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An Adamantane-Based Coordination Framework with the First Observation of Discrete Metal Sulfonate Clusters

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By employing a rigid adamantane-based unit as a spacer, a coordination solid with an open channel layered structure results showing the first observation of metal sulfonate clusters. The design approach employed enforces a structural mismatch of metal and ligand coordinative preferences.

Numerous studies have been reported with the goal of gaining control over the solid state assembly of infinite coordination solids. This is recognized as a complex task involving numerous interdependent synthetic and structural variables.[1] While some of these parameters, such as temperature or solvent, can be quite subtle, the size and shape of the ligand along with the particular metal−ligand interaction represent fundamental considerations in the self-assembly of coordination solids. In some cases, predictable structures have resulted from the assembly of components with well-defined geometries and bonding preferences,[2] for example, the construction of PtS analogues from square and tetrahedral units,[3] honeycomb-type structures from the connection of trigonal species,[4] or, of particular relevance to this work, the formation of diamondoid structures from tetrahedral units.[5]

While, with ligands such as carboxylates, the regularity of some discrete assembly motifs (paddlewheel, tetrahedral oxo clusters)[6] enables elegant design strategies (isoreticular synthesis) to be developed,[7] an analogous approach for sulfonates is precluded by the lack of structural data on homoleptic sulfonate complexes.[8,9] With regard to Ba^{2+}, with simple monosulfonate anions, virtually all structures adopt continuous-sheet layered motifs leading to their use as lubricants.[10] Only three examples of nonlayered sulfonate complexes are known. Fromm has reported the partial solvation of barium triflate with THF to form a 1-D column.[11] We have reported a metastable one-dimensional structure

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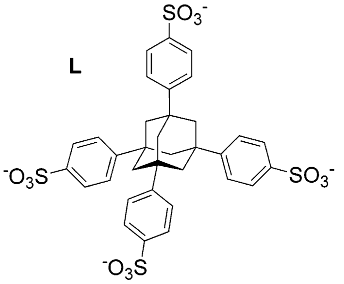
formed with Ba^{2+}, 2-pyridylethanesulfonate, and ethyl acetate guest molecules.[12] While this structure did convert to a layered motif with heating/desolvation, it did serve to illustrate, importantly, that the organic moiety of the sulfonate, and indeed the guest molecules, had a greater role than simply "filler" and that the overall structure was not dictated by the metal ion ligation. With this in mind, we sought to synthesize a highly structure-directing polysulfonated ligand which would completely disfavor the formation of a layered solid. The tetraanion of 1,3,5,7-tetrakis(4-sulfophenyl)adamantane, **L**, presents four ligating groups in an orientation which precludes, for both directional and proximal reasons, facile cross-linking of ligands into a simple layered solid. From solely the geometrical perspective, a product with an open diamondoid structure can be envisioned as the adamantane core[13] orients the four $-SO_3$ groups in a perfect tetrahedron and the addition of rigid phenyl spacers should promote void space in the structure. Upon complexation with Ba^{2+}, a product results which represents a structural compromise between the geometrical constraints imposed by the ligand and the coordinative preferences of the Ba^{2+} ion with the sulfonate groups. The infinite coordination solid, $[Ba_2(\mathbf{L})(H_2O)_4(dioxane)]\cdot(H_2O)_3(dioxane)_3$, **1**, broadly speaking, is a layered compound permeated by open channels. While compound **1** does still form an infinite two-dimensional framework, it is not one with the usual continuum of Ba^{2+} sulfonate interactions. Rather, these interactions are manifested as discrete clusters, the first observation of such aggregates in a metal sulfonate structure. Conversely, quite surprisingly, while three of the $-SO_3$ groups of the ligand coordinate multiple metal centers, the fourth is completely uncoordinated. These unusual structural features arise completely due to the mismatch of coordinative and structural tendencies in this system.

L



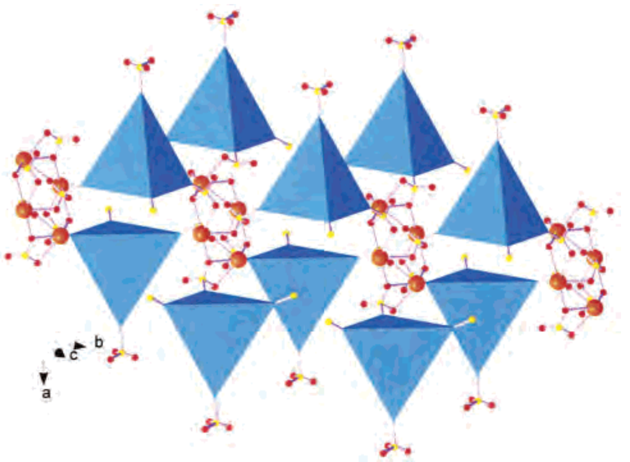


Figure 1. View of a section of a layer of compound **1** showing the coordination of the clusters. Molecules of **L** are represented as large tetrahedra. Note that each cluster is coordinated by six different ligands. For clarity, coordinated water molecules have also been removed and SO_3 groups, which are not ligated to the specific clusters shown, are represented by only the central S atom. Completely noncoordinating SO_3 groups are not truncated.

