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

**John Jacob Morris**

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SOLUTION AND SOLID-STATE STUDIES OF ALKALI  
METAL AGGREGATE ASSEMBLIES

A Dissertation

Submitted to the Graduate School  
of the University of Notre Dame  
in Partial Fulfillment of the Requirements  
for the Degree of

Doctor of Philosophy

by

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# SOLUTION AND SOLID-STATE STUDIES OF ALKALI METAL AGGREGATE ASSEMBLIES

Abstract

by

John Jacob Morris

The work presented in this dissertation investigates the use of various alkali metal aggregates as secondary building units, SBUs, for the formation of extended framework materials. Three main avenues of research have been studied, which each consider different approaches to better understand this class of materials.

The first topic is concerned with the manipulation of extended supramolecular structure of lithium aryloxide complexes using either self-assembled mixed-anion species or solvent additives (Chapters 2 and 3). Our group has previously shown that molecular cage aggregates of *s*-block metal complexes can successfully be utilized as SBUs to direct network assembly. For example, tetrameric cubanes of specific lithium aryloxides may be designed such that each metal center has a single open site for coordination to a Lewis base. In turn, employment of a ditopic linker results in these aggregates acting as tetrahedral nodes to form 3D diamondoid, and related lower dimensionality polymers. Another level of sophistication to these systems is presented here through the control of the number of metal atoms within each aggregate that may act as points of network

extension. A set of zero-, one-, two-, and three-dimensional materials have been synthesized by systematically varying the stoichiometry of the two components, 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OLi (ArOLi) and Me<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>OLi (ROLi), within single aggregates while using 1,4-dioxane (diox) as a ditopic linker. The homoleptic complex  $[(\text{ArOLi})_4 \cdot (\text{diox})_2] \supset 3(\text{diox})]_{\infty}$  forms a 3D diamondoid extended structure, where Li<sub>4</sub>O<sub>4</sub> cubanes act as tetrahedral nodes. Attempts to rationally alter the dimensionality of the network through the sequential replacement of ArOLi vertices by potentially chelating ROLi units have succeeded. The mixed-anion complexes  $[(\text{ROLi})(\text{ArOLi})_3 \cdot (\text{diox})_{1.5}] \supset 1/2(\text{C}_6\text{H}_{14})]_{\infty}$  and  $[(\text{ROLi})_4(\text{ArOLi})_2 \cdot (\text{diox})]_{\infty}$ , adopt 2D hexagonal net and 1D chain structures, respectively. Furthermore, the two complexes  $[(\text{ROLi})_3(\text{ArOLi})_3 \cdot (\text{diox})_{0.5}](\text{C}_6\text{H}_{14})]_{\infty}$  and  $[(\text{ROLi})_5(\text{ArOLi}) \cdot (\text{diox})_{0.5}]_{\infty}$  both form unusual 0D molecular dumbbell structures in the solid state. Incorporation of multiple ROLi units in the mixed-anion complexes not only results in reducing the number of possible sites for polymer extension through chelation, but also changes the aggregation state of the building block from tetrametallic Li<sub>4</sub>O<sub>4</sub> units to hexametallic Li<sub>6</sub>O<sub>6</sub> units.

The second area of investigation explores the molecular aggregation and extended network chemistry of substituted aryloxide ligands in combination with the heavier alkali metals Na, K, Rb, and Cs (Chapters 4-6). In particular, we reasoned that aggregates containing the larger alkali metals were appealing candidates as SBUs for high-connectivity systems since they should allow multiple sites for network extension (increased metal solvation), leading to interesting or novel network topologies. Ring and cage aggregates containing the large alkali metals potassium or rubidium have proven to be excellent building blocks for the creation of high-connectivity nets, as demonstrated

by their use as septahedral and nonahedral nodes. Highlights from this work include the characterization of  $[(4\text{-Cl-2,6-Me}_2\text{-C}_6\text{H}_2\text{OK})_2\cdot(\text{dioxane})_{3.5}]_\infty$  and  $[(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OK})_5\cdot(\text{dioxane})_5]_\infty$ , which form two new types of 7-connected nets, and  $[2\text{-}^i\text{Pr-C}_6\text{H}_4\text{ORb})_6\cdot(\text{dioxane})_{4.5}]_\infty$ , which is the first ever example of a 9-connected net.

