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An open channel coordination framework sustained by cooperative primary and secondary sphere interactions

Sean A. Dalrymple and George K. H. Shimizu*

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. E-mail: gshimizu@ucalgary.ca; Fax: 1 403 289 9488; Tel: 1 403 220 5347

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A three-dimensional coordination solid is presented in which every metal ion is stabilized by both primary and secondary sphere interactions to form an open channel structure.

Second sphere coordination refers broadly to any intermolecular interactions with the primary coordination sphere of a metal complex, that is, further interactions with those ligands directly bonded to the metal center. These inherently supramolecular phenomena are fundamental to the properties of any metal complex in a condensed phase and their effects on molecular complexes have been well studied.[1] Given that two commonly employed approaches to the generation of extended supramolecular solids are to sustain the network *via* metal ligand interactions[2] and/or by complementary hydrogen bonding interactions,[3,4] the use of second sphere interactions to assemble supramolecular solids seems almost a corollary. It is somewhat paradoxical then that extended solids generated deliberately utilizing these interactions are rare. The most well-studied families involve H-bonding between metal chlorides and protonated N species.[5] Hosseini *et al.* have also recently reported a metal cyanide/bisamidinium hydrogen bonded extended solid.[6] Kitagawa *et al.* have reported metal chloranilic acid structures augmented by H-bonds between aquo ligands and aromatic N ligands.[7] Our research group has been mainly studying the chemistry of the sulfonate (RSO_3^-) group in the primary coordination sphere of various metal complexes.[8] However, the bulk of available structural data of metal sulfonate complexes demonstrate the inability of sulfonate ions to displace solvent, usually water, from the primary coordination sphere.[9] The present work concerns a 3-D coordination polymer with a channel structure. Significantly, it is a rare example of a coordination solid sustained by cooperative primary and secondary sphere interactions.[10]

We have previously reported that the trianion of 1,3,5-tris(sulfomethyl)benzene, TSMB, forms discrete second sphere capsules with trivalent hexaaquo metal ions.[11] In these complexes, two molecules of the trisulfonated ligand each form six hydrogen bonds to each triangular face of the octahedral metal cations. A high degree of hydrogen bonding complementarity is observed between sulfonate groups and pairs of aquo ligands oriented in *cis* coordination sites on the metal center. The current work deals with the novel ligand hexakis(sulfomethyl)benzene (HSMB), henceforth denoted **L**. The ligand **L** possesses two segregated trisulfonate faces with 1,3,5- and 2,4,6-sulfomethyl substituents adopting mutually *syn* orientations. This conformational preference is frequently observed for persubstituted benzene derivatives and has been described as ‘steric gearing’ for its utility in preorganizing supramolecular hosts.[12] Owing to this, **L** behaves in a comparable manner to two molecules of the trisulfonate ligand, TSMB. The present work reports the structure of $\{[(Al(H_2O)_3)_2(\mathbf{L})]\cdot(H_2O)_{14.5}\}_\infty$, **1**, a three-dimensional network. This structure is stabilized by cooperative primary and secondary sphere effects to yield a neutral open framework solid with water-filled channels.

The hexaanion of hexakis(sulfomethyl)benzene, **L**, was synthesized as its sodium salt *via* the Strecker-type sulfonation of hexakis(bromomethyl)benzene with sodium sulfite. Complexation of **L** with $AlCl_3$ in aqueous solution followed by diffusion of acetone into the solution gave single crystals of $\{[(Al(H_2O)_3)_2(\mathbf{L})]\cdot(H_2O)_{14.5}\}_\infty$, **1**.†

