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Silver(I) Arylsulfonates: A Systematic Study of "Softer" Hybrid Inorganic–Organic Solids

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The present study represents the first systematic examination of the effects on the layered structure of simple silver aryl–monosulfonates as the breadth of the pendant aryl group is increased beyond that where a simple "phosphonate-like" motif is sustainable. Five new silver arenesulfonates are reported. On the basis of comparison with Ag benzenesulfonate, a threshold of ~6.4 Å is proposed and confirmed as the critical breadth of an aryl group for a simple layered motif to be observed in silver sulfonates. Ag 1,1′-biphenyl-4-sulfonate (**1**) and Ag 2-naphthalenesulfonate (**2**) are below this threshold and so form simple layered networks, termed type 1 solids. When the pendant group is broadened to a 1-naphthyl group, the layer incorporates coordinated water to maintain a layered structure giving Ag 1-naphthalenesulfonate hemihydrate (**3a**). This more diffuse structure is termed a type 2 solid. For anhydrous Ag 1-naphthalenesulfonate (**3**) and Ag 1-pyrenesulfonate (**4**), the additional breadth is compensated for by the formation of Ag–π interactions and the formation of type 3 solids. Interactions between the pendant groups are observed to play a significant role in the packing of the solid. All frameworks are characterized by single crystal and powder X-ray diffraction, IR, DSC-TGA, and elemental analysis. The significance of this adaptable framework is discussed along with implications for design of stacked arene arrays.

Hybrid inorganic−organic layered compounds are a broadly ranging and widely studied class of solids. The prototypical family of this genre is the metal phosphonates ($M^{n+}(RPO_3^{2-})_{n/2}$).[1] These compounds have been extensively studied and are valued for their ability to incorporate structural variation in the interlayer region while maintaining a regular two-dimensional motif. This attribute is owing to the structure-regulating, strong bonding between the metal ions of the layers and the phosphonate oxygen atoms which allows the organic R group to be varied from chromophores to crown ethers to chiral entities.

We,[2] and others,[3] have been interested in examining metal sulfonates as a family of layered solids. In contrast to the dianionic phosphonate ligands, monoanionic sulfonate groups are generally perceived as weaker ligands with respect to their coordinating ability. A considerable body of structural evidence supports this as, with most transition metal ions, sulfonate groups will not displace even solvent from the primary coordination sphere; this is particularly true for harder cations.[4] Silver(I) is an anomaly in this regard as, even from aqueous solution, anhydrous solids can be obtained where the primary coordination sphere of the metal ion is exclusively composed of sulfonate oxygen atoms.[5] The standard structural motif observed for these systems is that of two-dimensional sheets with each sulfonate group bridging

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multiple silver(I) ions, that is, a structure analogous to that of metal phosphonates. This analogy does not extend to the consistency of the microstructural features of the inorganic framework, however, as even a subtle change in the R group can lead to changes in the aggregation pattern between silver(I) ions and sulfonate groups. For example, a change in ligand from *p*-toluenesulfonate[5b] to benzenesulfonate[5c] retains a layered motif but results in a change in the coordination mode of the sulfonate group from μ^5 to μ^6. An initial implication of this observation is that the ligating couple of the sulfonate group and silver(I) would be ill suited for the formation of functional extended solids. However, increasingly, examples of flexible coordination solids are appearing which, despite having a dynamic structure, retain order and demonstrate functionality;[6] they represent complements to zeolite-like solids, rather than replacements. Thus, a desirable feature in these types of solids is that of structural adaptability rather than structural rigidity. In this light, silver(I) sulfonates seem ideally suited in that they possess a ligating group (SO_3^-) which can adopt many bridging coordination modes and a d^{10} metal center in silver(I). The d^{10} configuration is of note as it has no crystal field stabilization energy and hence no dominant geometrical preferences. Indeed, we have previously reported a network, sustained by silver(I) sulfonate interactions, which displays selective and reversible guest inclusion while undergoing extensive structural rearrangement in a highly ordered fashion.[7] We have also demonstrated topotactic intercalation of alcohols in a layered silver(I) sulfonate,[8] a significant result given that topotactic intercalation is a phenomenon typically observed only for solids very strongly bonded in two dimensions.

The current work extends the previous work on silver aromatic sulfonate coordination chemistry by examining the structural consequences of systematically increasing the breadth of the appended aryl group along different vectors from a benzene core. Pendant organic moieties are selected to extend both the height and, importantly, the breadth of the organosulfonates as illustrated in Scheme 1. As will be shown, there is a critical threshold below which the width of the R group must remain to sustain a layered solid. While this is somewhat intuitive, interesting results arise when this threshold is surpassed. We present here the structures of [Ag(4-biphenylsulfonate)]$_\infty$, AgL1, **1**; [Ag(2-naphthalenesulfonate)]$_\infty$, AgL2, **2**; [Ag(1-naphthalenesulfonate)]$_\infty$, AgL3, **3**; [Ag(H_2O)$_{0.5}$(1-naphthalenesulfonate)]$_\infty$, Ag(H_2O)$_{0.5}$L3, **3a**; [Ag(1-pyrenesulfonate)]$_\infty$, AgL4, **4**. Each structure demonstrates the ability of the silver(I) sulfonate skeleton to adapt to the individual steric requirements of the appended organic moiety. When the breadth of the appendage becomes too great to allow a simple layered structure, the network compensates to maintain ligation of the silver centers via additional Lewis base or cation$-\pi$ interactions. Furthermore, it is apparent that the interactions among the interlayer groups are also optimized, illustrating that, in these more weakly bonded solids, the organic group has a true structure directing role rather than one simply as a pendant from the inorganic layers. These complexes provide insight into the factors regulating structure in layered solids sustained by weaker interactions and affirm the adaptable nature of silver(I) sulfonates as a family of solids.