An expected finding during the study of the potassium 2-*tert*-butylphenoxide system was the encapsulation of molecular water inside a  $\text{K}_6\text{O}_6$  hexameric drum, forming  $[\{(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})\}\cdot(\text{dioxane})_4]_\infty$ . Encapsulation of neutral molecules within alkali metal aggregates is rare. The scope and cause of this unusual behavior was studied in detail (Chapter 5).

The final part of the dissertation explores the synthesis of organometallic polymers assembled from cation- $\pi$  interactions (Chapter 7). The objective was to utilize ferrocene, the prototypical metallocene, as a neutral, linear, ditopic  $\pi$ -linker to bridge between preformed alkali metal aggregates. The combination of  $\text{M}(\text{HMDS})$ , where  $\text{M} = \text{Na, K, Rb, Cs}$ , with ferrocene gives rise to one-dimensional polymeric chains of dimeric ring amides bridged through ferrocene. In addition, the rubidium and cesium analogues have close intermolecular agostic interactions with neighboring chains, such that the supramolecular structures may be considered as two-dimensional  $4^4$ -nets. These studies demonstrate that cation- $\pi$  interactions can be used to rationally build extended networks using appropriate conditions.

For My Family and Niki  
Thank You For Everything

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## ABBREVIATIONS

**1D** – One dimensional

**2D** – Two dimensional

**3D** – Three dimensional

**Bipy** – 4, 4'-Bipyridine

**BCU** – Body-Centered Cubic

**BDC** – Benzenedicarboxylate

**BPE** – Trans-bis(4-pyridyl)ethylene

**BTB** – 1,3,5-benzenetribenzoate

**BTC** – 1,3,5-benzenetricarboxylate

**BuLi** – Butyllithium

**CSD** – Cambridge Structural Database

**Cp** – Cyclopentadienyl

**DEM** – diethoxymethane

**Dia** – Diamondoid

**Diox** – 1,4-Dioxane

**DMF** – Dimethylformamide

**DME** – Dimethoxyethane

**DMF** – Dimethylformamide

**DMSO** – Dimethylsulfoxide

**DFT** – Density Functional Theory

**DZ** – Double- $\zeta$

**EQ** – Equation

**FAU** – Faujasite

**Fc** – Ferrocene

**FCU** – Face-Centered Cubic

**FMA** – fumarate

**HMDS** – Hexamethyldisilazide

**HMPA** – Hexamethylphosphoramide

**IP** – Isophthalate

**IR** – Infrared

**L-lac** – Lactate

**LiOAr** – Lithium aryloxide

**MeLi** – Methyllithium

**MOF** – Metal Organic Framework

**MS** – Mass Spectrometry

**NaOAr** – Sodium aryloxide

**NMR** – Nuclear Magnetic Resonance

**PCU** – Primitive Cubic

**PMD** – Pyrimidine

**PMDTA** – N, N, N', N'', N''-Pentamethyldiethylene triamine

**Pyr** – Pyridine

**Pz** – Pyrazolyl

**RCSR** - Reticular Chemistry Structure Resource

**SBU** – Secondary Building Unit

**SCO** – Spin crossover

**THF** – Tetrahydrofuran

**Tol** – Toluene

**TMEDA** – N,N,N',N'-Tetramethylethylenediamine

**TPM** – Tetra-(4-pyridyl)methane

**TPT** – 2,4,6-tris(4-pyridyl)triazine

**XRD** – X-ray diffraction

## NUMBERED COMPOUNDS

- 2.1** [ $\{(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{diox})_2\} \supset 3(\text{diox})$ ] $_{\infty}$
- 2.2** [ $\{(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_3 \cdot (\text{diox})_{1.5}\} \supset 1/2(\text{C}_6\text{H}_{14})$ ] $_{\infty}$
- 2.3** [ $\{(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})_3(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_3 \cdot (\text{diox})_{0.5}\}(\text{C}_6\text{H}_{14})$ ] $_{\infty}$
- 2.4** [ $(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})_4(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{diox})$ ] $_{\infty}$
- 2.5** [ $(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})_5(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi}) \cdot (\text{diox})_{0.5}$ ] $_{\infty}$
