The First Nonlayered Metal Sulfonate Structure: a 1-D Ba^{2+} Network Incorporating Hydrophobic Channels

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The phosphonate group, RPO$_3^{2-}$, has been extensively studied for its ability to bridge metal centers and form layered networks where the interlayer environment is regulated by the R group.[1] In these structures, the inorganic backbone is rigid and adopts a very regular motif, e.g., α- or γ-Zr phosphonate, with a broad range of pendant organic groups.[2] Our research group,[3] along with others,[4,5] has been studying the interesting structures based on the coordinative tendencies of the more weakly bonding sulfonate group, RSO$_3^-$. Despite the strong analogy to the phosphonate group, the coordination chemistry of sulfonates has been studied to a very limited extent. Examples which have been reported to date with silver(I)[3,4] and various alkali, alkaline earth, or transition metal organosulfonates[5] typically exhibit varying degrees of hydration, as would be expected for more weakly bonding ligands, *but invariably, the networks all adopt two-dimensional structures.* Specifically concerning barium, it has been widely accepted that all Ba sulfonates are layered networks and, on this basis, these compounds have found considerable use as lubricants.[6] The number of structurally characterized barium organosulfonates,[7] however, is actually very small and the previous assertion seems to have arisen largely as an extrapolation of the known layered structure of Ba methanesulfonate.[7a] With the ever-growing library of supramolecular complexes based upon weak interactions,[8] it is apparent that with weaker interactions comes more coordinative
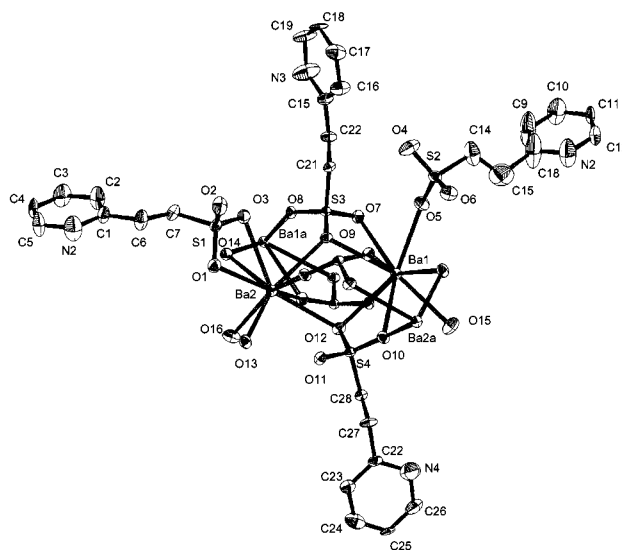

Figure 1. ORTEP representation of **1** with the numbering scheme. The view is slightly offset from the *a*-axis, showing the orientation and coordination mode of each of the four different molecules of **L**. Thermal ellipsoids of 30% probability are represented.

flexibility. A corollary of coordinative flexibility should be greater structural diversity. Herein, we present the structure and thermal analysis of [Ba(**L**)$_2$(H$_2$O)$_4$·EtOAc$_{0.5}$] (**L** = 2-pyridylethanesulfonate), **1**, the first metal sulfonate complex not to adopt a two-dimensional structure.[9] The complex is composed of one-dimensional inorganic columns with pendant pyridylethane groups which serve to define hydrophobic channels capable of organic guest inclusion.

Compound **1** forms a one-dimensional array composed of SO$_3$-bridged columns of Ba^{2+} ions. The columns extend along the *a*-axis with the pendant organic groups protruding in separate directions (Figure 1). Although there are four unique molecules of **L**, once symmetry considerations are met, the pendant groups actually diverge in six directions to give the columns an insectlike cross section. The nearest distance between columns is along the unit cell diagonal (15.070(9) Å). The distance between columns along either the *b*- or *c*-axis is one cell axis. The pendant pyridylethane groups of the organosulfonates do not pack efficiently to fill space. The result is channels, which run parallel to the BaSO$_3$ columns, lined with aromatic rings. The channels are approximately 7.7 × 9.1 Å, as defined by the shortest distances between transannular molecules of **L** (**L**/type 1−type 1, and **L**/type 2−type2, respectively). Within this hydrophobic domain are included highly ordered guest molecules of ethyl acetate.

