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Rational Assembly of Primitive Cubic Networks Using Hexameric Stacks of Sodium Aryloxides as Nodes

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The two sodium aryloxide complexes [{(4-R–$C_6H_4ONa)_6$·(dioxane)$_3$}$_\infty$], where R = Et (**1**) or F (**2**), have been prepared and found to form three-dimensional cubic networks in the solid state. Each structure is similarly composed of dioxane-connected Na_6O_6 aggregates that act as octahedral nodes in directing the assembly process. Although the localized metrical parameters within the hexameric cages are similar to each other, as well as to those of the molecular analogue [(4-F–$C_6H_4ONa)_6$·(THF)$_8$] (**3**), the gross architectures show significant variations. In particular, the smaller complex **2** ensures effective filling of space through transannular Na–F interaggregate interactions, resulting in substantial compression of the cubic framework.

The use of metal-containing aggregates to control the assembly of infinite network materials in a predictable manner is quickly emerging as a highly promising strategy.[1] Significant effort has been devoted to linking metal cages through divergent polydentate Lewis bases[2] and also by direct covalent bonding.[3] For the most part, these studies have concentrated on the use of transition metal complexes as secondary building units (SBUs). In contrast, although many classes of s-block metal complexes are known to have extensive molecular aggregation chemistry,[4] their use in network assembly has not been extensively pursued.[5] This deficit can be explained by the considerable problems associated with these species, such as the spherical, nonpolarizable nature of the cations, the limited preference for fixed metal geometries, and the lability of metal−ligand bonding resulting in complex dynamic solution equilibria between aggregated species.[4] All of these issues can lead to poor predictability and reproducibility in network synthesis. Hence, although the potential for the rational design of frameworks composed of s-block metals and linking ligands has certainly been recognized,[6] it was only recently that this goal was finally realized.[7,8] Specifically, our group used lithiated aryloxides to selectively preassemble tetrasolvated Li_4O_4 cubane aggregates that were subsequently connected through the divergent Lewis base dioxane to build polymeric assemblies.[8] This included 3D diamondoid networks, which are related to four points of extension from the tetrahedral SBUs.

To date, our studies have been directed toward the use of lithiated aggregates as SBUs, as the coordination chemistry of these complexes is by far the best understood within the s-block.[4] However, several factors attracted us to the possibility of expanding our work to the heavier group 1 analogues, including (i) widening the range of aggregate geometries available as SBUs, (ii) controlling the dimensions of the networks by the choice of the metal, and (iii) increasing the opportunities for metal solvation. A potential drawback is the accompanying substantial increase in ionic character, and hence, it is reasonable to question whether the desired metal aggregates possess the inherent stability to remain intact upon polymer formation.

Building on the success of the lithiated systems, we targeted sodium aryloxides as SBUs because these complexes contain relatively strong Na−O bonds and the THF solvate

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of simple sodium phenoxide is known to adopt a molecular hexameric stack (face-shared double cube) aggregate in the solid state, [{PhONa·THF}$_6$].[9] We theorized that, if such aggregates proved to be robust and if all six sodium centers were used as points of extension, these complexes could act as novel octahedral nodes to build cubic networks.[10] A further attraction was that, to our knowledge, this arrangement has not been previously observed for polymers composed of s-block metal aggregates.[11] In this communication, we highlight that this central objective has been achieved, providing strong encouragement for future studies in this area.

The two complexes [{(4-R−C$_6$H$_4$ONa)$_6$·(dioxane)$_3$}$_\infty$], where R = Et (**1**) or F (**2**), were readily prepared by the direct deprotonation of the parent phenol by NaH, using dioxane as the neat solvent medium.[12] In addition, the molecular analogue of **2**, [(4-F−C$_6$H$_4$ONa)$_6$·(THF)$_8$] (**3**), was successfully synthesized and characterized for comparative purposes.[12] Single-crystal X-ray analyses of **1**−**3** revealed that they each contain the desired hexameric Na$_6$O$_6$ core aggregation,[13] which can be considered as a triple stack of Na$_2$O$_2$ dimers.[14] Similar arrangements have been found for sodium thiolates, hydrazides, and various aryloxides.[9,15] Whereas the polymers **1** and **2** have all of their metal centers monosolvated by dioxane, the molecular complex **3** unexpectedly has a pair of terminal sodium centers solvated by two THF molecules (Figure 1).

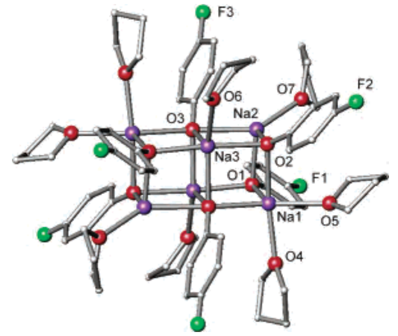

Figure 1. Molecular structure of **3** with hydrogen atoms omitted.