- 2.6** [ $(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi}) \cdot (\text{Me}_2\text{NC}_2\text{H}_4\text{OH}) \cdot (\text{diox})_{0.5}$ ] $_{\infty}$
- 3.1** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_2$ ] $_{\infty}$
- 3.2** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_{2.5}$ ] $_{\infty}$
- 3.3** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dmf})_4$ ]
- 3.4** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dioxane}) \cdot (\text{dmf})_2$ ] $_{\infty}$
- 3.5** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dioxane})_2$ ] $_{\infty}$
- 3.6** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxolane})_2$ ] $_{\infty}$
- 3.7** [ $\{(4\text{-Br-}2,6\text{-Me-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_2\} \{ (4\text{-Br-}2,6\text{-Me-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxane})_{2.5} \}$ ] $_{\infty}$
- 3.8** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dioxane})_1 \cdot (\text{dmf})_2$ ] $_{\infty}$
- 3.9** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_4 \cdot (\text{dmf})_4$ ]
- 3.10** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{OLi})_2 \cdot (\text{dioxolane})_2$ ] $_{\infty}$
- 4.1** [ $(4\text{-Cl-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{ONa})_2 \cdot (\text{dioxane})_3$ ] $_{\infty}$
- 4.2** [ $(4\text{-Br-}2,6\text{-Me}_2\text{-C}_6\text{H}_2\text{ONa})_2 \cdot (\text{dioxane})_3$ ] $_{\infty}$

- 4.3** [(4-Cl-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.4** [(4-Br-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.5** [(4-Cl-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>ORb)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.6** [(4-Br-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>ORb)<sub>2</sub>·(dioxane)<sub>3.5</sub>]<sub>∞</sub>
- 4.7** [(4-Cl-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OCs)<sub>7</sub>·(dioxane)<sub>1</sub>]<sub>∞</sub>
- 4.8** [(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>5</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 4.9** [(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>ORb)<sub>5</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 4.10** [(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OK)<sub>4</sub>·(thf)<sub>4</sub>]<sub>∞</sub>
- 5.1** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 5.1<sub>n</sub>** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 5.2** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(THF)<sub>6</sub>]
- 5.3** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>ORb)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>4</sub>·(dioxane)]<sub>∞</sub>
- 5.4** [{(2-*t*Bu-C<sub>6</sub>H<sub>4</sub>ONa)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>3</sub>]<sub>∞</sub>
- 5.5** [{(2-*i*Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>⊃(H<sub>2</sub>O)}·(dioxane)<sub>5</sub>·(dioxane)]<sub>∞</sub>
- 5.6** [(2-*i*Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 5.7** [{(2-<sup>*i*</sup>Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(H<sub>2</sub>O)<sub>2</sub>}·(dioxane)<sub>5.5</sub>]<sub>∞</sub>
- 5.8** [2-<sup>*i*</sup>Pr-C<sub>6</sub>H<sub>4</sub>ORb)<sub>6</sub>·(dioxane)<sub>4.5</sub>]<sub>∞</sub>
- 5.10** [(2-Me-C<sub>6</sub>H<sub>4</sub>OK)<sub>4</sub>·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 6.1** [(4-F-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(dioxane)<sub>4</sub>]<sub>∞</sub>
- 6.2** [(4-I-C<sub>6</sub>H<sub>4</sub>OK)<sub>6</sub>·(dioxane)<sub>6</sub>]<sub>∞</sub>
- 6.3** [(4-I-C<sub>6</sub>H<sub>4</sub>ORb)<sub>6</sub>·(dioxane)<sub>6</sub>]<sub>∞</sub>
- 6.4** [(4-Cl-C<sub>6</sub>H<sub>4</sub>OK)<sub>3</sub>·(dioxane)]<sub>∞</sub>
- 6.5** [(4-Br-C<sub>6</sub>H<sub>4</sub>OK)<sub>2</sub>·(dioxane)<sub>0.5</sub>]<sub>∞</sub>

