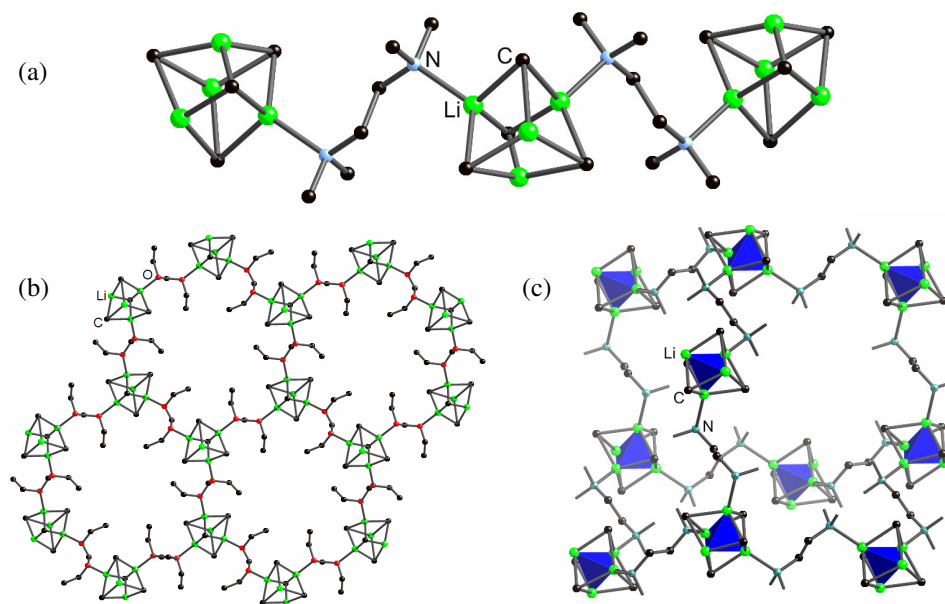
hydroperoxide.<sup>50</sup> In this case, zinc nitrate is reacted with L-lactic acid to give chiral SBUs, which are then connected by rigid non-chiral BDC to give an open homochiral framework.

#### 1.4 Alkali Metals In Extended Networks

A noticeable omission from the list of strategies directed towards the rational synthesis of extended networks is the use of *s*-block metals. Indeed, while sophisticated work has been carried out detailing the subtle factors involved in determining the molecular structures adopted by alkali metal complexes,<sup>51</sup> no sustained attempt has been made to rationalize polymer formation in this area. This may be explained by the potential problems associated with these species, such as the presence of complex dynamic solution equilibria between aggregated complexes, the spherical non-polarizable nature of the cations, the limited preference for fixed metal geometries, and the lability of the metal-ligand bonding. All of these issues may lead to poor predictability in network synthesis.<sup>52</sup> It is therefore unsurprising that the deliberate use of *s*-block metals as SBUs in the formation of coordination networks has been avoided.

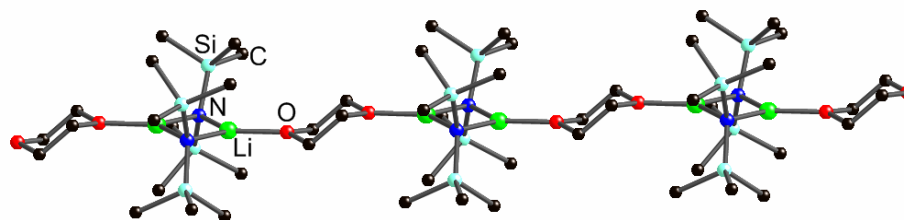
The formation of one-, two-, and three-dimensional coordination polymers is known in *s*-block metal chemistry.<sup>53</sup> However, these polymers have usually been prepared either inadvertently or in order to study localized metrical information.<sup>54</sup> A number of alkyllithium complexes have been synthesized in the presence of didentate Lewis bases, where the base unintentionally acted as a divergent linker.<sup>55</sup> For example, Williard reported the synthesis of  $[(\text{BuLi})_4 \cdot (\text{TMEDA})]_\infty$  (TMEDA = tetramethylethylenediamine) where  $\text{Bu}_4\text{Li}_4$  tetrameric cubanes are linked through