Relatively little variation is found for the metrical parameters within the individual cages. The Na−O(donor) bond lengths lie in the narrow range 2.292(1)−2.423(1) Å, with mean distances of 2.316, 2.348, and 2.369 Å for **1**, **2**, and **3**, respectively. Also, the Na−O(anion) distances lie in the range 2.210(1)−2.506(1) Å, with mean distances of 2.328, 2.340, and 2.356 Å for **1**, **2**, and **3**, respectively. Furthermore, the internal O−Na−O angles within the stacks all lie within 6° of the idealized value of 90° for a perfect face-shared cube, ranging between 86.78(2)° and 95.83(2)°, with mean values of 90.90°, 90.06°, and 89.65° for **1**, **2**, and **3**, respectively. In combination, these similar values indicate that the incorporation of the Na$_6$O$_6$ hexameric stacks within the 3D frameworks in **1** and **2** has little, if any, effect on the geometry of the aggregated cores.

Analysis of the extended structures of **1** and **2** reveals that all six of the sodium centers of the individual hexamers act as points of polymer extension by connecting to neighboring aggregates through bridging dioxane molecules. Overall, the cages act as octahedral SBUs to give the connectivity of distorted primitive cubic lattices as predicted (Figures 2 and 3). The cubic description of **1** and **2** is useful for visualization but is a simplification. Considering the nodal points to be at the centers of the Na$_6$O$_6$ cages, the frameworks have long edges associated with the terminal sodium centers and shorter edges at the central sodium centers.

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(12) Synthetic conditions: All compounds lose coordinating solvent upon removal from the mother liquor or exposure to vacuum; hence the determined yields (first crystalline batches) are based on the solvent content as determined by integration of their ^{1}H NMR spectra. Synthesis of **1**: 4-Fluorophenol (5 mmol, 540 mg) was added to a stirred suspension of sodium hydride (5 mmol, 120 mg) in dioxane (10 mL) to give a white precipitate. Complete dissolution was achieved by dilution with dioxane (5 mL) and strong heating. Slow cooling in a water bath (65−20 °C) resulted in the deposition of clear colorless X-ray quality crystals. Yield 320 mg, 39.1%. ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 3.57$ (2.7 H, s, OCH$_2$, dioxane), 6.08 (2 H, m, *m*-H, Ph), 6.54 (2H, m, *o*-H, Ph). ^{13}C NMR (75 Mz, DMSO-d_6) $\delta = 66.42$ (OCH$_2$, dioxane), 114.34 (d, $^3J_{HF} = 20.9$ Hz, *o*-C, Ph), 117.99 (d, $^2J_{HF} = 7.3$ Hz, *m*-C, Ph), 149.71 (d, $^1J_{HF} = 220.5$ Hz, *p*-C, Ph), 168.31 (*i*-C, Ph). Synthesis of **2**: 4-Ethylphenol (5 mmol, 610 mg) was added to a stirred suspension of sodium hydride (5 mmol, 120 mg) in dioxane (5 mL) to give a white precipitate. Complete dissolution was achieved upon heating. X-ray quality crystals were precipitated on the slow evaporation of the solvent within a glovebox. Yield 660 mg, 78.1%. ^{1}H NMR (300 Mz, DMSO-d_6) $\delta = 1.07$ (3H, t, $^3J_{HH} = 7.5$ Hz, CH$_3$, Et), 2.34 (2H, q, $^3J_{HH} = 7.5$ Hz, CH$_2$, Et), 3.57 (2.2 H, s, OCH$_2$, dioxane), 6.14 (2 H, d, $^3J_{HH} = 8.4$ Hz, *m*-H, Ph), 6.54 (2H, d, $^3J_{HH} = 8.1$ Hz, *o*-H, Ph). ^{13}C NMR (75 MHz, DMSO-d_6) $\delta = 18.82$ (CH$_3$, Et), 27.60 (CH$_2$, Et), 66.39 (OCH$_2$, dioxane), 118.44 (*o*-C, Ph), 122.87 (*m*-C, Ph), 127.94 (*p*-C, Ph), 168.87 (*i*-C, Ph). Synthesis of **3**: 4-Fluorophenol (5 mmol, 540 mg) was added to a stirred suspension of sodium hydride (5 mmol, 120 mg) in THF (5 mL) to give a clear solution. Cooling at −45 °C resulted in the deposition of clear colorless crystals. Yield 600 mg, 78.9%. ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 3.61$ (1 H, m, OCH$_2$, THF), 1.76 (1 H, m, CH$_2$, THF), 6.09 (2 H, m, *m*-H, Ph), 6.54 (2H, m, *o*-H, Ph). ^{13}C NMR (75 Mz, DMSO-d_6) $\delta = 25.18$ (CH$_2$, THF), 67.07 (OCH$_2$, THF), 114.34 (d, $^3J_{HF} = 20.9$ Hz, *o*-C, Ph), 117.89 (d, $^2J_{HF} = 7.3$ Hz, *m*-C, Ph), 148.3 (d, $^1J_{HF} = 219.8$ Hz, *p*-C, Ph), 167.93 (*i*-C, Ph).

