

X-ray and Neutron Diffraction Studies of Water-Encapsulated inside Potassium Aryloxy Aggregates: Complementary Host–Guest Stabilization of Mono- and Dihydrated Cages

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The controlled hydrolysis of potassium 2-*tert*-butylphenoxide or 2-isopropylphenoxide leads to the unexpected encapsulation of the water inside K_6O_6 hexameric drum aggregates. Encapsulation of the neutral molecules is enabled in these instances through the formation of strong hydrogen bonds and dative interactions between the host and guest.

Alkali-metal complexes are notoriously air- and moisture-sensitive.¹ Indeed, despite their best efforts, a relatively frequent occurrence for researchers in s-block organometallic chemistry is the unanticipated appearance of O^{2-} , O_2^{2-} , and OH^- anions as components of complex crystal structures.² These species normally result from the reaction of the highly oxophilic metal reagents with adventitious water or dioxygen. These observations are important because the formation of such mixed-anion complexes may significantly alter the reactivity and selectivity of the parent reagent.³ Also, the deliberate generation of these small anions has been used to stabilize large aggregates of main-group complexes, where they act as points of cage “nucleation”.⁴ In comparison, there are no reports of neutral water encapsulation by an alkali-metal cage aggregate. However, the formation of water-containing supramolecular capsules is well-known for self-assembled cages using transition metals and organic linkers.⁵ Because the neutral water molecule carries a pair of hydrogen centers, it would be expected to create substantial repulsive interactions with surrounding highly electropositive alkali-metal

ions. Nevertheless, water is a ubiquitous ligand for alkali-metal salts, with hundreds of known crystal structures.⁶ Most commonly, it acts as a terminal ligand, but it can also serve as a μ^2 or even a μ^3 bridge. We now report the first examples of water encapsulation inside alkali-metal cage aggregates, as authenticated by X-ray and neutron diffraction analyses.

The present study originates from our ongoing interest in developing the use of alkali-metal aggregates as secondary building units for the assembly of coordination polymers.⁷ During these investigations, high-quality crystals were obtained from the equimolar reaction of 2-*tert*-butylphenol with potassium hexamethyldisilazide in 1,4-dioxane. Subsequent single-crystal X-ray diffraction analysis revealed the formation of a hexameric “drum” aggregate, coordinated to six dioxane molecules.^{8,9} Two of the solvents terminally bind to the aggregate, while the remaining four dioxanes bridge to neighboring hexamers, leading to the formation of two-dimensional 4⁴-nets (see the Supporting Information).

Refinement of the X-ray data indicated a substantial residual peak near the center of the trimeric K_3O_3 ring of the asymmetric unit (space group $C2/c$). The most reasonable assignment for this site is the unexpected inclusion of a water molecule because anion incorporation would render the complex charged. Symmetry expansion through the crystallographic inversion center leads to a pair of water molecules, each with a partial occupancy of $\sim 50\%$ (the oxygen centers are nominally separated by 1.28 Å). Thus, each hexamer in

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- (1) Wakefield, B. J. *Organolithium Methods*; Academic: London, 1988.
- (2) Wheatley, A. E. H. *Chem. Soc. Rev.* **2001**, *30*, 265.
- (3) McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *J. Am. Chem. Soc.* **1985**, *107*, 1815.
- (4) *Molecular Clusters of the Main Group Elements*; Driess, M., Nöth, H., Eds.; Wiley-VCH: Weinheim, Germany, 2004.
- (5) Pluth, M. D.; Raymond, K. N. *Chem. Soc. Rev.* **2007**, *36*, 161.

(6) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.

(7) (a) Morris, J. J.; Noll, B. C.; Honeyman, G. W.; O'Hara, C. T.; Kennedy, A. R.; Mulvey, R. E.; Henderson, K. W. *Chem.—Eur. J.* **2007**, *13*, 4418. (b) Morris, J. J.; Noll, B. C.; Henderson, K. W. *Cryst. Growth Des.* **2006**, *6*, 1071. (c) MacDougall, D. J.; Morris, J. J.; Noll, B. C.; Henderson, K. W. *Chem. Commun.* **2005**, 456.

(8) Boyle, T. J.; Andrews, N. L.; Rodriguez, M. A.; Campana, C.; Yiu, T. *Inorg. Chem.* **2003**, *42*, 5357.