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(8) For layered guanidinium sulfonate networks based upon H-bonding, see: (a) Holman, K. T.; Ward, M. D. *Angew. Chem., Int. Ed.* **2000**, 39, 1653. (b) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575. (c) Swift, J. A.; Pivovar, A. M.; Reynolds, A. M.; Ward, M. D. *J. Am. Chem. Soc.* **1999**, *121*, 5887. (d) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941.
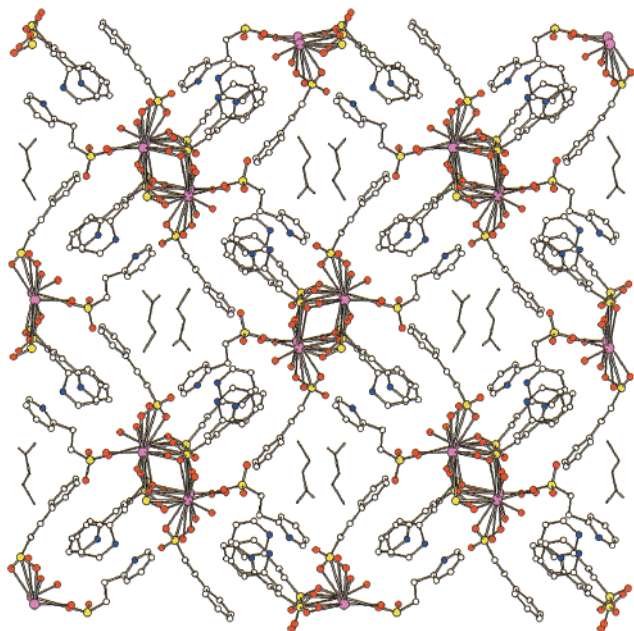
(9) This statement refers to either homoleptic sulfonate complexes or hydrated sulfonate complexes. Obviously, many metal complexes exist which incorporate sulfonates in addition to other ligands, and these complexes adopt a wide range of structures. For a review of triflate binding, see: Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

Figure 2. View down the *a*-axis showing the orientations of the 1-D columns in the structure and the hydrophobic channels which run parallel. The 6-fold divergent arms off the central column are also visible. Ethyl acetate molecules are shown as stick figures.

Figure 2 shows the arrangement of the one-dimensional columns, with their 6-fold divergent organic groups, and the resulting solvent-filled channels.

There are two crystallographically unique Ba^{2+} ions in the structure. Ba1 is 10-coordinate and has an irregular geometry. The coordination sphere is composed of seven sulfonate oxygen atoms, from five different sulfonate groups, two bridging water molecules, and one terminal water molecule. Ba2 is nine-coordinate and has a geometry best described as a tricapped trigonal prism. The coordination sphere is composed of six sulfonate oxygen atoms, from five different sulfonate groups, two bridging water molecules, and one terminal water molecule. There are four crystallographically unique molecules of **L** in the structure, each with a different mode of coordination. The first bonds only to Ba2 in a chelating fashion via two oxygen atoms (Ba2−O1 = 2.885(2) Å, Ba2−O3 = 2.948(2) Å). The second molecule of **L** forms only a single bond to a barium center (Ba1−O5 = 2.722(2) Å). The third **L** molecule adopts a μ^4 coordination mode where one oxygen atom bridges two Ba^{2+} centers (Ba1−O9 = 2.872(2) Å, Ba2−O9 = 2.801(2) Å), and each of the remaining two oxygens forms a single bond to a different Ba^{2+} center (Ba1−O7 = 3.227(2) Å, Ba1′−O8 = 2.744(2) Å). The final molecule of **L** also bridges four Ba^{2+} ions but in a different manner. Two oxygen atoms each bridge two barium centers (Ba1−O10 = 3.113(2) Å, Ba2−O10 = 2.740(2) Å, Ba1−O12 = 2.897(2) Å, Ba2−O12 = 2.819(2) Å) while the third, O11, is uncoordinated. There are no π-stacking interactions between any combination of pyridine rings in the structure.