Experimental Section

General Procedures and Instrumentation. TGA/DSC analyses were performed on a Netzsch 449C simultaneous thermal analyzer under a dynamic N_2 atmosphere at a scan rate of 5 °C/min, with samples heated in pierced hermetically sealed pans. The preparation of L1 was derived from kinetic-based studies previously reported for the chlorosulfonation of biphenyl.[9] 1-Pyrenesulfonic acid was prepared by published methods.[10] All chemicals were purchased from Aldrich Chemical Co. and used as received.

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 Kα 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.[11] 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-97[12] 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. Details are available in Table 1, and 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.

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Table 1. Crystal Data and Refinement Summaries for AgL1, AgL2, AgL3, [AgL3(H_2O)$_{0.5}$], and AgL4

formula	$C_{12}H_9O_3S_1Ag_1$	$C_{10}H_7O_3S_1Ag_1$	$C_{10}H_8O_{3.5}S_1Ag_1$,	$C_{10}H_7O_3S_1Ag_1$,	$C_{16}H_9O_3S_1Ag_1$,
	AgL1	AgL2	[Ag(L3)(H_2O)$_{0.5}$]	AgL3	AgL4
fw	341.12	315.09	316.09	315.09	389.16
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	Pc (No. 7)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	5.1120(3)	19.955(4)	15.991(3)	16.468(3)	14.9140(4)
b (Å)	5.219(2)	6.015(1)	5.448(1)	5.059(1)	5.61900(10)
c (Å)	23.622(2)	8.622(2)	11.230(2)	23.804(5)	18.3330(6)
α (deg)	94.15(2)	90	90	90	90
β (deg)	91.00(2)	91.76(3)	95.87(3)	107.37(3)	124.8151(11)
γ (deg)	119.21(2)	90	90	90	90
V (Å^3)	547.6(2)	1034.4(4)	973.2(3)	1892.7(7)	1261.33(6)
Z	2	2	2	4	4
D_{calcd} (g/cm^3)	2.069	1.011	1.079	1.106	2.049
μ (mm^{-1})	2.021	1.065	1.132	1.164	1.769
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
data [$I > 2\sigma(I)$]/params	2367/126	2125/136	4085/286	4350/299	2866/190
GOF	1.081	0.976	1.235	1.044	1.047
final R indices [$I > 2\sigma(I)$]	R1 = 0.057	R1 = 0.062	R1 = 0.030	R1 = 0.026	R1 = 0.029
	wR2 = 0.137	wR2 = 0.192	wR2 = 0.082	wR2 = 0.053	wR2 = 0.084
final R indices (all data)	R1 = 0.1067	R1 = 0.1916	R1 = 0.0393	R1 = 0.0459	R1 = 0.041
	wR2 = 0.1765	wR2 = 0.2171	wR2 = 0.1006	wR2 = 0.566	wR2 = 0.116

Preparation of Silver 1,1′-Biphenyl-4-sulfonate, AgL1, 1. Biphenyl (2.00 g, 13.0 mmol) was dissolved in freshly distilled (CaH_2) dichloromethane (40 mL) in a 1-neck 100 mL round-bottomed flask. The flask was fitted with a rubber septum pierced with a needle to act as a vapor bleed. Chlorosulfonic acid (1.51 g, 13.0 mmol, 1.0 equiv) was added dropwise at ambient temperature over the course of 1 min with vigorous stirring. Initially, a bright red solution results, which rapidly gives way to a light yellow and slightly turbid reaction mixture. The septum was replaced with a reflux condenser, and the reaction was refluxed for 2.5 h. Reduction of the volume of dichloromethane to ca. 10 mL precipitates the monochlorosulfonated product contaminated with unreacted biphenyl (∼10%). No evidence of the formation of the dichlorosulfonated biphenyl was observable by ^{1}H NMR. The crude product was filtered off and washed with ice cold dichloromethane (2 × 1 mL). A second precipitate of crude product was obtained from the filtrate by cooling to −20 °C for 1 h (crude yield: 2.5 g). Removal of biphenyl can be achieved by iterative recrystallizations from dichloromethane; however, as this is accompanied by a severe reduction in the yield of the chlorosulfonated product, conversion to the sulfonate was the preferred method. Accordingly, hydrolysis of the 1,1′-biphenyl-4-sulfonyl chloride was performed by dissolving 0.50 g of the crude product in a 1:10 acetone/H_2O solution (7 mL), and stirring at ambient temperature for 30 min. The acetone fraction was removed under reduced pressure, and the now insoluble biphenyl contaminant was separated by filtration. Addition of 12 N HCl (5 mL) to the filtrate precipitated the sulfonic acid as a white solid. This solid was filtered off and dried in vacuo, yielding the monohydrate of HL1, 0.40 g isolated. Anal. Calcd: C, 57.13; H, 4.79. Found: C, 56.58; H, 4.55. The acid was dissolved in H_2O (5 mL), and $AgNO_3$ (0.270 g, 1.58 mmol, 1.0 equiv with respect to the isolated sulfonic acid) in aqueous solution (1 mL) was added. Evaporation of the solution to ∼2 mL under reduced pressure and cooling to 4 °C precipitated the silver salt, which was filtered, washed with water (2 × 0.5 mL), and dried in air. Yield: 0.510 g, 94% based on isolated sulfonyl chloride. ^{1}H NMR (200 MHz, MeCN-d_3): δ = 8.92 (d, 2H, J = 7.69), 8.08 (d, 2H, J = 7.01), 7.89 (d, 2H, J = 8.37), 7.65−7.40 (m, 3H) ppm. ^{13}C{^{1}H}NMR (50.29 MHz, MeCN-d_3): δ = 129.93, 128.64, 128.01, 127.50, 127.34 ppm. FT-IR (cm^{-1}, KBr): 3351.2(br, w), 3055.1(w), 1653.0(w), 1505.4(m), 1162.9(s), 1050.1(s), 969.2(m), 799.1(m), 768.3(s), 687.1(s), 611.2(s), 566.1(m), 514.7(m). TGA/DSC: 270.0−351.4 °C TG featureless (5.09 J/g, endo), 408.9 °C decomp of L1. ESI-MS (neg ion, MeOH/H_2O): calcd M$^-$ = 233.03 for $C_{12}H_9SO_3$; found 233.54. Anal. Calcd for $C_{12}H_9SO_3Ag$: C, 42.25; H, 2.66. Found: C, 42.03; H, 2.59.