divergent TMEDA to give a one-dimensional coordination polymer (Figure 1.6a).<sup>56</sup> TMEDA usually acts as a terminal didentate base.<sup>57</sup> Indeed, the introduction of excess TMEDA to BuLi results in a molecular dimer with chelated metal centers.<sup>58</sup> Stalke reported the synthesis of  $[(\text{MeLi})_4 \cdot (\text{DEM})_{1.5}]_\infty$  (DEM = diethoxymethane), which forms a two-dimensional coordination framework through bridging of  $\text{Me}_4\text{Li}_4$  cubanes by DEM (Figure 1.6b).<sup>59</sup> Weiss reported the synthesis of the three-dimensional polymer  $[(\text{MeLi})_4 \cdot (\text{TMEDA})_2]_\infty$  (TMEDA = tetramethylethylenediamine), which is constructed from  $\text{Me}_4\text{Li}_4$  cubanes linked through divergent TMEDA (Figure 1.6c).<sup>60</sup> The  $\text{Me}_4\text{Li}_4$  tetramer acts as a tetrahedral node to give a three dimensional diamondoid network.



**Figure 1.6** (a) A 1D coordination polymer formed from  $\text{Bu}_4\text{Li}_4$  tetramers and TMEDA. Only the  $\alpha$ -carbon of the butyl group is shown for clarity. (b) A 2D sheet of  $\text{Me}_4\text{Li}_4$  tetramers bridged by DEM. (c) The adamantane subunit of the 3D diamondoid network of  $\text{Me}_4\text{Li}_4$  tetramers bridged by TMEDA. The blue tetrahedrons highlight the four lithium centers in the aggregate.

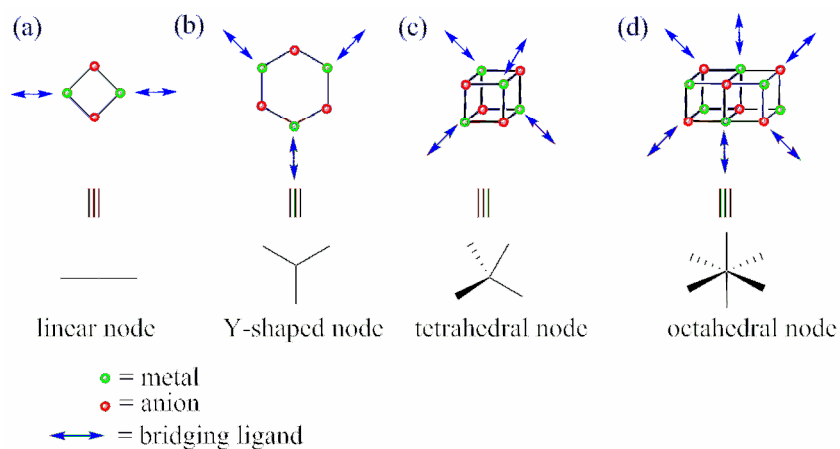
All of the above are examples of the inadvertent synthesis of extended coordination networks. There are also several related examples of amidolithium and amidosodium aggregates.<sup>61</sup> For example, Willard reported the synthesis of  $[(\text{LiHMDS})_2 \cdot (\text{dioxane})]_\infty$  (HMDS = hexamethyldisilazide), where  $\text{Li}_2\text{N}_2$  ring dimers are disolvated by dioxane to give a linear one-dimensional coordination polymer (Figure 1.7).<sup>62</sup>



**Figure 1.7** A one-dimensional coordination polymer formed from  $(\text{LiHMDS})_2$  ring dimers solvated by 1,4-dioxane.