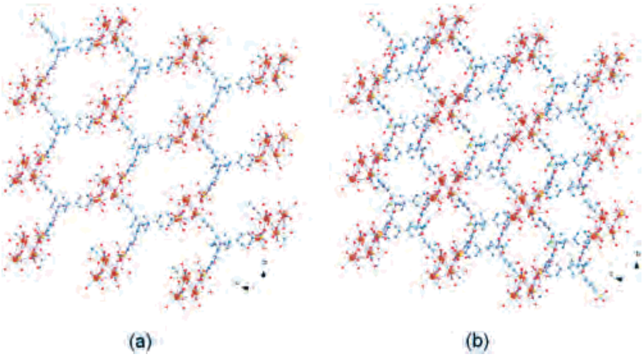


Figure 2. (a) View down onto a layer of compound **1**, with the organic moieties of **L** to one side of a layer removed, showing the distorted honeycomb arrangement. (b) View of **1** showing a complete layer with overlapping hexagonal motifs.

The new tetrasulfonated ligand, **L**, was readily prepared in a three-step synthesis.[14] Single crystals of complex **1** were grown by slow diffusion of dioxane into an aqueous solution of $Ba_2\mathbf{L}$ formed in situ.[15] Compound **1** forms a two-dimensional open grid structure where the layers lie in the *bc* plane. The layers are composed of Ba_4 clusters bridged by six sulfonate groups originating from six different molecules of **L**, three projecting to each side of a given layer. Thus, each molecule of **L** uses three of its four sulfonate groups to coordinate to different Ba^{2+} centers, leaving one sulfonate group uncoordinated and directed away from the layer (Figure 1). Looking down upon a single molecule of **L** along the *a*-axis, the symmetry of the three ligating sulfonates is effectively trigonal. Not surprisingly then, the basic motif adopted by the ligands, to one face of a layer, is a (distorted) honeycomb motif (Figure 2a). The ligands to the opposite side of the layer have the same (inversion-related) structure. The molecules of **L** to opposite sides of the layers, however, do not align perpendicularly opposite

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(14) $H_4\mathbf{L}$ was prepared in three steps beginning with adamantane. Details provided as Supporting Information.

(15) Crystal data for compound **1**: $Ba_2C_{50}H_{54}O_{24}S_4$, fw = 1441.7 g mol^{-1}, colorless plates, triclinic, space group $P\bar{1}$, $a = 13.9845(28)$ Å, $b = 14.7922(30)$ Å, $c = 15.3637(31)$ Å, $\alpha = 75.43(3)°$, $\beta = 82.74(3)°$, $\gamma = 77.75(3)°$, $V = 2996.9(3)$ Å^3, $Z = 2$, $D_c = 1.715$ Mg m^{-3}, $R = 7.58\%$, $R_w = 18.26\%$, and GOF = 1.031 for 736 parameters using 8890 ($F_o > 2.0\sigma(F_o)$) reflections. Mo Kα radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) 2.225 mm^{-1}. The structure was collected on a Nonius Kappa CCD diffractometer at −100 °C. The structure was solved by direct methods and refined by full-matrix least squares, based on F^2, by using SHELXL-97.[19] Barium and sulfur atoms were located first and the remaining atoms found by difference Fourier maps. All non-hydrogen atoms were refined anisotropically.

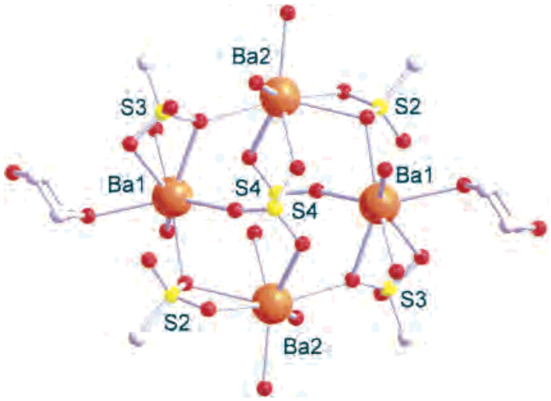

Figure 3. The tetrabarium cluster formed in compound **1**. Two types of sulfonate groups bridge the edges while another caps the faces of the square arrangement.

their symmetry-related partners. The base of the adamantane units of related trans-layer ligands are situated ~4.5 Å apart. The overall result is that, viewed down the *a*-axis, the layers represent two sets of overlaid distorted honeycomb grids with shared vertices (Figure 2b). The structure of **1** is quite open with a series of pores permeating the framework.