Preparation of Silver 2-Naphthalenesulfonate, AgL2, 2. Sodium 2-naphthalenesulfonate, (1.00 g, 4.35 mmol) was converted to its acid form by passage down a cation exchange column as an aqueous solution (10 mL). Evaporation of the solvent yielded crude HL2 as a yellow semisolid. This was redissolved in a 1:1 MeOH/MeCN solution (20 mL). Ag_2CO_3 (0.722 g, 4.35 mmol, 1 equiv) was added and the mixture sonicated at room temperature for 30 min. After the evolution of CO_2(g) had ceased, the reaction was filtered and concentrated under reduced pressure to 10 mL. Et_2O (20 mL) was added to precipitate the silver salt as a white solid. Yield: 1.21 g, 89.0%. FT-IR: (cm^{-1}, KBr): 3048.3(w), 1348.9(m), 1189.3(s), 1144.2(s) 1126.7(s), 1092.8(s), 1026.3(m), 958.9(m), 910.9(m), 86.59(m), 830.4(m), 743.8(m), 667.2(m), 558.2(m), 497.7(w), 474.5(m), 427.3(m). DSC/TGA: 309.9−317.5 °C (36.46 J/g, endo) TGA featureless, 321.7−336.9 °C (93.02 J/g, endo) TGA featureless, 337 °C decomp of L2. Anal. Calcd for $Ag_1C_{10}H_7O_3S$: C, 38.23; H, 2.25. Found: C, 38.83; H, 2.25. Large single crystal plates were obtained from i-Pr_2O diffusion into a MeOH solution of **2**. Polycrystalline material of the same phase could also be obtained when crystallized from water.

Preparation of L3 as its Ag(MeCN) adduct, Silver Tris-(acetonitrile)-1-naphthalenesulfonate. To a 1:1 solution of water and acetone (25 mL) was suspended 1-naphthalene sulfonyl chloride (1.00 g, 4.43 mmol). Upon dissolution, a colorless oil separated which was left to vigorously stir for 20 h at room temperature. The acetone was removed under reduced pressure. $AgNO_3$ (0.748 g, 4.43 mmol, 1.0 equiv) was then added as an aqueous solution (5 mL) to remove chloride as AgCl. Filtration of the reaction afforded a colorless solution, which was evaporated under reduced pressure to give crude HL3 as a yellow oil. MeCN (20 mL) was added followed by Ag_2O (0.509 g, 2.21 mmol, 0.5 equiv), and the mixture was sonicated for 30 min at room temperature until the suspension lost its turbidity. The reaction was filtered through a Celite plug and washed with MeCN (2 × 2 mL), and the combined filtrates were reduced in volume to 10 mL. Addition of i-Pr_2O (10 mL) and cooling to −10 °C precipitated the product as a white powder. ^{1}H NMR (200 MHz, d_3-MeCN): δ = 8.92 (d, 1H, J = 8.21), 8.09 (d, 1H, J = 7.35), 7.90 (d, 2H, J = 8.54), 7.56−7.40 (m, 3H) ppm.

$^{13}C\{^1H\}$ NMR (50.29 MHz, d_3-MeCN): δ = 143.43, 134.87, 131.17, 130.03, 128.93, 128.03, 127.11, 126.74, 126.09, 125.41 ppm. ESI-MS (H_2O, *m*/*z*): calcd 207.23 for HL3, found 206.83. FT-IR (cm^{-1}, KBr): 3524.7(w, br), 3399.2(w, br), 3053.3(w), 2994.8(w), 2923.8(w), 1646.5(w), 1505.5(m), 1345(w), 1205.3(s), 1181.2(w), 1142.9(s), 1153.9(s), 1056.1(s), 968.5(m), 826.1(w), 800.96(s), 768.4(s), 692.9(s), 614.7(s), 614.7(s), 510.9(s). DSC/TGA: 41.8−60.2 °C (132.0 J/g endo) −13.56% obsd (−14.10% calcd for loss of 3 MeCN), 108.2−118.3 °C (43.49 J/g endo) −14.78% obsd (−14.10% calcd for loss of 3 MeCN), 214.8−234.7 °C (28.25 J/g) TGA featureless, 245.5−267.7 °C (51.87 J/g) TGA featureless, 265.5 °C decomp of L5. Anal. Calcd for $Ag_1C_{10}H_7O_3S$-(H_3C_2N): C, 40.47; H, 2.83; N, 3.93. Found: C, 37.14; H, 2.48; N, 3.16. Yield: 1.80 g, 94.1%. Single crystals, which revealed the formulation of this complex as {[AgL3(MeCN)$_3$][Ag(MeCN)$_3$]}-L3,[13] were grown by vapor phase diffusion of Et_2O into a MeCN solution of the product.