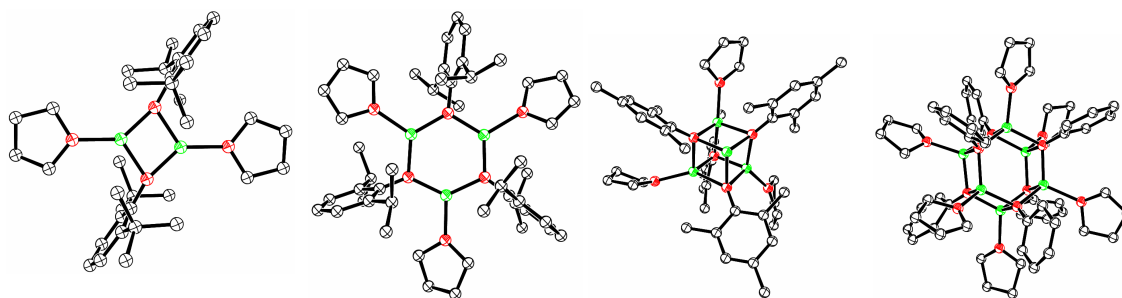
## 1.5 Alkali Metal Aggregates In Network Assembly

The coordination chemistry of molecular *s*-block metal complexes has been an active area of research. Indeed, the molecular aggregation behavior of numerous types of metal-ligand combinations are now well established.<sup>52</sup> The initial work in our group was aimed at using a series of readily prepared *s*-block aggregates as SBUs. A highly attractive feature of *s*-block SBUs is the diversity of metal aggregate geometries and compositions available as nodes. Since the location of the metal centers and the anions within these aggregates are known in advance, we could use this information to rationally design one-, two-, and three-dimensional coordination networks. Figure 1.8 displays a selection of commonly found aggregation states for *s*-block complexes: dimers, trimers, tetrameric cubanes, and prismatic hexamers, and relates these to their corresponding nodal geometries.



**Figure 1.8** Relationship between selected metal aggregates and their nodal geometries: (a) disolvated ring dimer, (b) trisolvated ring trimer, (c) tetrasolvated tetrameric cubane, and (d) hexasolvated prismatic hexamer.

A starting point for this project was the use of lithium aryloxides. Extensive studies have established predictable aggregation patterns for molecular lithium aryloxides in both solution<sup>63</sup> and the solid state.<sup>64</sup> These complexes contain strong Li-O bonding, and numerous aggregate types are available as SBUs. In addition, they are readily prepared from the parent phenol by direct deprotonation using bases such as organolithiums. Two main factors influence the aggregation state in these complexes: (i) steric demands of the substituents on the aryl ring, and (ii) the relative strength of the Lewis base present. For example, increasing the steric bulk at the *ortho*-positions of the aryl ring results in a decrease the aggregation state of the lithiated complex. This is highlighted in a series of THF solvated lithiated aryloxides (ArOLi) as shown in Figure 1.9, which form dimers (Ar = 2,6-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), trimers (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), tetrameric cubanes (Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), and prismatic hexamers (Ar = C<sub>6</sub>H<sub>5</sub>).<sup>65</sup>



**Figure 1.9** Molecular structures of a series of THF-solvated lithium aryloxides,  $[(\text{ArOLi})\cdot(\text{THF})]_n$ .

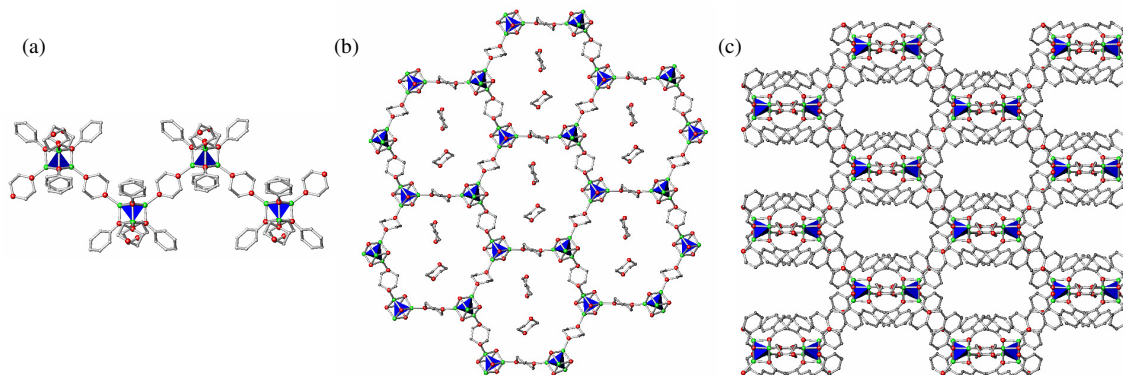
Each of the metal atoms within these aggregates has one coordination site occupied by a monodentate THF donor molecule. Replacement of the terminal Lewis bases by divergent linker molecules may result in the formation of extended coordination networks. The most likely extended structures to be produced in each case are one-dimensional polymers from disolvated dimers; two-dimensional nets from ring trimers; three-dimensional diamondoid networks using tetrameric cubanes; and primitive cubic networks using prismatic hexamers. There are of course numerous possibilities for both the connectivity and topology of the supramolecular assemblies that may be formed via the interaction of the four aggregate types shown above. However, it is becoming clear that a relatively few, high-symmetry structures dominate network topologies.<sup>66</sup>

