

Structural Constraints in the Design of Silver Sulfonate Coordination Networks: Three New Polysulfonate Open Frameworks

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Received August 15, 2005

Three new silver sulfonate metal–organic frameworks are presented along with a design strategy for future generations. $\{[Ag_6(\text{mesitylenetrisulfonate})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}\}_\infty$ (**1**), $\{Ag_4(\text{durenetetrasulfonate})(\text{H}_2\text{O})_2\}_\infty$ (**2**), and $\{[Ag_4(1,3,5,7\text{-tetrakis}(4,4'\text{-sulfophenyl})\text{adamantane})(\text{H}_2\text{O})_2] \cdot 1.3\text{H}_2\text{O}\}_\infty$ (**3**) represent a series of open-framework silver sulfonate solids where the organic linker plays a key role in determining the overall structure. Compound **1** forms a pillared layered structure, while compounds **2** and **3** form 3-D nets derived from cross-linking of 1-D columns of silver sulfonates. All three solids incorporate water molecules, which can be removed to yield a solid stable to in excess of 300 °C. Powder X-ray diffraction studies and vapor sorption experiments show, for **1** and **2**, that the solids retain their structure when guests are removed and, for all three, that water vapor is resorbed stoichiometrically by the solids. An idealized silver sulfonate framework is proposed, and upon comparison to the reported structures, guidelines are proposed for structural constraints in the design of future generations of 1-D and possibly 0-D aggregate structures.

Introduction

Increasingly, coordination solids that demonstrate porosity or reversible guest sorption are being reported.¹ A logical design paradigm in the construction of such frameworks is to have metal and ligand components with well-defined coordinative preferences to favor the formation of large pores.² The elegance of this strategy is that, once suitable metal ions and ligand functional groups are recognized, variation in the geometry and size of the organic linker can

afford a tremendous breadth of structural motifs. However, oftentimes, in attempts to sustain an open structure, geometries of metal ions and conformations of ligands are prone to distortion, often leading to undesired, frequently dense, structural motifs. In our research, we have been taking a contrasting approach. We have focused our efforts on the coordination chemistry of both metal ions and ligating groups without highly directional coordinative preferences. The rationale is that, while rigid components may assemble to give a robust structure, ideal and sustained complementarity between components is crucial to forming the desired network. The use of both metal ions and ligating groups with less directional coordinative tendencies could allow for a more adaptable assembly process and enable the formation of new framework solids.³ Notably, as will be shown, these solids can be quite robust and sustain guest exchange.

It has been shown by our group,⁴ and others,⁵ that sulfonate groups, which are generally regarded as weakly coordinating, can adopt a range of different bridging modes with metal centers, particularly with silver(I).^{6,7} Structurally, silver(I) sulfonates are related to the well-studied metal phosphonate

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family,⁸ adopting the classic layered motif of hybrid inorganic–organic solids. For metal phosphonates, the interlayer region may be made porous by alternating pillaring groups with nonpillaring monophosphonate or phosphate groups.⁹ For silver(I) arenemonosulfonates, we have shown that the structures are highly dependent on the lateral breadth of, and interactions between, the pendant R group on the sulfonates.⁷ As with the metal phosphonates, in the absence of strongly structure-directing factors, dense solids are obtained. This work targets the formation of open silver sulfonate solids by the selection of organic cores for the sulfonate ligands. Essentially, polysulfonate linkers are chosen such that the formation of a dense solid is prohibited. For the first two compounds presented, this is achieved by appending multiple sulfonomethyl groups to an arene core in a divergent manner. The final compound uses a tetrahedrally divergent tetrasulfonate ligand to orient sulfonate groups at a distance to completely disfavor the formation of a layered structure.

Here we report three new open-framework metal sulfonate structures: $\{[\text{Ag}_3(\text{L1})(\text{H}_2\text{O})_{2.5}]\cdot\text{H}_2\text{O}\}_\infty$ (**1**, where L1 = α,α',α'' -mesitylenetrisulfonate), $\{[\text{Ag}_4(\text{L2})(\text{H}_2\text{O})_2]\}_\infty$ (**2**, where L2 = $\alpha,\alpha',\alpha'',\alpha'''$ -durennetetrasulfonate), and $\{[\text{Ag}_4(\text{L3})(\text{H}_2\text{O})_2]\cdot 1.3\text{H}_2\text{O}\}_\infty$ [**3**, where L3 = 1,3,5,7-tetrakis(4,4'-sulfophenyl)adamantane]. Compound **1** forms a pillared layered structure with interlayer guests. Compounds **2** and **3** both form open-channel 3-D structures anchored by 1-D columns of silver sulfonate aggregates, rather than layers. These represent the first examples of homoleptic silver sulfonates with columnar (1-D) architectures. Differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) and powder X-ray diffraction (PXRD) data show, despite

being sustained by weaker ligating groups, that compounds **1–3** are quite robust. Vapor sorption experiments show that all of the structures can resorb lost guests.

Experiment Section

General Procedures and Instrumentation. TGA/DSC analyses were performed on a Netzsch 449C simultaneous thermal analyzer under a dynamic N₂ atmosphere at a scan rate of 5 °C/min, with samples heated in pierced hermetically sealed pans. All chemicals were purchased from Aldrich Chemical Co. and used as received. L1¹⁰ and L3¹¹ were prepared by previously reported procedures.