(9) A water-solvated potassium aminosilanolate has previously been characterized: Reiche, C.; Kliem, S.; Klingebiel, U.; Noltemeyer, M.; Voit, C.; Herbst-Irmer, R.; Schmatz, S. *J. Organomet. Chem.* **2003**, *667*, 24.

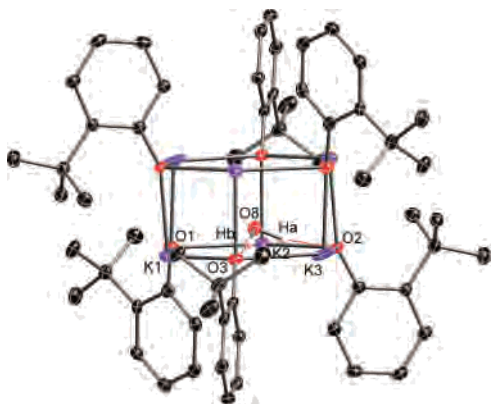


Figure 1. Section of the joint X-ray and neutron structure of **1**. The encapsulated water molecule with attached hydrogen atoms is shown in one of the two possible sites. Other hydrogen atoms and coordinated dioxane molecules are removed for clarity.

the crystalline lattice contains a single encapsulated water molecule, giving the molecular formula $\{(2\text{-}^t\text{BuC}_6\text{H}_4\text{OK})_6\cdot(\text{H}_2\text{O})\}\cdot(\text{diox})_4$ (**1**; Figure 1).

Considering the unique nature of the neutral molecular encapsulation within **1**, we wished to unambiguously identify the guest present. This proved to be problematic by conventional means. The hydrogen positions could not be assigned from the X-ray data because of the location of the guest molecule over two sites. Also, ^1H NMR and IR analyses were not helpful because of broadening of the signals. The use of neutron diffraction analysis was then targeted because this technique is ideally suited for the location of hydrogen atoms. Subsequently, neutron diffraction data of **1** were obtained at the Intense Pulsed Neutron Source at Argonne National Laboratory using a time-of-flight Laue single-crystal diffractometer.^{10,11} The atomic positions of the X-ray diffraction structure were used as a starting point in the refinement. Because of the large number of parameter variables, a joint refinement using X-ray and neutron reflections was used in the final model. Only the neutron data were used to calculate the difference Fourier map in order to find all hydrogen atom positions. As illustrated in Figure 1, the refinement of **1** clearly identified the central guest molecule to be neutral water. In turn, an analysis of the metrical parameters within **1** provides valuable insights into the stabilization of this unusual structure.

The two hydrogen atoms of the water molecule, Ha and Hb, have bond distances of 0.963(16) and 1.009(16) Å to the central oxygen atom, O8, with an Ha–O8–Hb angle of 108.0(13)°. Therefore, encapsulation by the hexameric prism does not significantly perturb the structure of the water molecule.¹² Each hydrogen of the water has a close interaction to a neighboring aryloxy oxygen, with distances of 1.726(16) Å for Ha–O2 and 1.721(17) Å for Hb–O3 and

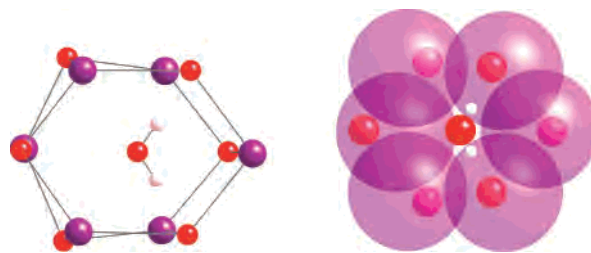


Figure 2. Ball-and-stick and Corey–Pauling–Koltun space-filling views of the $[\text{K}_6\text{O}_6\cdot\text{H}_2\text{O}]$ core of the calculated structure.

with angles of 167.69° for O8–Ha–O2 and 169.94° for O8–Hb–O3. These data support the formation of strong hydrogen bonds within the cage.¹²

The two K_3O_3 rings of the hexameric prism define almost perfect planes, and the oxygen of the water molecule is asymmetrically located at distances of 1.88 and 0.68 Å between these mean planes. In turn, this leads to relatively short distances of 2.730(2), 2.751(2), and 2.723(2) Å between O8 of the water molecule and the three potassium centers of the closest ring, K1, K2, and K3, respectively (the remaining K–O8 distances are all >3 Å). These internal K–O interactions are comparable with the mean K–O_{Ar} distance of 2.657 Å, in range of 2.521(1)–2.761(1) Å.