## 1.6 Use of Tetrameric $\text{Li}_4\text{O}_4$ Cubanes as SBUs

Initial studies focused on linking neutral, pre-assembled, lithiated SBUs using an external, neutral, divergent Lewis base. The commonly encountered  $\text{Li}_4\text{O}_4$  tetrameric cubanes form by lithium aryloxides ( $\text{ArOLi}$ ) was targeted.<sup>67</sup> These complexes are excellent SBU candidates as the metals are held in an approximately tetrahedral arrangement with one coordination site available for solvation, and there is a wide range

of substituted phenols available for systematic studies.<sup>65</sup> The didentate donor dioxane was selected as the divergent external linking Lewis base due to its capacity to act as solvent media, its inability to chelate a lithium center, and its similarity to THF.

A series of dioxane coordinated lithium aryloxides were synthesized and characterized by X-ray diffraction. Figure 1.10 highlights the structural characterization, by single-crystal XRD, of the three representative complexes of  $[(\text{ArOLi})_4(\text{dioxane})_n]_\infty$ , where (a)  $\text{R}=\text{Ph}$ ,  $n=3$ ; (b)  $\text{R}=4\text{-Et-C}_6\text{H}_4$ ,  $n=2.5$ ; and (c)  $\text{R}=1\text{-naphth}$ ,  $n=2$ .<sup>67</sup>



**Figure 1.10** Sections of the polymeric structures of the: (a) 1D zig-zag chain, (b) framework atoms of the 2D hexagonal network with two guest solvent molecules per macrocycle, and (c) 3D diamondoid network. Vertices of the blue tetrahedra represent the four lithium centers within each cubane.

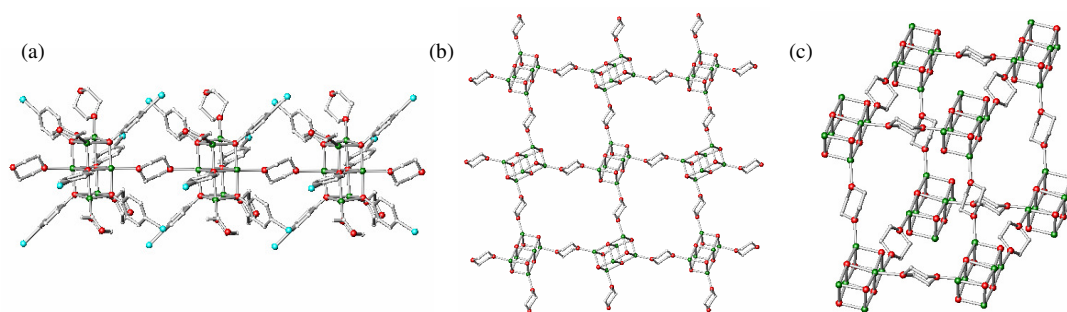
The complexes in Figure 1.10 illustrate the pronounced effect of relatively small changes in sterics on the extended structure adopted. The complex  $[(4\text{-Et-C}_6\text{H}_4\text{OLi})_4(\text{dioxane})_{2.5}]_\infty$ , gives a two-dimensional  $6^3$ -net with large hexameric rings. Starting from this complex, decreasing the size of the aryloxide results in a one-dimensional polymer, whereas increasing the aryloxide results in the formation of a 3D network. Although previous calculations have shown that dioxane bridging between two lithium tetramers is thermoneutral,<sup>67</sup> there will be a substantial increase in entropy