Preparation of Silver 1-Naphthalenesulfonate Hemihydrate: Ag(H_2O)$_{0.5}$L3, 3a. {[AgL3(MeCN)$_3$][Ag(MeCN)$_3$]}L3 (200 mg, 0.458 mmol) was dissolved in H_2O (2 mL). Evaporation of this solution over 7 days yielded very thin single crystalline plates at the air−water interface. Polycrystalline material could be obtained by evaporation under reduced pressure at 20−25 °C. FT-IR (cm^{-1}, KBr): 3404.6(w, br), 3049.5(w), 1500.4(m), 1199.9(s), 1159.8(s), 1043.0(s), 968.1(m), 805.7(s), 767.8(s), 687.5(s), 613.0(s), 613.0(s), 517.2(s). DSC/TGA: 116−124 °C (68.48 J/g, endo) −2.75% obsd (−2.70% calcd for loss of 0.5 H_2O), 219.6−234.4 °C (46.90 J/g, endo) TGA featureless, 242.1−258.0 °C (65.80 J/g, endo) TGA featureless, 292.9 °C decomp of L3. Anal. Calcd for $C_{10}H_7O_3S_1$-(H_2O)$_{0.5}$: C, 37.16; H, 2.50. Found: C, 36.84; H, 2.08. Yield: 150 mg, 99%.

Preparation of Silver 1-Naphthalenesulfonate AgL3, 3, from Solution. Polycrystalline Ag(H_2O)$_{0.5}$L3 (100 mg, 0.301 mmol) was dissolved in 5 mL of MeOH with heating. Addition of Et_2O (2 mL) precipitated the product as a white solid, which was filtered off and washed with Et_2O (2 × 2 mL). FT-IR (cm^{-1}, KBr): 1652.7(m), 1505.9(s), 1148.6(s, br), 1047.6(s), 968.5(m), 797.7(m), 767.6(m), 687.3(m), 611.6(m), 566.5(m), 509.26(m). DSC/TGA: 222.5−240.5 °C (86.09 J/g, endo) TGA featureless, 278.2 °C decomp of L3. Anal. Calcd for $C_{10}H_7O_3S$: C, 38.22; H, 2.25. Found: C, 38.74; H, 1.84.

Preparation of Silver 1-Naphthalenesulfonate, AgL3, 3, via Thermolysis. Polycrystalline Ag(H_2O)$_{0.5}$L3 (100 mg, 0.301 mmol) was dispersed over the bottom of a 50 mL beaker and dried in a 200 °C oven for 2 h to yield a white powder. FT-IR (cm^{-1}, KBr): 1650.1(m), 1505.0(s), 1152.8(s, br), 1040.9(s), 960.3(m), 801.9(m), 767.1(m), 684.5(m), 600.4(m), 565.9(m), 511.8(m). DSC/TGA: 222.5−240.5 °C (86.09 J/g, endo) TGA featureless, 273.1 °C decomp of L3. Anal. Calcd for $C_{10}H_7O_3S$: C, 38.22; H, 2.25. Found: C, 37.90; H, 1.93. Yield 93 mg, 100%.

Preparation of Silver(I) 1-Pyrenesulfonate, AgL4, 4. 1-Pyrenesulfonic acid (0.77 g, 2.72 mmol) was dissolved in 10 mL of MeCN; Ag_2CO_3 (0.37 g, 1.36 mmol, 0.5 equiv) was then added, generating a green suspension. The reaction mixture was sonicated at room temperature until the green turbidity disappeared and the evolution of CO_2 ceased. The solution was filtered and the solvent removed under reduced pressure to yield a crude white solid that was redissolved in MeOH (15 mL) and filtered again. The pure complex was obtained via precipitation from this solution upon addition of an equal volume of Et_2O and cooling to 4 °C. Single crystals of this network were obtained by vapor diffusion of *i*-Pr_2O into a saturated MeOH solution of the product. Yield: 0.91 g, 86%. ^1H NMR (200 MHz, MeCN-d_3):[3] δ = 9.27 (d, J = 9.4 Hz, 0.4 H), 8.62 (d, J = 8.03 Hz, 0.6 H), 8.27−8.05 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR: δ = 142.3, 133.1, 132.2, 131.7, 128.9, 128.4, 128.2, 126.5, 126.4, 126.3, 126.2, 125.8, 125.3, 124.9 ppm. FT-IR (cm^{-1}, KBr): ν = 3043.5(w), 1382.4(w), 1227.3(s), 1111.0(s), 1046.3(s), 1001.1(s), 852.4(s), 755.5(m), 710.2(m), 665.0(s), 613.3(m), 555.1(m), 516.3(w). TGA/DSC: TG and DSC featureless to 272.7 °C: decomp of L4. ESI-MS: (neg ion, MeCN): calcd M^- = 281.03 for $C_{16}H_9SO_3$; found 281.04. Anal. Calcd for $C_{16}H_9SO_3Ag$: C, 49.38; H, 2.33. Found: C, 48.88; H, 2.21.

Conversion of Ag(H_2O)$_{0.5}$L3, 3a, to AgL3, 3. Initially, compound **3** was obtained by dissolution of **3a** (or Ag(MeCN)$_3$L3) into MeOH or EtOH, followed by precipitation with *i*-Pr_2O. Compound **3** could also be obtained by heating compound **3a** or Ag(MeCN)$_3$L3 at 150 °C for 2 h to remove the solvent in these structures. In each of these cases, PXRD analysis of the dried compounds showed that the same polycrystalline compound was formed in each case and the patterns matched that of the simulated PXRD from the single crystal structure determination.