(13) Crystal data for **1**: C$_{30}$H$_{39}$Na$_3$O$_6$, monoclinic, $P2_1/c$, $a = 10.3777(1)$ Å, $b = 16.5849(2)$ Å, $c = 17.9530(2)$ Å, $\beta = 95.596(1)°$, $V = 3075.22(6)$ Å^3, $T = 100$ K, $Z = 4$, $\rho_{calc} = 1.219$ Mg m^{-3}, Mo Kα $\lambda = 0.71073$ Å, 43096 reflections collected and 10 149 unique reflections ($R_{int} = 0.0245$), final R1 = 0.0365 for 8038 observations with $I > 2\sigma(I)$, R1 = 0.0487 (wR2 = 0.1032) for all unique data. Crystal data for **2**: C$_{24}$H$_{24}$F$_3$Na$_3$O$_6$, triclinic, $P\bar{1}$, $a = 10.3782(2)$ Å, $b = 11.1745(2)$ Å, $c = 12.9564(2)$ Å, $\alpha = 65.384(1)°$, $\beta = 77.787(1)°$, $\gamma = 64.896(1)°$, $V = 1235.87(4)$ Å^3, $T = 100$ K, $Z = 2$, $\rho_{calc} = 1.436$ Mg m^{-3}, Mo Kα $\lambda = 0.71073$ Å, 337 236 reflections collected and 8267 unique reflections ($R_{int} = 0.0218$), final R1 = 0.0348 for 7109 observations with $I > 2\sigma(I)$, R1 = 0.0406 (wR2 = 0.1012) for all unique data. Crystal data for **3**: C$_{68}$H$_{88}$F$_6$Na$_6$O$_{14}$, triclinic, $P\bar{1}$, $a = 11.9721(3)$ Å, $b = 13.3007(3)$ Å, $c = 13.9938(3)$ Å, $\alpha = 65.713(1)°$, $\beta = 64.905(1)°$, $\gamma = 64.905(1)°$, $V = 1779.07(7)$ Å^3, $T = 100$ K, $Z = 1$, $\rho_{calc} = 1.289$ Mg m^{-3}, Mo Kα $\lambda = 0.71073$ Å, 83 097 reflections collected and 11788 unique reflections ($R_{int} = 0.0419$), final R1 = 0.0409 for 9381 observations with $I > 2\sigma(I)$, R1 = 0.0557 (wR2 = 0.1153) for all unique data.

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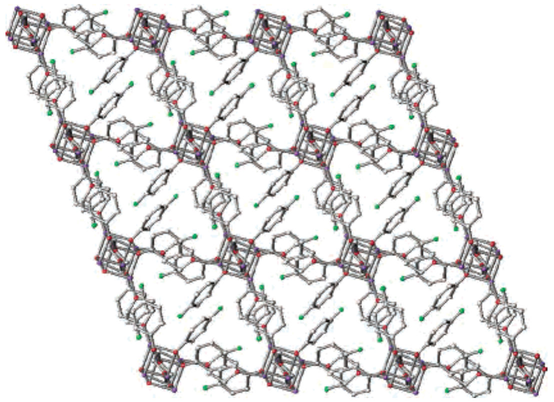

Figure 2. Section of the extended structure of **2** viewed along the crystallographic *c* axis. Hydrogen atoms are omitted for clarity.

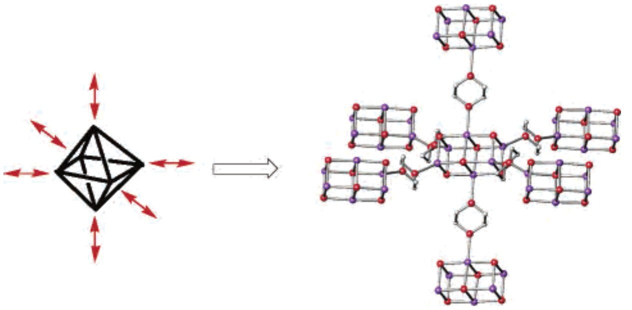

Figure 3. Section of the framework of **1** showing one Na_6O_6 unit connecting to six neighboring aggregates and highlighting the relationship between the SBU and an octahedral node.