The structure of **1** can be perceived as being built up from repeat units of one molecule of **L**, in an all-*trans* conformation, capping an $[Al(H_2O)_3]^{3+}$ unit on each trisulfonate face (Al–O3 = 2.374(5) Å). The previously mentioned *cis*-aquo sulfonate hydrogen bonding motif is again maximized as six H-bonds are formed to the triaquo face (O3–O1 = 2.787(4) Å). The Al centers are not three-coordinate and solely ligated by water molecules, rather, they are octahedral where the non-aquated triangular face is composed of three sulfonate oxygen atoms from three different sulfonate groups (Al–O3 = 2.382(4) Å), that is, primary sphere ligation. The crystallographically equivalent unit of this framework is one sixth of a ligand and one third of an Al center. Each sulfonate group employs two oxygen atoms to form secondary sphere interactions with two aquo ligands, while the third oxygen atom forms a primary sphere interaction with an adjacent Al center. The complete ligation of a single molecule of **L** is shown in Fig. 1.

Structure **1** ultimately links into a three-dimensional framework sustained by both the primary and secondary sphere bonding to each Al center as shown in Fig. 2.

An interesting aspect of the structure of **1** is visualized upon viewing the structure down a diagonal 45° off from the *c*-axis (Fig. 3). Open channels of dimensions 7.1 × 7.1 Å (~4.1 × 4.1 Å with van der Waals considerations) permeate the framework along the *b*-axis. For each molecule of **L**, 14.5 molecules of water are found in the channels as determined crystallographically and corroborated by the TGA data. Notably, the Cr^{3+} and Fe^{3+} complexes of L are isostructural with **1**.[13]

Thermogravimetric analyses and powder X-ray diffraction of compound **1** indicate that the solid undergoes a structural change upon desolvation. Compound **1** loses the guest water molecules at ambient temperature but then forms a second ordered phase, which retains the coordinated aquo ligands and is stable to 300 °C.[14]

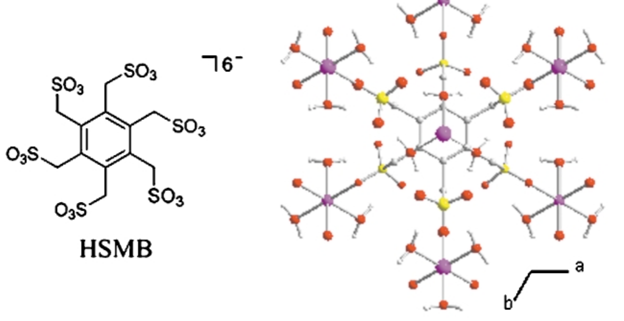

Fig. 1 Left: line drawing of **L**. Right: Perspective view of the primary and secondary sphere ligation of a molecule of **L**. For clarity, only the triaquo face of the Al center situated above the benzene ring is shown. All Al centers are crystallographically equivalent. Note the all-*trans* conformation of **L**. Al, pink; S, yellow; O, red; C, grey; H, white.

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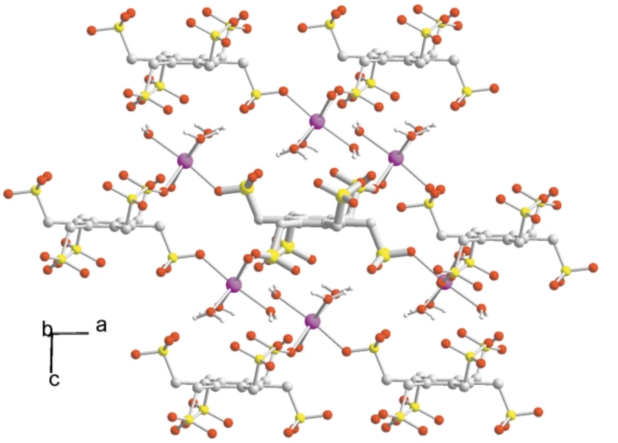

Fig. 2 View of **1** down the *b*-axis showing the connectivity of a single molecule of **L** in three dimensions. One molecule of **L**, situated centrally, is shown with thickened bonds.