General X-ray Crystallography. Crystals suitable for X-ray analysis were chosen under an optical microscope and quickly coated in oil before being mounted in a nylon loop and frozen under a stream of cryogenic nitrogen gas (−100 °C) for data collection. Standard graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) was employed, and a full hemisphere of data was obtained regardless of the crystal system indicated by data observed in initial scans of the crystal. Single-crystal X-ray data were collected on a Nonius Kappa CCD diffractometer using a data acquisition strategy determined from the HKL2001 suite of programs.¹² Likewise, data were processed, and intensities were corrected for Lorentz and polarization effects and for absorption using this software. All structures were solved by direct methods using SHELXS-97¹³ and refined on F^2 by full-matrix least-squares procedures with SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.5 times the isotropic equivalent of their carrier atoms. Final atomic coordinates, thermal parameters, and a complete listing of bond lengths and angles are deposited and are available from the Cambridge Crystallographic Data Centre. Pertinent structure refinement data for **1–3** are given in Table 1.

Preparation of Silver α,α',α'' -Mesitylenetrisulfonate, $\{[\text{Ag}_3(\text{L1})(\text{H}_2\text{O})_{2.5}]\cdot\text{H}_2\text{O}\}_\infty$ (1**).** α,α',α'' -Mesitylenetrisulfonic acid (0.25 g, 0.59 mmol) was dissolved in 10 mL of H₂O; Ag₂CO₃ (0.24 g, 0.88 mmol, 1.5 equiv) was then added, generating a cloudy white suspension. The reaction mixture was stirred at room temperature until the white turbidity disappeared and the evolution of CO₂ ceased. The volume was reduced by a third to give a saturated solution, which was then filtered. Single crystals of network **1** were obtained by vapor diffusion of acetone into the saturated H₂O solution of the product at 4 °C over a 3-week period. Yield: 0.22 g, 50%. FT-IR (cm^{−1}, KBr): ν 3448.2(br), 1640.1(s), 1607.3(s), 1459.8(s), 1416.1(s), 1268.6(s), 1224.9(vs), 1142.9(s), 1050.1(s), 1017.3(s), 886.2(w), 766.0(s), 705.9(s), 662.2(w), 591.2(m), 569.4(m), 520.2(m). TGA/DSC: 25–75 °C, −2.78% obsd and −3.65% calcd for loss of 3H₂O; 320 °C, decomposition of L1.

Preparation of Silver $\alpha,\alpha',\alpha'',\alpha'''$ -Durennetetrasulfonate, $\{[\text{Ag}_4(\text{L2})(\text{H}_2\text{O})_2]\}_\infty$ (2**), and Silver 1,3,5,7-Tetrakis(4,4'-sulfophenyl)adamantane, $\{[\text{Ag}_4(\text{L3})(\text{H}_2\text{O})_2]\cdot 1.3\text{H}_2\text{O}\}_\infty$ (**3**).** Compounds **2** and **3** were prepared in a manner analogous to that of **1**, employing $\alpha,\alpha',\alpha'',\alpha'''$ -durennetetrasulfonic acid and tetrakis(4,4'-sulfophenyl)adamantane, respectively. For compound **2**, yield: 0.58 g, 82%.

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Table 1. Crystal Data and Refinement Summaries for Compounds 1–3

| formula | $C_9H_{13}O_{12.5}S_3Ag_3$, [Ag ₃ (L1)(H ₂ O) _{2.5}]·H ₂ O (1) | $C_{10}H_{16}O_{14}S_4Ag_4$, [Ag ₄ (L2)(H ₂ O) ₂] (2) | $C_{34}H_{28}Ag_4O_{15.5}S_4$, [Ag ₄ (L3)(H ₂ O) ₂]·1.3H ₂ O (3) |
|---|---|---|---|
| fw | 740.98 | 315.09 | 1244.28 |
| cryst syst | triclinic | monoclinic | monoclinic |
| space group | <i>P</i> 1 (No. 1) | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>P</i> 2 ₁ / <i>c</i> (No. 13) |
| <i>a</i> (Å) | 8.7275(17) | 9.929(2) | 11.462(2) |
| <i>b</i> (Å) | 9.782(2) | 5.088(1) | 6.8727(14) |
| <i>c</i> (Å) | 10.946(2) | 19.249(4) | 24.986(5) |
| α (deg) | 97.94(3) | 90 | 90 |
| β (deg) | 90.96(3) | 99.77(3) | 98.79(3) |
| γ (deg) | 107.81(3) | 90 | 90 |
| <i>V</i> (Å ³) | 879.5(3) | 919.95 | 1945.2(7) |
| <i>Z</i> | 2 | 2 | 2 |
| <i>D</i> _{calcd} (g/cm ³) | 2.798 | 3.188 | 2.119 |
| μ (mm ⁻¹) | 3.728 | 4.539 | 2.270 |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 |
| data [<i>I</i> > 2 σ (<i>I</i>)]/param | 7352/497 | 1702/146 | 3000/265 |
| GOF | 1.196 | 1.095 | 1.031 |
| final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>) | <i>R</i> 1 = 0.0204, <i>wR</i> 2 = 0.0545 | <i>R</i> 1 = 0.0378, <i>wR</i> 2 = 0.0903 | <i>R</i> 1 = 0.0505, <i>wR</i> 2 = 0.1379 |
| final <i>R</i> indices (all data) | <i>R</i> 1 = 0.0227, <i>wR</i> 2 = 0.0779 | <i>R</i> 1 = 0.0575, <i>wR</i> 2 = 0.1188 | <i>R</i> 1 = 0.0576, <i>wR</i> 2 = 0.1444 |