The unexpected encapsulation of water, therefore, appears to be due to a combination of the water's strong hydrogen bonding to the aryloxy anions and its dative interactions to the surrounding potassium centers.¹³ An ab initio study at the computationally manageable HF/6-31G* level supports this assessment. Geometry optimizations were completed on the full molecules $\{(2\text{-}^t\text{BuC}_6\text{H}_4\text{OK})_6\}\cdot(\text{diox})_6$ and $\{(2\text{-}^t\text{BuC}_6\text{H}_4\text{OK})_6\cdot(\text{H}_2\text{O})\}\cdot(\text{diox})_6$ (Figure 2). These basic calculations confirm that water encapsulation not only is feasible but is actually energetically favored over the water-free parent molecule by –14.7 kcal/mol.

Repeated attempts to prepare an anhydrous derivative using meticulously dried and degassed reagents, solvents, and glassware simply resulted in lower yields of **1** (~5%). Interestingly, the deliberate addition of large excesses of water to the reaction still produced **1**. For example, using a 2:1 molar equivalent ratio of water to aryloxy resulted in the precipitation of **1** in 64% yield. The reaction of KOH with the phenol in 1,4-dioxane also produced crystals of **1** despite the in situ generation of equimolar quantities of water.¹⁴ Therefore, the hexameric monohydrate appears to be remarkably stable to further hydration.

To determine if water encapsulation is specific to **1** or a more general phenomenon for this class of compounds, the closely related ligand 2-isopropylphenol was studied. Subsequently, the complex $\{(2\text{-}^i\text{PrC}_6\text{H}_4\text{OK})_6\cdot(\text{H}_2\text{O})\}\cdot(\text{diox})_5$ (**2**) was successfully prepared and its structure elucidated by single-crystal X-ray diffraction. The aggregated structure of **2** is essentially identical with that of **1**, with water again encapsulated within a prismatic K_6O_6 hexamer (Figure

(10) Schultz, A. J.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999.

(11) Schultz, A. J.; De Lurgio, P. M.; Hammonds, J. P.; Mikkelsen, D. J.; Mikkelsen, R. L.; Miller, M. E.; Naday, I.; Peterson, P. F.; Porter, R. R.; Worlton, T. G. *Physica B* **2006**, *385–386*, 1059–1061.

(12) Jeffery, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(13) (a) Barr, D.; Raithby, P. R.; Schleyer, P. v. R.; Snaith, R.; Wright, D. *S. J. Chem. Soc., Chem. Commun.* **1990**, 643. (b) Lambert, C.; Schleyer, P. v. R.; Pieper, U.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 77.

(14) Mikulcic, P.; Raithby, P. R.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 428.