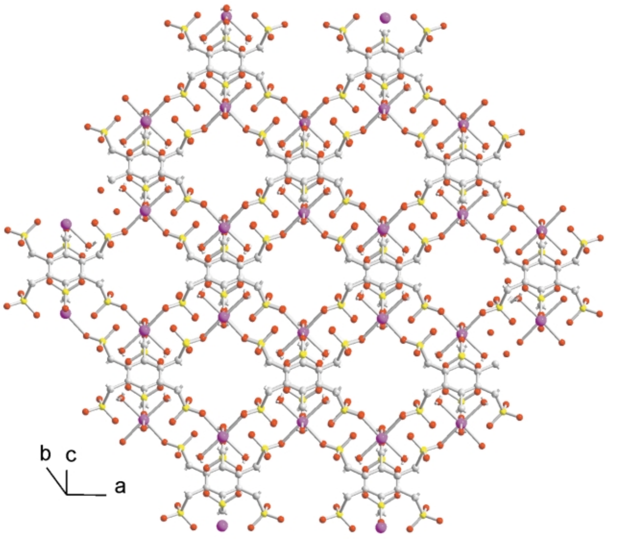

Fig. 3 Solvent-filled channels present in **1**. Guest water molecules have been deleted. The channel dimensions are ~7.1 × 7.1 Å.

The predictable ordering of molecular species in the solid state is the fundamental premise of the discipline known as crystal engineering. Second sphere phenomena, though omnipresent in condensed phases, have rarely been employed in the deliberate construction of extended solids.[4–7] This work illustrates that second sphere interactions involving sulfonate groups have considerable potential in the construction of designed solids. From the perspective of those generating coordination solids, the use of sulfonate groups, a functional group that frequently will not displace solvent from the primary coordination sphere of a metal complex, may seem counter-intuitive. However, forming extended solids through complementary second sphere interactions would represent an analogous approach to those observed in the assembly of many families of wholly organic extended solids.[3] In **1**, the *cis*-aquo/sulfonate hydrogen bonding complementarity is prominent in the second sphere and these interactions are further reinforced by primary sphere ligation.

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Notes and references

† *Crystal data* for $\{[(\mathrm{Al(H_2O)_3})_2(\mathbf{L})]\cdot(\mathrm{H_2O})_{14.5}\}_\infty$, **1**: $C_{12}H_{22}Al_2O_{38.33}S_6$, $M = 1027.97$, trigonal, space group $R3m$, $a = b = 11.986(2)$, $c = 24.641(5)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 3065.7(9)$ Å^3, $Z = 3$, $Dc = 1.670$ g cm^{-3}, μ(Mo Kα) = 0.494 mm^{-1}, crystal size 0.25 × 0.22 × 0.15 mm. Data for **1** were collected on a Nonius Kappa CCD diffractometer at −100 °C and solved using the SHELXTL software package.[15]A total of 5856 reflections were processed of which 877 were unique and considered significant with $I_{net} > 2\sigma(I_{net})$. Final residuals for $I_{net} > 2\sigma(I_{net})$ were $R = 0.0663$ and $R_w = 0.0884$ (GoF = 1.094) for 63 parameters. CCDC 188681. See http://www.rsc.org/suppdata/cc/b2/b205952e/ for crystallographic data in CIF or other electronic format.

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13 Both structures are trigonal, $R3m$. For Cr^{3+}, $a = b = 11.988(2)$, $c = 24.758(5)$ Å. For Fe^{3+}, $a = b = 11.979(2)$, $c = 24.671(5)$ Å.

14 PXRD analysis of a sample of **1** heated to 100 °C showed conversion to a denser phase then stable to ~310 °C. TGA/DSC analyses were performed on a Netzsch STA449C under N_2 at a scan rate of 5 °C min^{-1}. PXRD data were obtained on a Scintag X2 Powder X-ray diffractometer at the Steacie Institute for Molecular Sciences of the National Research Council of Canada.

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