Results and Discussion

The structures obtained with this family of compounds can be classified into three general categories. In this work, for the sake of clarity, these will be referred to as type 1, type 2, and type 3. Type 1 structures are those sustained exclusively by bonding between Ag ions and sulfonate oxygen atoms. Type 2 structures involve a continuum of interactions between Ag ions and sulfonate oxygen atoms but with ancillary ligation by additional simple Lewis bases. Type 3 networks involve coordination between Ag ions and sulfonate oxygen atoms but with additional coordination of Ag by the π system of the appended arene. Basic structural descriptions of the different complexes will initially be provided followed by comparisons of most relevant structural features.

Structures of the Type 1 Solids, [Ag(4-biphenylsulfonate)]$_\infty$, AgL1, 1, and [Ag(2-naphthalenesulfonate)]$_\infty$, AgL2, 2. Compound **1** contains the most basic modification of the benzenesulfonate core with another aromatic unit, that is, direct linear extension of the vector from the sulfonate to the aryl group. The lateral breadth of the appended biphenyl moiety is the same as a single phenyl ring (∼4.47 Å defined by the peripheral H−H distance measured perpendicularly to the C−S bond). As could be expected, this structure does not result in drastic changes to the overall motif, and a simple type 1 layered structure is obtained as shown in Figure 1. The perpendicular interlayer distance has a value of 23.56 Å with the biphenyl moieties forming a bilayer arrangement. The thickness of an individual layer is approximately 3.89 Å, defined by the trans-layer S atom separations, resulting in a gallery height of 19.66 Å. Looking at an individual layer (Figure 2), there is only one type of Ag center, and it has a distorted octahedral geometry. As with the Ag benzenesulfonate structure,[5c] compound **1** possesses a μ^6 (κ^2O1, κ^2-O2, κ^2O3) bridging mode for the SO_3 group. The Ag−O distances are all different and range from 2.412(6) to 2.540(6) Å, typical for silver sulfonate complexes.

(13) Unit cell parameters for {[Ag**L3**(MeCN)$_3$][Ag(MeCN)$_3$]}**L3**: orthorhombic, space group $P2_12_12_1$ (No. 19), a = 13.9039(2) Å, b = 14.7133(3) Å, c = 11.0340(2) Å, $\alpha = \beta = \gamma$ = 90°, V = 696.85(2) Å^3.

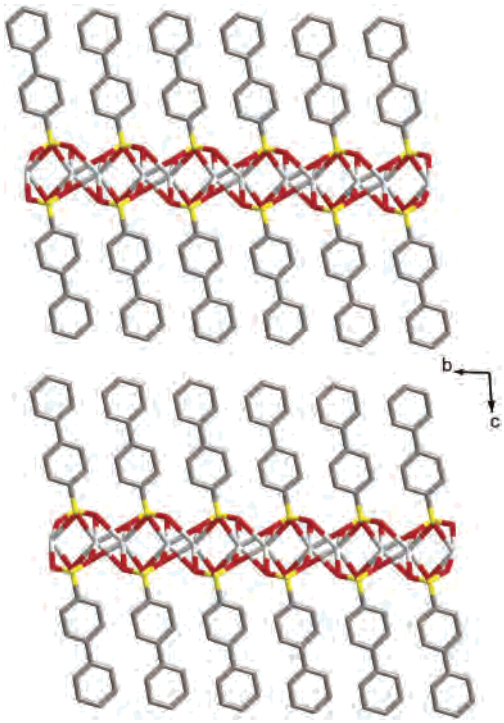


Figure 1. [Ag(4-biphenylsulfonate)]$_\infty$, **1**, showing parallel sheets along the *a*-axis.

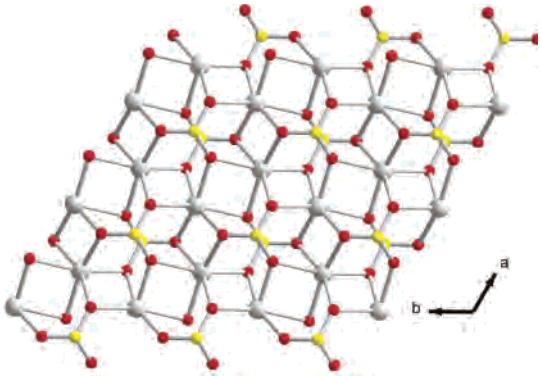


Figure 2. View onto a single layer of compound **1** showing the μ^6 bridging mode of the SO_3 group and the six-coordinate Ag center.

To date, Ag benzenesulfonate had been the only structure, regardless of metal ion, where the SO_3 group adopted the unusual μ^6 mode. A very upright orientation of the R group is required to allow coordinative saturation of the sulfonate. In Ag benzenesulfonate, the phenyl ring is virtually perfectly perpendicular to the layers. In **1**, the aryl group is tilted off the perpendicular axis by 19.0°. This, however, is not a sufficient distortion to prevent the SO_3 group from adopting the μ^6 bridging mode. A further similarity between Ag benzenesulfonate and compound **1** is that both structures have aryl groups which are disordered dynamically about a 2-fold axis. This arises due to the imperfect packing of the aryl moieties in the interlayer when anchored spatially by the metals. As would be expected from the disorder, there are no π interactions between any of the biphenyl rings despite the layers packing with sufficient density to form a bilayer structure. The trace of the unit cell onto an individual layer gives a pseudorhombohedral (5.112 × 5.219 Å^2) cross