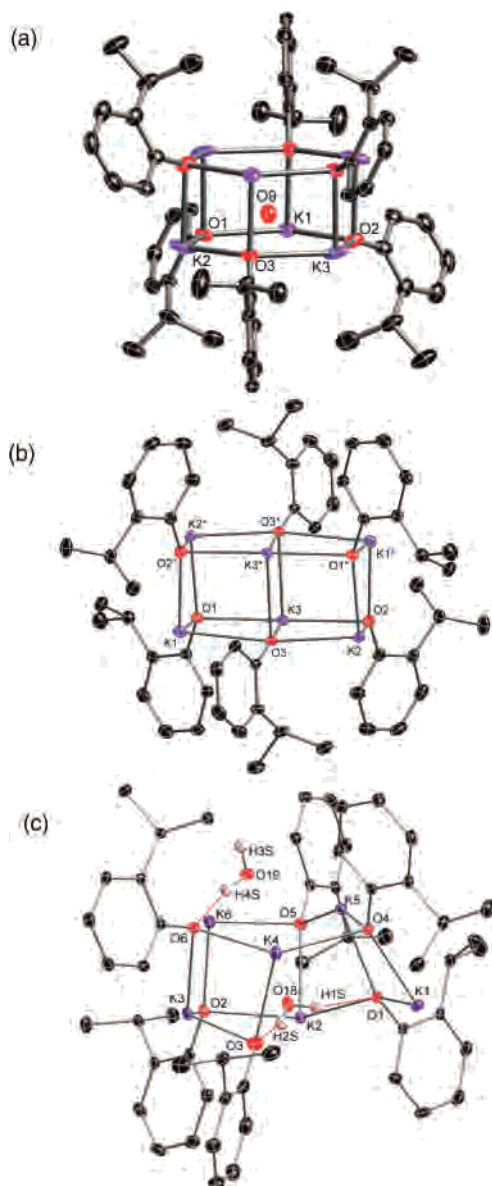


Figure 3. Sections of (a) the prismatic monohydrate **2** (hydrogen atoms of the water were not located), (b) the water-free triple stack of dimers **3**, and (c) the dihydrate **4**. Hydrogen atoms (except those located in the X-ray difference map for the water in **4**) and dioxane molecules are removed for clarity.

3a). The smaller isopropyl groups now allow for the coordination of eight dioxanes. Two of the dioxanes bond terminally to the cage, leaving six dioxanes to bridge to neighboring aggregates to form a three-dimensional (3D) primitive cubic network, with free dioxane molecules filling the channels.

Pleasingly, using this system, we were able to prepare the water-free derivative $[(2\text{-}^i\text{PrC}_6\text{H}_4\text{OK})_6 \cdot (\text{diox})_5]_\infty$ (**3**), which was structurally characterized and is shown in Figure 3b. The most striking feature of **3** is that a hexameric aggregate is found again, but it now adopts a compact “triple stack of dimers” motif.⁸ Interestingly, both prismatic hexamers and triple stacks of dimers have previously been reported for alkali-metal aryloxides.⁸ However, little rationalization has appeared to explain why both structural isomers appear. Retention of hexameric

aggregation in **2** and **3** clearly illustrates the stability of this arrangement for these metal–ligand–solvent systems. Incorporation of water only requires opening of the two central K–O_{Ar} contacts in **3** to give the prismatic isomer. The extended structure of **3** is a 3D cubic net similar to that of **2** but without the enclathrated dioxane solvent.

The subtle change of *tert*-butyl to isopropyl also critically alters the sensitivity of the system to hydration. Increasing the molar ratio of water to aryloxide from 1:6, used to prepare **2**, to 2:6 allows isolation of the dihydrate $[(2\text{-}^i\text{PrC}_6\text{H}_4\text{OK})_6 \cdot (\text{H}_2\text{O})_2] \cdot (\text{diox})_{5.5}]_\infty$ (**4**; Figure 3c). The crystal structure of **4** again consists of linked hexameric units consistent with **1–3**, but now the additional water breaks open an edge of each K₃O₃ ring, where K6–O6 is 3.695 Å, K1–O3 is 4.652 Å, and the remaining K–O_{Ar} distances are <3 Å.

One of the water molecules can still be considered to be within the loose cage, with O18 lying 0.14 Å above the closest K₃O₃ mean plane. This water again hydrogen bonds to a pair of aryloxide anions and interacts with two potassium centers [K3–O18 is 2.788(1) Å and K2–O18 is 2.883(1) Å]. The second water sits 1.50 Å out of the closest K₃O₃ mean plane, forming two dative interactions, K6–O19 at 2.727(1) Å and K5–O19 at 2.807(1) Å. Because it is no longer encapsulated, this second water molecule forms only a single hydrogen bond to an aryloxide, with the remaining hydrogen directed toward a dioxane molecule of a neighboring cage [H3s–O10 is 2.018(2) Å and O19–H3s–O10* is 170.53(2)°]. Finally, the extended structure of **4** is interesting, adopting an unusual 4⁴-net bilayer motif.

A final point of note is that the thermal ellipsoids of all six potassium centers are elongated in **2**, whereas only K3 and K3' are elongated in **1**. This suggests that the waters in **2** are disordered over all six possible binding sites, which is likely a consequence of the smaller isopropyl groups allowing more flexing of the structure.

In conclusion, the characterization of **1–4** demonstrates that guest water molecules can be encapsulated within appropriately designed alkali-metal host aggregates. Indeed, considering that the identification of water within **1** and **2** may easily have been overlooked, it is likely that similar neutral solvates have previously been prepared but not recognized. We are presently extending our studies to determine the specificity of water encapsulation to a broader range of substituted aryloxides and also to other alkali-metal aggregates.

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Supporting Information Available: Experimental and computational details and X-ray and neutron data (PDF and CIF), including details of the extended structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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