FT-IR (cm⁻¹, KBr): ν 3574.9(s), 3466.6(br), 1576.4(w), 1459.8(s), 1409.6(w), 1206.7(s), 1173.8(vs), 1128.9(s), 1104.6(s), 1038.2(s), 1021.4(s), 766.8(m), 728.3(w), 668.5(m), 599.8(s), 545.6(m), 529.3(m), 514.4(m). TGA/DSC: 50–125 °C, -3.01% obsd and -3.92% calcd for loss of 2H₂O; 325 °C, decomposition of L2. For compound 3, yield: 0.39 g, 80%. FT-IR (cm⁻¹, KBr): ν 3446.7-(br), 3466.6(br), 1700.1(m), 1495.9(m), 1398.1(m), 1357.6(m), 1226.7(vs), 1124.4(s), 1037.1(s), 1008.7(s), 834.6(s), 715.6(vs), 667.9(w), 623.0(s), 578.0(m). TGA/DSC: 25–275 °C, -4.71% obsd and -4.77% calcd for loss of 3H₂O; 375 °C, decomposition of L3.

Results and Discussion

In a 1:1 ratio, silver(I) and a monosulfonate ion will adopt a structure composed of layers of Ag ions bridged by SO₃ groups with the organic R group directed into the interlayer, the classic hybrid inorganic–organic motif.^{6a,b,7} The ideal anchoring of the organic moieties is such that, with simple aryl substituents, a dense interlayer results where interactions between R groups play a significant role in determining the mode of ligation of the SO₃ group to the Ag ions. For example, in silver 2-naphthalenesulfonate,⁷ the naphthyl groups adopt a herringbone motif like in naphthalene itself. This is in direct contrast to metal phosphonates, where the metal oxo–ligand interaction is the dominating structure-directing factor. To further examine the extent of the structure-directing role of the linker groups in silver sulfonates, three different polysulfonate cores were synthesized and complexed with silver(I). Structural descriptions of these three compounds are presented followed by more general commentary on the family.

Structure of 1. The overall structure of compound 1 can be described as a pillared layered motif where sheets of SO₃-bridged Ag ions are separated by mesitylene units. Each molecule of L1 has one sulfonate group coordinating to one layer and two sulfonate groups ligating to an adjacent layer. Along the *a* axis, adjacent mesitylene units are flipped. Notably, the pillars are not densely packed and guests are included in the channels. Figure 1 shows a view parallel to the Ag sheets. The channels perpendicular to the *bc* plane have dimensions of 8.50(5) Å × 4.25(5) Å, as defined by

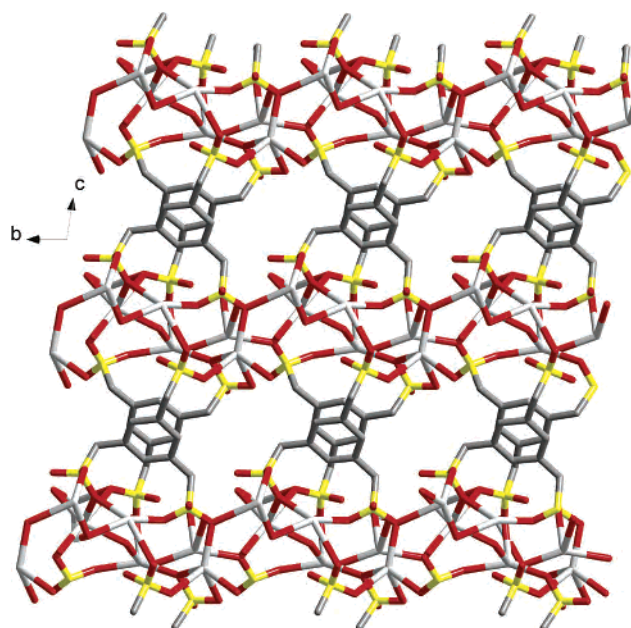


Figure 1. View of compound 1 showing the pillared layer structure. Note the alternating pattern of mesitylene cores and the interlayer voids.

the transannular C8–C18 and C7–C17 distances, and are occupied by two crystallographically unique water molecules. The perpendicular interlayer distance is 10.95(1) Å. The aromatic rings of adjacent L1 molecules are canted with respect to the metal sulfonate layers (the *ab* plane) at approximately 45°. The rings are also π -stacked along the *a* axis with a separation of 3.850(2) Å and an offset of ~1.4 Å. The thickness of an individual layer is approximately 4.65–(5) Å, defined by the trans-layer O-atom separations, resulting in a gallery height of 6.30 Å. Looking at an individual layer (Figure 2), there are six unique Ag centers in the structure as well as two unique ligands. One Ag center, Ag1, is four-coordinate, four (Ag2, Ag3, Ag4, and Ag6) are five-coordinate, and one (Ag5) is six-coordinate. None of the centers has an ideal geometry for its respective coordination number, illustrating the relevance of the pliant coordination sphere of Ag(I).¹⁴ With the exception of Ag2, which is ligated by five sulfonate O atoms, the Ag centers are coordinated to both sulfonate and water O atoms. Ag1 bonds