associated with polymer formation due to the gain in translational freedom of the liberated solvent molecules.<sup>68</sup> Clearly, there is an optimum length for the aryloxide ligands of the SBU in order to efficiently fill the hexameric rings of the two-dimensional sheets. If the ligands are too short this will result in energetically unfavorable voids at the center of the ring, and conversely, if the ligands are too long the 2D arrangement will be destabilized by transannular interactions.<sup>69</sup> This analysis is consistent with the 1D chain structure observed when the *para*-substituent is small (H, Me, F or Cl). Minimal extension at this position (Et, OMe, <sup>i</sup>Pr) leads to the formation of two-dimensional hexagonal sheets, whereas lateral substitution of the aromatic (Ar = 1-naphth or 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) gives three-dimensional diamondoid networks. This initial series of complexes act as a proof-of-concept that pre-assembled *s*-block complexes may be used as SBUs in the construction of coordination polymers. Furthermore, small changes in the substitution pattern of the ligands may lead to substantial changes in the resulting network topology.

### 1.7 Use of Hexameric Na<sub>6</sub>O<sub>6</sub> Aggregates as SBUs

Complexes of the heavier Group 1 metals are appealing candidates for SBUs. Of the heavier alkali metals, the alkoxides and aryloxides of both sodium and potassium have been reasonably well studied.<sup>70</sup> A potential drawback of moving from lithium to the heavier *s*-block metals is a significant weakening of the metal-ligand bond strength, which may in turn lead to increased aggregate lability and a decrease in the predictability of the nature of the SBU. The study of Li<sub>4</sub>O<sub>4</sub> aryloxide aggregates was extended to include the heavier Na<sub>6</sub>O<sub>6</sub> aryloxide aggregates as potential sodium based SBUs.<sup>71</sup> It was proposed that the hexameric aggregates should act as octahedral SBUs if all of the metal

centers are solvated by a divergent Lewis base. In turn, this should lead to the formation of a three-dimensional primitive cubic network. The set of *para*-halide substituted derivatives are particularly useful in illustrating the effect of sterics on network structure. Figure 1.11 highlights the structural characterization of the three representative complexes of  $[(4\text{-R-C}_6\text{H}_4\text{ONa})_6\text{.}(\text{dioxane})_n]_\infty$ , where: (a)  $\text{R} = \text{I}$ ,  $n = 5$  and forms a one-dimensional coordination polymer, (b)  $\text{R} = \text{Br}$ ,  $n = 4$  and forms a two-dimensional square planar net, and (c)  $\text{R} = \text{F}$  and  $n = 3$  and forms a three-dimensional primitive cubic network.<sup>72</sup> This system again demonstrates that the desired hexameric  $\text{Na}_6\text{O}_6$  SBU can be used to systematically control the resulting network topology by altering the size of the substituent at the *para*-position. Further investigation of alkyl-substituted derivatives show similar behavior, forming either the 1D, 2D, or 3D networks discussed above. Moreover, these results show that even the heavier *s*-block elements may be used as robust SBUs.



**Figure 1.11** Sections of the polymeric structures of the: (a) 1D linear chain, (b) 2D square net (framework atoms only), and (c) 3D cubic lattice (framework atoms showing a single cubic unit), formed from triple-stack  $\text{Na}_6\text{O}_6$  SBUs bridged by dioxane.

## 1.8 Outline of Research

The overall aim of the work presented in this thesis is an investigation into the use of various alkali metal aggregates as SBUs for the formation of extended framework



materials. Each chapter in this manuscript is written as a self-contained unit that uses different approaches to better understand this class of materials. The background and focus of each chapter will be highlighted in individual introductions. Chapter 2 explores the manipulation of extended supramolecular structure using self-assembled lithium mixed-anion complexes. Chapter 3 studies the use of solvent additives to alter the supramolecular structure of lithium aryloxide complexes. The main focus of Chapters 4, 5, and 6 is the synthesis of high-connectivity networks using the heavier alkali metals in combination with substituted phenols. These three chapters are broken up by the type of substitution on the aryl ring. The final chapter explores the synthesis of organometallic polymers assembled from cation- $\pi$  interactions.

## 1.9 References

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