DSC and TGA were performed on crystals of **1**.[10] The data correspond to loss of the ethyl acetate molecules from ambient temperature up to 50 °C, followed by loss of water up to 100 °C. The fully desolvated network is then stable to 380 °C. PXRD data of **1**, at the different stages of desolvation, show that structural rearrangement accompanies the loss of solvent. The PXRD of

the fully desolvated sample is consistent with a layered network. Neither addition of ethyl acetate to this solid nor addition of ethyl acetate to the hydrated sample restores the original framework. However, the fact that the 1-D structure is obtained at all is a clear indication that the layered motif is not overwhelmingly favored and the potential for new families of frameworks exists. For example, more robust solids can be envisioned by employing polysulfonate ligands to line the channels.

The structure of **1**, the first structurally characterized complex of **L**, presents a number of interesting features. The one-dimensional framework is the first exception to the trend of RSO_3^- complexes to form layers. The structure contains columns with 6-fold diverging pendant arms, which arrange to generate infinite aromatic channels. These channels include hydrophobic guests despite there being 4 equiv of water as part of this same framework. Compound **1** is reminiscent of the pentiptycene polymers studied by Wrighton and Swager.[11] In these organic polymers, 4-fold divergent pendant groups of pentiptycene units are employed to generate porosity, in addition to defining the hydrophobic nature of the interpolymer channels. The present result provides an inorganic example of one-dimensional *n*-fold divergent units generating void space in an extended architecture.[12] In a broader sense, this work demonstrates that there is a rich coordination chemistry of the sulfonate ion, literally other dimensions, which has yet to be explored and that the consequence of the SO_3^- unit being weakly coordinating may simply be greater structural diversity rather than structural instability.

(10) Thermal analyses were performed on a Netzsch STA 449C from 25 to 600 °C at a heating rate of 10 °C/min. Accurate initial masses for the sample were difficult to obtain owing to the loss of ethyl acetate at ambient conditions. For loss of ethyl acetate: calcd 7.40%, obsd 3.25%. For loss of H_2O: calcd 6.00%, obsd 5.56%.

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(13) †**1**: To a solution of 2-pyridylethanesulfonic acid (2.01 g, 10.73 mmol) in H_2O (20 mL) was added a solution of $Ba(OH)_2 \cdot H_2O$ (1.03 g, 5.439 mmol) in H_2O (50 mL), and this mixture was stirred for 12 h at 25 °C. The mixture was filtered to give a clear solution. Upon diffusion of ethyl acetate, thin colorless needles of **1** suitable for X-ray data collection were obtained. Elemental analysis was performed on a sample dried to 100 °C. Calcd: C, 32.99; H, 3.16. Found: C, 32.85; H, 3.30. Crystal data for compound **1**: $Ba_2C_{32}H_{52}N_4O_{18}S_4$, fw = 1183.70 g mol^{-1}, colorless needles, monoclinic, space group $P2_1/c$, $a = 9.6932(5)$ Å, $b = 21.4518(12)$ Å, $c = 21.1781(12)$ Å, $\beta = 97.866(1)°$, $V = 4362.3(4)$ Å^3, $Z = 4$, $D_c = 1.802$ mg/m^3, $R = 5.41\%$, $R_w = 12.11\%$, and GOF = 0.980 for 541 parameters using 11337 ($F_o > 2.0\sigma(F_o)$) reflections. Mo Kα radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) 2.062 mm^{-1}. Data collection temperature = −100 °C. The structure was collected on a Siemens SMART CCD diffractometer using the ω scan mode (1.36° < 2θ < 28.85°) and solved using the NRCVAX suite of programs. Gabe, E. J.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr*. **1989**, *22*, 384.