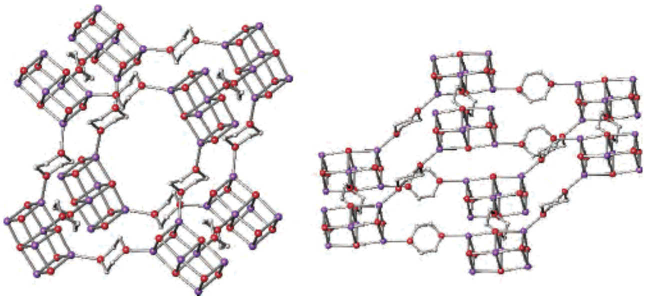

Figure 4. Sections of the extended structures of **1** and **2** showing only the framework atoms of single cubic units. The angle adopted highlights the distortion of **2** from a perfect cubic arrangement.

Also, the angles made between neighboring centroids vary substantially for the complexes. In **1,** these angles lie in the relatively narrow range 85.5−94.5°, whereas those in **2** are much more diverse, spanning 50.7−129.3° (Figure 4). This distortion is clearly manifested in the O−Na−O angles made between the central anionic oxygens and the dioxanes bound to the terminal sodium centers. In **1**, these angles are 123.4(3)° and 136.1(3)°, whereas in **2**, they are 140.8(3)° and 170.2(3)°. This latter angle in **2** results in the observed compression of the framework.

Close examination of the bonding environment around this terminal sodium center in **2** reveals that the near-linear O(3)−Na(2)−O(5) angle opens up a coordination site on the metal (Figure 5). In turn, this vacancy is occupied by a relatively short Na(2)−F(1*) interaction of 2.545(1) Å, arising from an interaggregate contact across one of the faces of the cubic structure. This Na−F distance is in accord with similar reported contact distances. For example, the shortest Na−F distances in the contact ion pair [Na•(18-crown-6)•PF_6] are approximately 2.4−2.5 Å.[16] In fact, the presence of these Na−F interactions is very likely to be critical in the stabilization of the 3D framework. The cubic cavities in **1** are efficiently filled by 4-Et−$C_6H_4O^-$ groups, with the closest interaggregate H−H contact distances being ~2.4 Å.[17] Maintaining this near-cubic geometry but replacing the ethyl groups by the smaller fluorine atoms would result in unacceptably large voids (predicted closest F−F distances >3.5 Å). The transannular Na−F interactions therefore act in concert to zip the structure together, leading to efficient localized packing and stabilization of the 3D assembly. Interestingly, this additional interaction results in a distorted trigonal-bipyramidal arrangement around one of the terminal sodium centers, which can be directly compared to the disolvated metal centers found in the molecular analogue **3**.

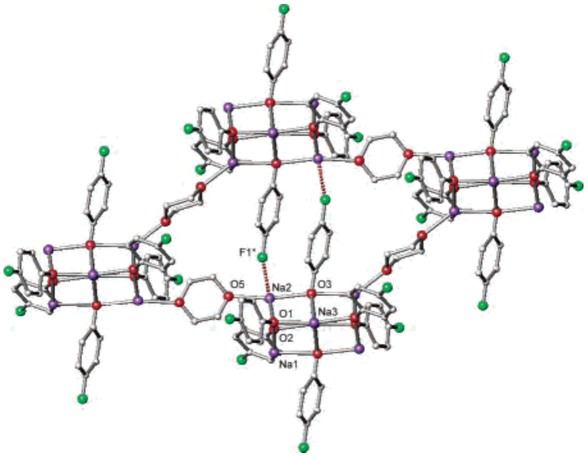

Figure 5. View of **2** along the crystallographic *a* axis showing the square face of the cubic network containing Na−F interactions. Additional dioxane molecules and hydrogen atoms are removed for clarity.

In conclusion, characterization of **1** and **2** demonstrates not only that aggregates of the heavier alkali metals are robust and can be used to direct 3D assembly in a predictable fashion but also that these networks exhibit a surprising degree of flexibility. This feature might be of importance in the use of related materials in selective host−guest chemistry.[18] We are presently investigating the structures formed by an extended series of group 1 organyloxides solvated by dioxane, and a complete analysis of the relationship between the sterics present and the supramolecular architecture adopted will be elaborated elsewhere.

Supporting Information Available: Crystallographic data for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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