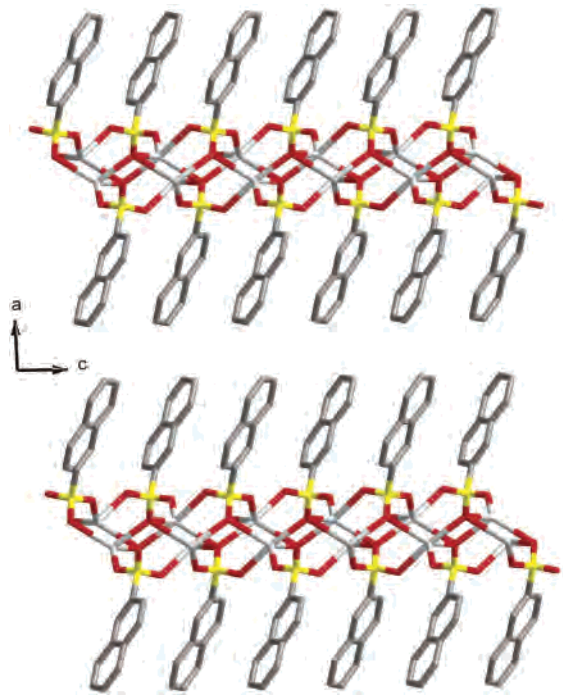


Figure 3. Ag 2-naphthalenesulfonate, **2**, viewed parallel to the layers showing the pendant naphthyl groups.

sectional area of 23.287 Å^2 which is more than sufficient to contain the breadth of the ligand, both the SO_3 group and the vertical biphenyl group. Further discussion on this point will follow when all structures have been presented.

Compound **2** possesses a 2-naphthalenesulfonate appendage so the additional phenyl ring is fused at an angle of 135° from the sulfonate group of the "parent" benzenesulfonate. This increases the lateral breadth of the R group to 5.73 Å, again perpendicularly to the C−S bond. The resulting solid again possesses a type 1 layered structure with no included solvents as shown in Figure 3. A bilayer arrangement is again observed with an interlayer distance of 19.946 Å. The thickness of an individual layer is approximately 4.39 Å resulting in a gallery height of 15.55 Å. The 2-naphthyl groups are tilted at an angle with respect to the layers of 77.9(6)°. While the macroscopic structural features of **2** are similar to those of **1**, a closer inspection of the layer (Figure 4) reveals a number of differences. There is one unique Ag ion in the structure, which is five-coordinate with a distorted square pyramidal geometry. This is in contrast to the six-coordinate center in **1** illustrating the adaptability of the d^{10} metal center. The distances from Ag1 to the five sulfonate oxygen atoms range from 2.467(9) to 2.855(4) Å. The bridging mode of the sulfonate group in 2 is μ^5 (κ^1O1, κ^3O2, κ^1O3). The most unusual microscopic feature is the κ^3 coordination of one of the oxygen atoms. Consequently, the S−O bond lengths are not uniform. The S1−O2 bond is elongated reflecting a resonance form with more single bond character between S1 and O2 (S1−O2 = 1.55(1) Å), and double bond character for O1 and O3 (S1−O1 = 1.462(9) Å, S1−O3 = 1.468(9) Å). The trace of the unit cell onto the layer gives a rectangular (6.015 × 8.622 Å^2) cross sectional area of 51.861 Å^2 for two sulfonate groups or, more

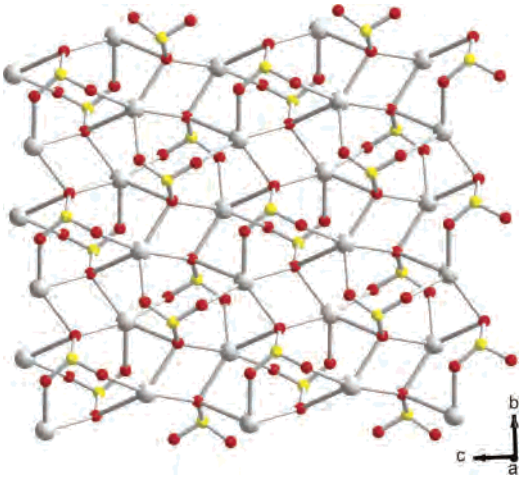


Figure 4. View onto a single layer of **2**, showing the μ^5 bridging of the SO_3 group as well as the κ^3 coordination of one sulfonate oxygen atom.

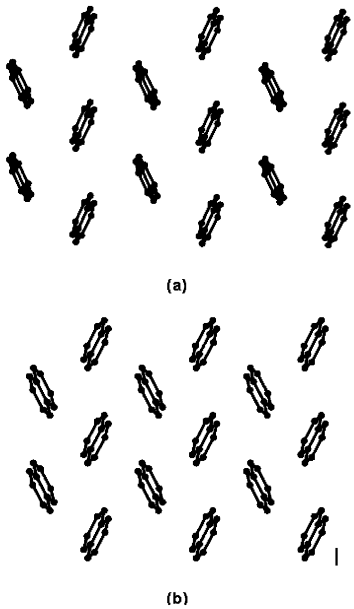


Figure 5. An illustration, via comparison of single crystal X-ray structures, of the herringbone π-stacking pattern adopted by (a) naphthalene itself,[15] and (b) the naphthyl groups in compound **2**.

meaningfully, 25.931 Å^2 for one sulfonate group. This is sufficient space for the 2-naphthyl group, and the type 1 structure results although the coordination number of Ag has decreased from six in **1** to five in **2**.