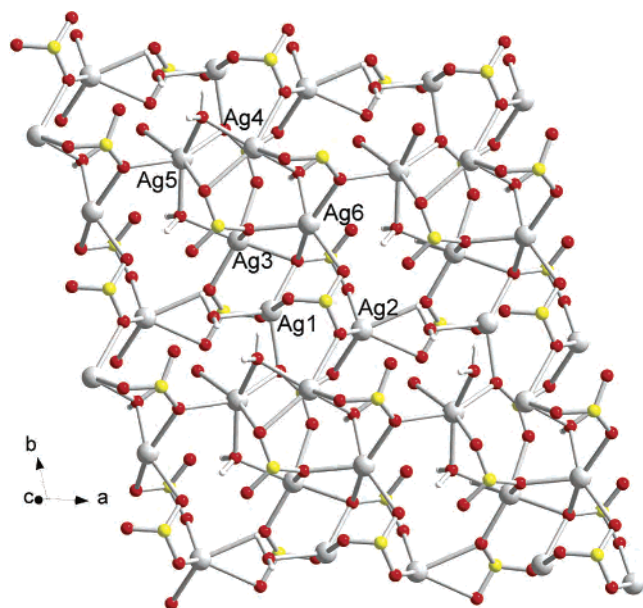


Figure 2. View onto a single layer of compound **1** showing the continuous structure. Visible are coordinated water molecules, depicted with H atoms.

to three sulfonate O atoms and one molecule of water, Ag3 to four sulfonate and one water, Ag4 to three SO₃ and two water, Ag5 to three SO₃ and three water, and Ag6 to four SO₃ and one water. The Ag–O sulfonate distances range from 2.323(4) to 2.772(4) Å, typical for silver sulfonate complexes, and the Ag–O water distances range from 2.325(4) to 2.791(5) Å. In addition to coordinate bonds between the silver metal centers and the sulfonate groups, a number of hydrogen bonds are also present, which serve to fortify the layered interactions. Hydrogen bonds exist between O atoms of the sulfonate groups and the terminally coordinated water molecules [O19⋯O6 = 2.747(5) Å] as well as the bridging water molecules [O20⋯O12 = 2.722(5) Å, O20⋯O15 = 2.811(5) Å, O21⋯O7 = 2.706(6) Å, and O22⋯O13 = 2.719(5) Å]. The water molecules in the channels are also hydrogen bonded to the coordinated water molecules on the silver centers [O22⋯O24S = 2.691(6) Å]. Additional hydrogen bonds most likely exist in the sulfonate groups; however, these were not located for the noncoordinated water molecules. The Ag–O sulfonate distances range from 2.387(6) to 2.598(6) Å for Ag1 and from 2.274(6) to 2.443(6) Å for Ag2, along with the ligated water molecule [Ag2–O7S = 2.312(7) Å].

Structure of 2. Compound **2**, based on the 1,2,4,5-tetramethylbenzene (durene) core, also forms a 3-D structure, but it is not that of a pillared layered type. Rather, the silver sulfonate aggregation takes the form of 1-D columns, which run along the *b* axis. These columns are then further cross-linked along the *a* and *c* directions by the durene cores, as shown in Figure 3. The distance between columns is 9.929(2) Å along the *a* axis and 9.786(2) Å along the *c* axis. The structure of the columns is shown in Figure 4. There are

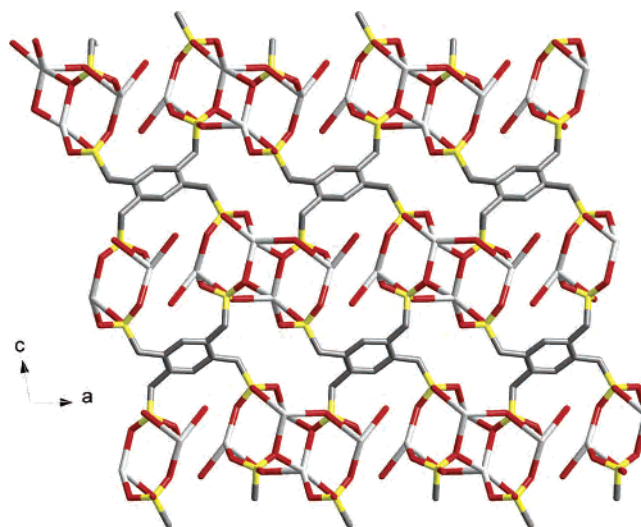


Figure 3. View down the *b* axis of compound **2**, where the 1-D columns would be pointing out of the page. Each durene core links four different columns.