- 6.6** [(4-Br-C<sub>6</sub>H<sub>4</sub>ORb)<sub>5</sub>·(dioxane)<sub>5</sub>]<sub>∞</sub>
- 6.7** [(4-<sup>i</sup>Pr-C<sub>6</sub>H<sub>4</sub>OK)<sub>2</sub>·(dioxane)<sub>0.5</sub>]<sub>∞</sub>
- 7.1** [{(Me<sub>3</sub>Si)<sub>2</sub>NNa}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.2** [{(Me<sub>3</sub>Si)<sub>2</sub>NK}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.3** [{(Me<sub>3</sub>Si)<sub>2</sub>NRb}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.4** [{(Me<sub>3</sub>Si)<sub>2</sub>NCs}<sub>2</sub>·(Cp<sub>2</sub>Fe)]<sub>∞</sub>
- 7.5** [{(Me<sub>3</sub>Si)<sub>2</sub>NRb}<sub>2</sub>·(Cp<sub>2</sub>Fe)<sub>0.6</sub>·(C<sub>7</sub>H<sub>8</sub>)<sub>0.8</sub>]<sub>∞</sub>
- 7.6** [{(Me<sub>3</sub>Si)<sub>2</sub>NCs}<sub>2</sub>·(Cp<sub>2</sub>Fe)<sub>0.5</sub>·(C<sub>7</sub>H<sub>8</sub>)]<sub>∞</sub>
- 7.7** [(Me<sub>3</sub>Si)<sub>2</sub>NK·(Tol)]<sub>2</sub>
- 7.8** [{(Me<sub>3</sub>Si)<sub>2</sub>NCs}<sub>2</sub>·(Tol)]<sub>∞</sub>
- 7.9** [K·(Cp<sub>2</sub>Fe)<sub>2</sub>·(Tol)<sub>2</sub>]<sup>+</sup>[Mg(HMDS)<sub>3</sub>]<sup>-</sup>
- 7.10** [{Na(Fcpz)}·{Na(DME)<sub>3</sub>}]<sub>∞</sub>
- 7.11** [K<sub>2</sub>(Fcpz)·(DME)<sub>3</sub>]<sub>∞</sub>
- 7.12** [Rb<sub>2</sub>(Fcpz)·(DME)<sub>3</sub>]<sub>∞</sub>
- 7.13** [Cs<sub>2</sub>(Fcpz)·(DME)<sub>3</sub>]<sub>∞</sub>
- 7.14** [{(Me<sub>3</sub>Si)<sub>2</sub>NK}·(<sup>t</sup>Bu-C<sub>6</sub>H<sub>5</sub>)]<sub>2</sub>
- 7.15** [{(Me<sub>3</sub>Si)<sub>2</sub>NK}·(Me<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)]<sub>2</sub>
- 7.16** [{K·((C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr)<sub>2</sub>]<sup>+</sup>{Mg(HMDS)<sub>3</sub>]<sup>-</sup>]<sub>∞</sub>
- 7.17** [{K·((C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr)<sub>1.5</sub>·(Mes)]<sup>+</sup>{Mg(HMDS)<sub>3</sub>]<sup>-</sup>]<sub>∞</sub>