Whereas in **1** the linearly extended biphenyl groups were disordered, in **2**, the additional breadth of the 2-naphthyl group brings the organic groups into contact. The naphthyl group in **2** packs in the classic herringbone motif inherent to simple aromatic hydrocarbons.[14] Packing of the naphthyl R-group has a similar array of π-stacking interactions as that of naphthalene itself[15] but is expanded by ~0.2 Å along the two axes defined by the π-face and -edge contacts of the naphthyl ring (Figure 5). Undoubtedly, the overall structure represents a compromise between the favorable nature of

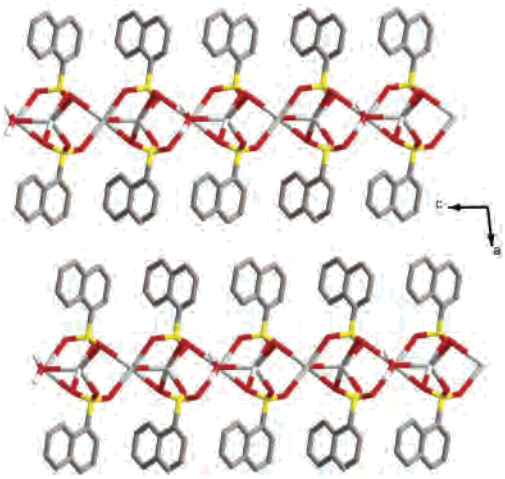


Figure 6. Ag 1-naphthalenesulfonate hemihydrate, **3a**, shown parallel to the layers. Note the coordinated water molecules (visible at the left of the image with H atoms on the oxygen).

these interactions and the metal ligand interactions in the silver sulfonate layers.

Structure of the Type 2 Solid, $[Ag(H_2O)_{0.5}$(1-naphthalenesulfonate)$]_\infty$, $Ag(H_2O)_{0.5}L3$, 3a. Compound **3a**, in addition to **3**, incorporates a 1-naphthalenesulfonate group. With the SO_3 group ideally anchoring the organic moiety perpendicularly to the layer of metals and with the appended benzene ring in this case fused 90° to the SO_3 linkage, the lateral breadth of the organic group, now a value of 6.93 Å, becomes very significant in this case. In preparations from water, compound **3a** results. Typically, even from aqueous solutions, simple silver monosulfonates form anhydrous solids, but **3a** is an exception. The overall structure is similar to that of **1** and **2** in that it is maintained as a bilayer motif (Figure 6). The interlayer distance of 15.91 Å and a layer thickness of approximately 4.10 Å result in a gallery height of 11.81 Å. There are two independent ligands which are tilted from the perpendicular by 9.4° and 8.8°. A look at the layer structure reveals important differences in this structure compared to **1** and **2**. The additional breadth of the 1-substituted naphthalene surpasses the critical threshold for retaining homoleptic sulfonate ligation of silver. In order to maintain the lamellar structure and satisfy the bonding requirements of silver, bridging water molecules are incorporated into the layer structure as shown in Figure 7. This allows the silver ions and sulfonate groups to be further spaced to accommodate the 1-naphthyl group. Owing to this more dispersed structure, the two crystallographically distinct sulfonate groups each bridge only four Ag centers, both in a κ^1O, κ^1O, κ^2O coordination mode. There are two distinct silver centers in the layer. The first silver center, Ag1, has a nearly square pyramidal geometry consisting of four bonds from four sulfonate oxygen atoms in the equatorial plane (Ag1−O = 2.368−2.510(4) Å) and coordination to a water molecule in the apical position (Ag1−O7 = 2.489(4) Å). The Ag2 center is also five-coordinate, having a distorted trigonal bipyramidal geometry composed of bonds from four sulfonate oxygen atoms (Ag2−O = 2.419−2.509(4) Å) with the fifth interaction arising from bonding with the coordinated

(14) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley and Sons Ltd.: Toronto, 2000; p 19.
(15) Ahmed, F. R.; Cruickshank, D. W. J. *Acta Crystallogr*. **1952**, *5*, 852.

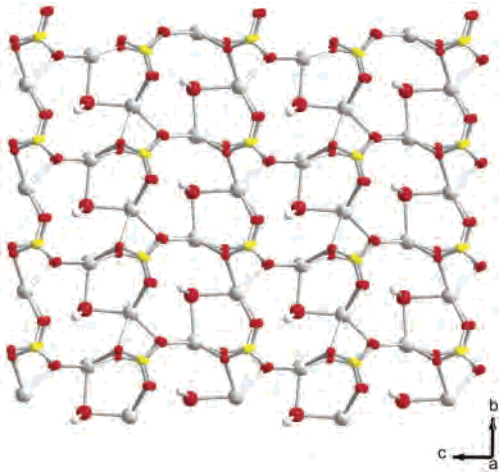


Figure 7. View onto the layer of **3a** showing the μ^5 coordination of the SO_3 groups. Note the coordinated water molecules, shown with H atoms, expanding the layers.

water molecule (Ag2−O7 = 2.425(4) Å) in the structure. The more diffuse structure of the layer is reflected in the unit cell which now has a trace in the *bc*-plane of 30.59 Å^2 per sulfonate group (∼5 Å^2 greater than in **2**). A herringbone π-stacking motif in this compound is also observed but is different than that in naphthalene or compound **2**. Edge to π-face interactions run perpendicular to the 1,4,5,8-positions of the naphthyl ring in **3a**, ranging from 3.55 to 4.01 Å, as opposed to stacking perpendicular to the 2,3,6,7-positions in the former compounds.

Structures of the Type 3 Solids, [Ag(1-naphthalenesulfonate)]$_\infty$, AgL3, 3, and [Ag(1-pyrenesulfonate)]$_\infty$, AgL4, 4. Given the ability of **L3** to form solvated structures with silver(I), and of particular note compound **3a**, where solvent inclusion is a stabilization factor for formation of a layered structure, an unsolvated form of this complex was prepared to further this study. Initially, compound **3** was obtained by heating compound **3a** at 150 °C for 2 h to remove the solvent. PXRD analysis of the dried compounds showed that a new polycrystalline compound was formed. It was also found that dissolution of **3a** in MeOH or EtOH, followed by precipitation with *i*-Pr_2O, also led to the same unsolvated compound as identified by PXRD.