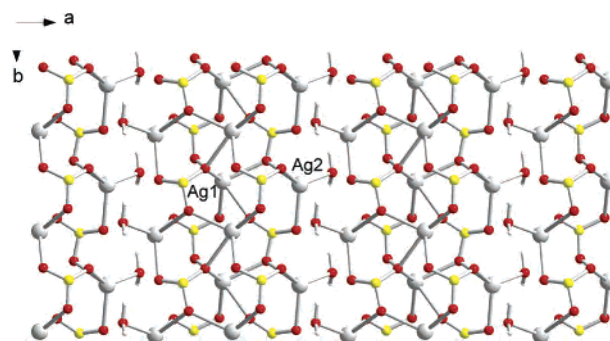


Figure 4. View showing, top to bottom, two columns of compound **2** separated by a ribbon of coordinated water molecules. No continuous layer is observed.

two types of Ag(I) ions, Ag1, a trigonal-bipyramidal center with homoleptic sulfonate ligation, and Ag2, a distorted tetrahedral center ligated by three SO₃ groups and a molecule of water. The coordinated water molecules are directed between the 1-D aggregates and undergo H-bonding interactions with two sulfonate O atoms of neighboring columns [O7S–O4 = 2.932(7) and O7S–O4A = 3.250(7) Å]. Along the *c* axis, there are no interactions between adjacent arene groups; they are tilted 48° with respect to the columns and do not overlap laterally at all. The most notable feature of this compound is the formation of 1-D columns as the homoleptic silver sulfonate aggregation motif. There are only two reports where 1-D columns of silver sulfonates are commented on, and both of these incorporate additional ligation to either further coordinate the metal center¹⁵ or alter the stoichiometry of silver sulfonate in the aggregate.^{6c}

Structure of 3. Compound **3**, like compound **2**, has a 3-D motif composed of 1-D columns cross-linked in the other two dimensions by the organic linker. In this case, the spacing between columns is considerably greater, and the overall structure of cross-linked columns is immediately

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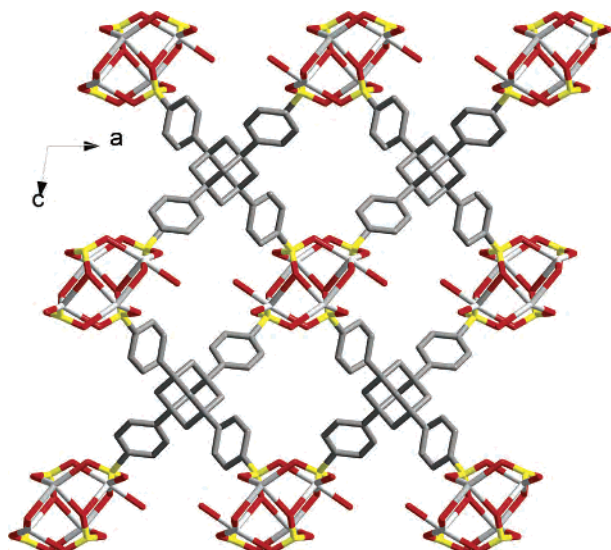


Figure 5. View of compound **3** showing the cross-linking of inorganic columns, directed out of the page, by the tetraphenyladamantane units. 1-D voids are shown between organic linkers.

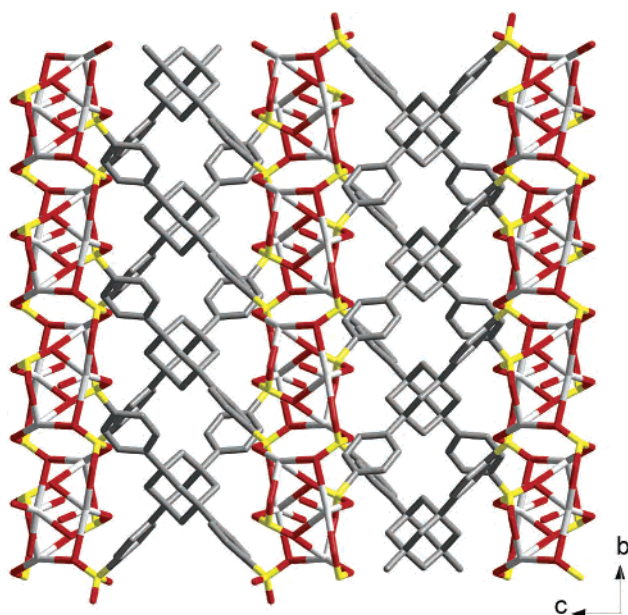


Figure 6. View of compound **3**, perpendicular to that in Figure 5, showing the columnar structure and the cross-linking role of the tetraphenyladamantane units. Note the voids to not permeate this direction.

evident, as shown in Figure 5. Two types of channels are defined by the adamantane cores of the ligand. The first is primarily occupied by coordinated water molecules and has approximate dimensions of 7.4×5.9 Å. The second is occupied by disordered water molecules (1.3 modeled per formula unit) and has dimensions of 8.3×6.0 Å. The distance between adjacent columns is $11.46(1)$ Å along the *a* axis and $12.49(1)$ Å along the *c* axis. The framework formation induces some strain upon the adamantane core, as evidenced by the S···S distances in a single ligand. Ideally equal, in the direction of the *a* axis, this distance measures $8.519(4)$ Å, while in the direction of the *c* axis, it measures $9.164(4)$ Å. The structure of a single column is shown in Figure 6. Crystallographically, two types of silver(I) centers comprise the column. Ag1 is a tetrahedral center with

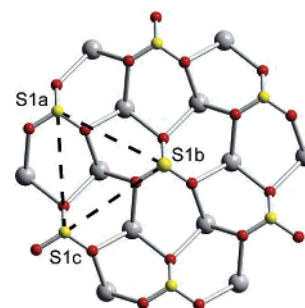


Figure 7. View of a single side of a layer of silver benzenesulfonate, which is defined as the ideal silver sulfonate network, for purposes of comparison. The three S–S distances depicted are $S1a-S1b = 5.160(2)$ Å, $S1b-S1c = 5.198(2)$ Å, and $S1a-S1c = 5.257(2)$ Å.

homoleptic sulfonate coordination, four sulfonate O atoms from four different L3 molecules. Ag2 also coordinates to four sulfonate O atoms from four different ligands but has an additional molecule of water ligated. The geometry of Ag2 is a slightly distorted square pyramid with water in an equatorial site. All sulfonate groups ligate four Ag atoms where two O atoms each coordinate one Ag center and the third O atom bridges between two Ag centers. Adjacent columns are offset by $3.436(1)$ Å, half the length of the *b* axis.