The dimensions of the openings in a single hexagonal assembly, as defined by trans-annular phenyl−phenyl distances of different molecules of **L**, measure approximately 12.6(1) × 18.5(1) × 15.5(2) Å. The pores are occupied by several disordered water molecules and three molecules of dioxane. There are two crystallographically unique Ba^{2+} atoms in the structure; both have irregular seven-coordinate geometries. Ba1 is coordinated by two η^1 and one η^2 sulfonate groups, two molecules of water, and one molecule of dioxane. Ba2 is coordinated by three η^1 and one η^2 sulfonate groups and two water molecules. Conversely, the three sulfonate groups involved in forming the cluster are all multiply bridging (on S2, μ_2, η^2; on S3, μ_2, η^2; on S4, μ_3, η^3). Surprisingly, one sulfonate group is completely uncoordinated. The nonligating sulfonate groups are oriented perpendicularly to either side of a given layer. They point into the channels of the two adjacent layers to stitch the framework together in the third dimension. These $-SO_3$ groups form a complex network of hydrogen bonding with both coordinated and free water molecules. The molecules of guest dioxane are disordered and situated slightly above and below the plane of Ba ions roughly in the middle of the hexagon formed by the ligands to each side of a layer (Figure 2a).

The Ba_4 clusters (Figure 3) which form the vertices of the honeycomb grids represent the first observation of discrete metal sulfonate clusters. The structure of the cluster is quite simple in that the metal ions form virtually a perfect square with angles that sum to 180.0° (∠Ba1−Ba2−Ba1 = 90.67°, ∠Ba2−Ba1−Ba2 = 89.33°). The μ_3 sulfonate groups are oriented across opposite faces of the square while the μ_2 sulfonate groups bridge the edges. Sulfonate oxygen−barium distances in the cluster are typical for Ba^{2+}−sulfonate interactions and range from 2.70(2) to 2.87(4) Å. This cluster has been foreshadowed by the two 1-D structures.[11,12] Barium, with its high coordination number and typically irregular geometries, is perhaps not a surprising candidate to form a greater breadth of aggregate structures.[16]

DSC and TGA were performed on crystals of **1**.[17] The data show loss of solvent molecules in two steps, the first from ambient temperature to 215 °C (22.1%) and a second from 215 to 330 °C (5.1%) corresponding roughly to the loss of uncoordinated (three dioxane, three water) and coordinated (one dioxane, four water) solvent, respectively.[18]

Framework **1** has components with competing, rather than complementary, structural tendencies. Tetrafunctional adamantane-based ligands, particularly rigid ones, typically direct diamondoid assemblies, and Ba sulfonates almost exclusively form layered solids. This particular tactic has its roots in the coordination chemistry of molecular metal complexes. *Specifically, by mismatching the coordinative preferences of a particular metal and ligand, interesting chemistry may result due to strained geometries and/or atypical ligation. Extending this thinking to an infinite coordination solid should equally provide opportunities for exceptional results*. In this case, from the perspective of the metal ligation, the first observation of discrete metal sulfonate clusters is made, and from the supramolecular vantage point, an interesting open channel framework structure is formed where, surprisingly, only three of the sulfonate groups are employed. In the general scheme, for metal sulfonate chemistry, this work illustrates that there are new topologies of sulfonate frameworks which may be formed by appropriate selection of ligands to direct the aggregation of the metal sulfonate moieties into discrete clusters.

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Supporting Information Available: Preparations and relevant spectroscopic data for **L** and compound **1**. CIF file for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Thermal analyses were performed on a Netzsch STA 449C from 25 to 500 °C at a heating rate of 10 °C/min. Accurate initial masses for the sample were difficult to obtain owing to the loss of volatile guests at ambient conditions.

(18) This fully desolvated network is then stable to 510 °C, but PXRD analysis showed the solid to be amorphous at this stage. Upon exposure to water vapor, the network resorbs coordinated solvent molecules (two water molecules per Ba center) but does not revert to its nascent form. It does not resorb dioxane. Water vapor was used as the network has slight, but not insignificant, solubility in water.

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