Structural Constraints and Rationalizations for Polydentate Silver(I) Sulfonates

In a previous work,⁷ we defined the “ideal” silver sulfonate structure as that adopted by silver benzenesulfonate.^{6b} This solid possesses a 2-D hybrid inorganic–organic solid structure with layers composed of a hexagonal grid of Ag ions, bridged in a μ^6 fashion, by sulfonate groups. The pendent phenyl ring is nearly perpendicular to the layer plane. A view onto a single layer of this solid is shown in Figure 7. For purposes of assessing structural constraints enforced by the ligands in this work, a relevant parameter is the nearest sulfur–sulfur distance in a layer because this can be viewed as the ideal anchoring distance to a single layer for a di- or polysulfonate ligand. This distance in silver benzenesulfonate is ~ 5.2 Å. This value must then be considered relative to the distance between sulfonate groups dictated by each organic ligand core. It should be noted that this sulfur–sulfur distance does have some flexibility associated with it. For example, silver 2-naphthalenesulfonate, with a broader R group, maintains a layered motif by the silver sulfonate layer, rearranging to sulfur–sulfur distances of $4.53(1)$ and $6.01(1)$ Å to accommodate the broader pendant group.⁷ However, it should be noted that these two values are still centered roughly on the 5.2-Å value.

For L1, owing to the mesitylene core, the only option for the sulfonate groups to coordinate in a lamellar solid would be for two to coordinate to a single layer in a meta orientation and one to coordinate to another layer. For L2, owing to the tetrasubstituted core, two sulfonate groups ligated to the same side of a layer in ortho-, meta-, and para-substitution patterns exist as possibilities. For ortho substitution, the two SO₃ groups would be required to be almost overlaid and so this pattern is disfavored. For para substitution, the aryl ring

would be required to lay almost parallel to the layers and force the generation of void space between adjacent ligands; this is also unfavorable. Thus, the most likely coordinating mode of L2 is also to have two sulfonate groups interacting with a single layer in a meta fashion, and this is ultimately what is observed.

Looking at the structure of compound **1**, there are two independent molecules of L1 and so two different values of S–S separation, 5.731(2) and 6.364(2) Å, enforced by the meta-coordination mode of the ligands to the layers. Both of these distances exceed the separation of sulfonate S atoms in the ideal layered silver sulfonate structure (recall 5.2 Å). In the case of compound **1** though, the observed motif is still that of a true layered solid. This is because L1 possesses a third sulfonate group (S2 and S4 in each of the two independent molecules of L1) that is less spatially restricted in regards to how it interacts with a given layer as the other two sulfonate groups in a given molecule of L1 are ligating to an adjacent layer. Indeed, when one examines the S–S distances between S2 and S4 and their neighboring sulfonate groups, the distances average 5.224(4) and 5.071(4) Å for S2 and S4, respectively. Moreover, the mean of these distances is 5.148 Å, which is just under the S–S separation in silver benzenesulfonate. Thus, the “single” sulfonate group acts as a filler to bridge the gaps defined by the *m*-xylyl spacers, and these sulfonate groups play a critical role in permitting the observed formation of a typical inorganic–organic hybrid solid. As mentioned, the intraligand, meta-oriented S–S separation exceeds that which would allow a layered solid to form. It is notable that the interligand S–S distance between these groups is considerably shorter than the intraligand distance. The shortest distances between meta-oriented S atoms intermolecularly are 4.945(2) and 5.110(2) Å, again more in the range expected for an ideal silver sulfonate layer.

Compound **2**, with its durenene core, can be viewed as having two sets of *m*-xylyl spacers constraining the structure. Only half of L2 is crystallographically unique, and so there are only two independent sulfonate groups. The meta S–S distance in L2 is 5.835(2) Å, again considerably above the ideal distance defined earlier. In the case of L2 though, in contrast to L1, both sides of the ligand are constrained by the ligand core, and there is no “filler” group to complete the formation of a layer. This results in the observed 1-D structure rather than a 2-D network typical for silver sulfonates. The shortest distances within a single column in compound **2** are 4.589(2) Å along the *a* axis and 5.088(2) Å along the *b* axis. These are both sets of interligand distances and are interestingly shorter than distances in a typical layer. Because the *m*-xylyl fragment only slightly exceeds the ideal sulfonate separation distance, it would not be expected that the columns would be greatly separated and the gap between columns can be efficiently filled by two coordinated molecules of water (Figure 4).

In the case of L3, the organic spacer has been enlarged to a 4-substituted tetraphenyladamantane core. In its lowest-energy structure, this core orients sulfonate S atoms a distance of 12.65 Å apart, well beyond that required to

preclude a simple layered solid. In compound **3**, the result is again 1-D columns of silver sulfonate aggregation, which are then cross-linked in the other two dimensions. The network induces considerable strain on the organic core, and the S–S distances observed in a given molecule of L3 are 9.070(2) Å along the *a* axis and 9.697(2) Å along the *b* axis. S–S distances along the diagonals of the *a* and *b* axes, as represented in Figure 5, are 11.59(2) and 12.20(2) Å. These distances are, for the larger part, considerably shorter than those in the minimized structure but are still enough to direct a 1-D network. The use of the much larger spacer in L3 than in L2 produces larger pores running through the solid, as described earlier, because both coordinated and guest water molecules are present. A possibility, which did not materialize, was that 0-D clusters of silver sulfonates could have been observed. We have previously reported L3 along with its Ba²⁺ structure. This solid formed open-grid 2-D sheets with tetrabarium clusters as nodes. To date, this remains the only solid reported that contains discrete metal sulfonate clusters.

Compounds **2** and **3** represent the first structures where 1-D columns of homoleptic silver sulfonate interactions have been observed. This observation is completely due to the choice of the ligand spacer. This is of note for several reasons. Silver(I) salts can often be air-, moisture-, and/or light-sensitive. Silver sulfonates are somewhat anomalous because they are none of the above. This stability could certainly be judged to originate from the 2-D structure, but both compounds are quite stable, as will be discussed shortly. *As far as implications for the design of other silver sulfonate networks, it would seem that any spacer that would juxtapose sulfonate groups rigidly at a distance of greater than roughly 5.2 Å should completely disfavor a layered solid and would likely result in 1-D columns. When that thinking is further extended, any ligand that imposed such a structural constraint in two dimensions could dictate the formation of 0-D clusters.*

Stability and Sorption Properties of Compounds 1–3. Compounds **1–3** were all air- and light-stable. This is not necessarily a given because a considerable number of silver-(I) salts decompose under such conditions. To further probe the stability of these complexes, TGA of the compounds was performed. Compound **1** showed an immediate onset of mass loss corresponding to the loss of water, which continued to 75 °C. Losses of channel and coordinated water are merged into one continuous mass loss. The desolvated structure was then stable to 320 °C. For compound **2**, because only coordinated water molecules are present, the onset of mass loss is a bit higher at 50 °C. All of the water molecules are lost by 125 °C, from which point no further changes are observed until decomposition at 325 °C. Compound **3** loses water molecules, both channel and coordinated, from 25 to 275 °C. This solid is then stable until 375 °C. The desolvated thermal stabilities of these compounds are quite high relative to the majority of coordination solids. Given the sizable plateau of stability exhibited by each of **1–3**, PXRD was performed to elucidate whether the structure, or at least some degree of order, was retained by the solids after the water

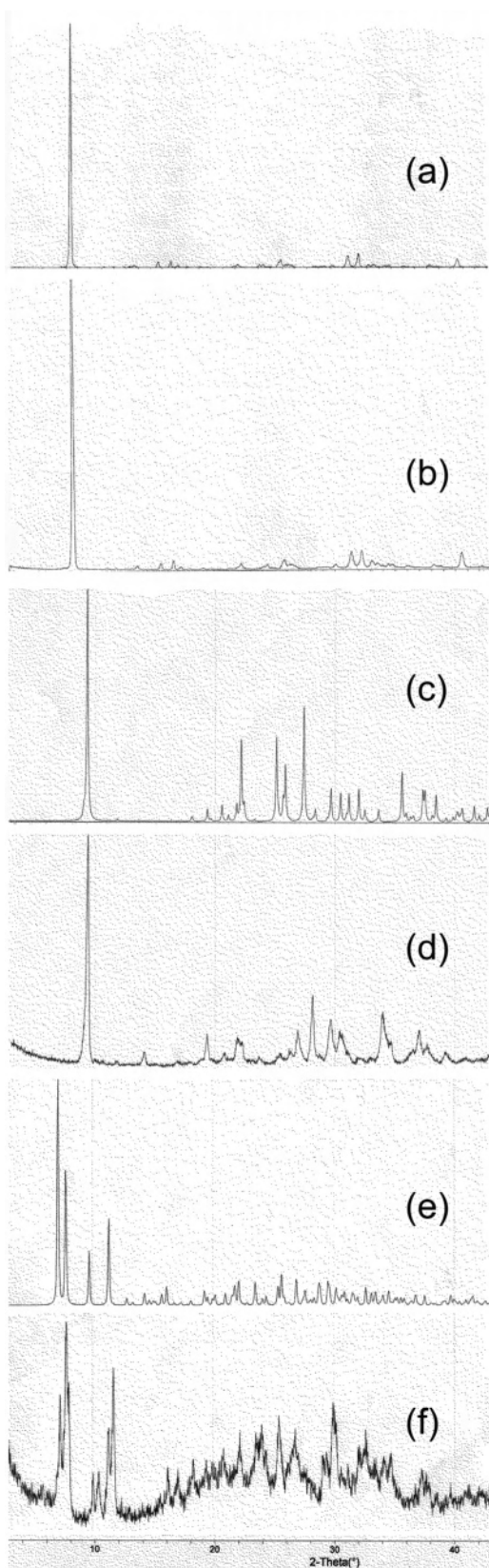


Figure 8. PXRD data: **1**, hydrated (a) and dehydrated (b); **2**, hydrated (c) and dehydrated (d); **3**, hydrated (e) and dehydrated (f).

molecules had been removed thermally. Figure 8 shows the results of these studies.

Compound **1**, with the true pillared layered structure, is quite robust. When the PXRD is run at 100 °C, a sufficient

temperature to remove the channel and coordinated water molecules, the PXRD pattern is virtually identical. Treated similarly, compound **2**, a structure of cross-linked 1-D columns, shows a shift in the mid- 2θ range of peaks. This is to be expected because, in **2**, the water molecules are coordinated but, more importantly, separate the columns. Their loss should, therefore, be accompanied by a contraction of the solid. Notably, this contraction does not come at the cost of long-range order. Compound **3**, also with a cross-linked 1-D structure, shows a greater loss of order upon heating than the other two solids reported here. That said, the compound does still display peaks, albeit broadened, in the PXRD at lower values of 2θ consistent with the parent structure.

The ability of compounds **1–3** to resorb guests was also examined by dehydrating each sample on the TGA and then running moist air over each. In the cases of compounds **1** and **2**, rapid re-uptake of water was observed. The mass increase reached a plateau at an amount corresponding to the stoichiometry of lost water. This result is significant for the functionality of the solids. For **1** and **2**, the resorption is portended by the very similar PXRD patterns after dehydration because minimal rearrangement should be required to accommodate water molecules. In the case of compound **3**, water uptake was considerably slower but also reached a stoichiometric amount. As will be discussed in the ensuing paragraph, sulfonate structures have an inherent flexibility with respect to their coordinating ability. We have observed exactly this “spongelike” resorption of guests with other silver networks¹⁶ as well as with Ba^{2+} .¹⁷ It is also a phenomenon observed in a number of other coordination solids where desolvation/solvation processes are accompanied by loss of order in the desolvated phase.¹⁸

Adaptability of Silver(I) Sulfonates. Silver sulfonates have been discussed in light of the less directional interactions sustaining the networks. Essentially, the coupling of a functional group with a multitude of ligating modes, the sulfonate, with a pliant metal ion, the d^{10} silver(I) center, results in solids predisposed to a dynamic nature and/or adaptable structures. This is observed even within 2-D solids because there is no truly consistent bridging mode of the sulfonate or no regular coordination geometry of the silver ions.^{6a,b,7} This work takes our ongoing work quite literally to another dimension because we have selected organic linkers to deliberately disfavor the formation of simple 2-D layered networks. The result is that, in the cases of **2** and **3**, the silver sulfonate aggregation motif has adapted to form 1-D columns while still retaining a stable solid. This result is perhaps well placed in context by contrasting it with a phosphonate analogue. We have synthesized the ligand

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1,3,5,7-tetrakis(4,4'-phosphonophenyl)adamantane, the phosphonate analogue of L3.¹⁹ Most divalent transition-metal cations will typically precipitate a layered inorganic–organic hybrid solid if mixed with a phosphonate ligand, which permits the formation of a layered structure, and in this regard, Ni²⁺ is not an exception.²⁰ However, when the phosphonate analogue of L3 was mixed with Ni²⁺, single crystals may be obtained, which show an ion pair composed of hexaaquonickel(II) cations and the phosphonate ligand as a true counterion.¹⁹ The deduction to be made from this observation is that the coordinative preferences of the metal ion and ligating group were incompatible with the structural motif being enforced by the rigid ligand core, resulting in the formation of a solvent-separated ion pair. This is in direct contrast to the formation of 1-D columns observed in the case of silver sulfonates, and so we refer to these sulfonate aggregates as adaptable.³

Conclusions

Three new silver(I) sulfonate compounds have been presented, each containing a different polysulfonated organic core. Compound **1**, containing a mesitylene core, had a classic pillared layered structure. Compound **2**, with a durene core, and compound **3**, with a tetraphenyladamantane core, possessed structures composed of 1-D inorganic columns cross-linked by the organic spacers into 3-D networks. Compounds **2** and **3** represent the first examples of 1-D silver sulfonate aggregates. All three compounds incorporated water in their structures whether as coordinated or free solvent,

and all three showed thermal stability in excess of 300 °C upon dehydration. Compounds **1** and **2** showed good retention of structure upon dehydration, while compound **3** showed partial loss of long-range order. All three compounds, however, showed the ability to resorb water when subjected to water vapor.

Rules are proposed for the self-assembly of silver sulfonates and the design of ligands. On the basis of comparison to an “ideal” lamellar silver sulfonate, a value for the nearest intralayer S–S distances of 5.2 Å was defined. The ligand spacers were then compared to this value with respect to what structural constraints they imposed upon the solid network and rationalizations made about the resultant framework. In summary, ligands that provide a rigid constraint of >5.2 Å with respect to the distances between their sulfonate S atoms have good potential to direct the structure away from a layered solid to 1-D aggregates. With such distances as long as 12 Å, as observed in compound **3**, 1-D aggregates can still be formed and used to open pores in the solid. A corollary of this would be that ligands that could be designed to enforce a S–S separation of >5.2 Å in two dimensions could be used to direct the formation of 0-D inorganic clusters of silver sulfonates.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for support of this research and for a postgraduate scholarship to S.A.D.

Supporting Information Available: X-ray crystallographic files for compounds **1–3**, in CIF format, are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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