In compound **3**, in the absence of any ancillary ligation, it would not be expected, with the breadth of the 1-naphthyl appendage, that a simple layered structure would be attained. Indeed, a two-dimensional solid is obtained, but the layers are not sustained exclusively by Ag sulfonate interactions (Figure 8). The construction of the layers in **3** can be viewed as a ribbon of sulfonate bridged Ag centers running parallel to the crystallographic *b*-axis. Off this column are projected four naphthyl groups above and below the tape of $AgSO_3$ aggregation. Two of the four naphthyl groups then form organometallic bonds to silver centers, in an η^2 π mode from the 6,7-positions of the ring. There are two unique silver centers, each of which is six-coordinate, and two unique ligands in the structure. Ag1 has a trigonal prismatic geometry. It coordinates only to sulfonate groups and comprises the core of the one-dimensional ribbon. Ag2 has an irregular geometry consisting of four bonds to sulfonate

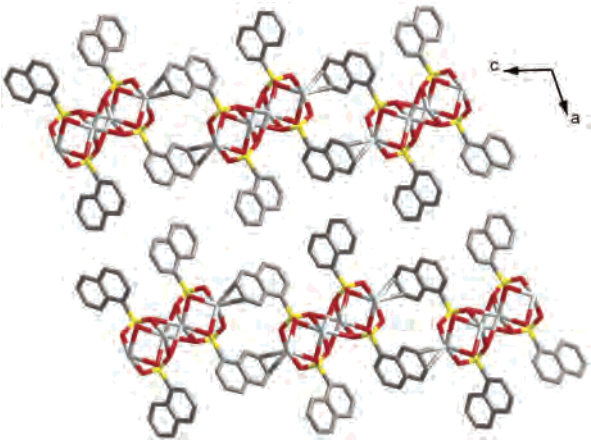


Figure 8. Ag 1-naphthalenesulfonate, **3**, shown parallel to the layers. Half of the naphthyl groups form π interactions with silver centers to satisfy bonding requirements.

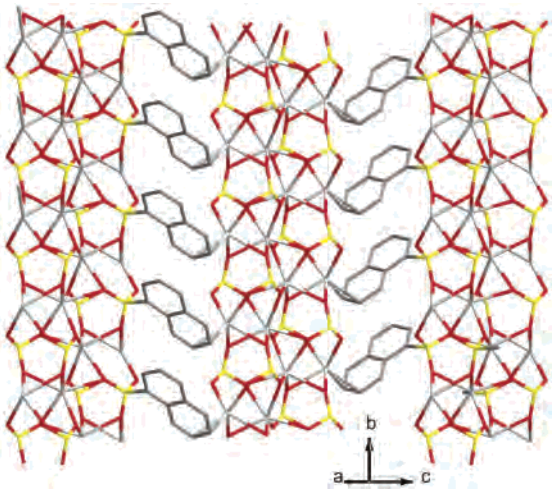


Figure 9. View onto a single layer of **3**. The layer is not composed of continuous $AgSO_3$ aggregates but takes the form of columns cross-linked by the 1-naphthyl units.

oxygen donors and two π interactions with the naphthyl ring. Equivalently, there are two types of organosulfonate ion present. Both sulfonate groups present the same μ^5, η^3 coordination mode and are juxtaposed across the plane of the tape. Both sulfonate groups connect three Ag1 centers (Ag1−O = 2.436(2)−2.549(2) Å) and two Ag2 centers (Ag2−O = 2.354(2)−2.631(3) Å). The π-bonds of the naphthyl ring to the Ag2 centers (Ag2−C7 = 2.506(2) Å, Ag2−C8 = 2.552(3) Å) are within normal ranges for this type of interaction giving an overall coordination mode of μ^6, η^5 for this ligand. Naphthyl rings from a given layer are π stacked. The Ag-bound naphthyl rings are stacked such that each six-membered ring forms π interactions only to one face. The stacking is in a face-to-face manner with one of the six-membered rings of an adjacent naphthyl group (Figure 9) with a mean C−C distance over all 6 carbon atoms of 3.683 Å. The nonmetalated naphthalene rings stack in a less eclipsed face-to-face manner but are slightly closer stacking at 3.51 Å. There are no π stacking interactions between any of the aryl groups from different layers.

For [Ag(1-pyrenesulfonate)]$_\infty$, AgL4, **4**, further lateral breadth is again added to the pendant organic group to

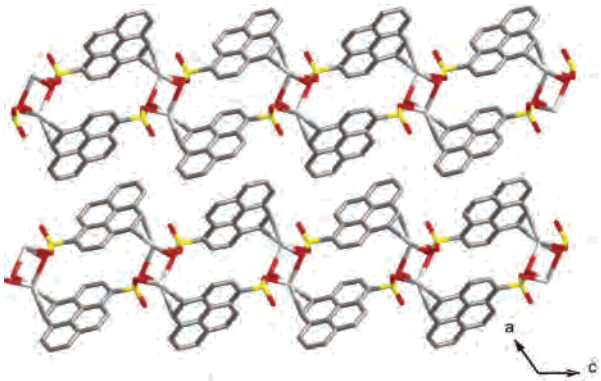


Figure 10. Ag 1-pyrenesulfonate, **4**, viewed along the layers. The larger pyrene units require all the organic units to tilt to form π interactions with adjacent Ag centers.

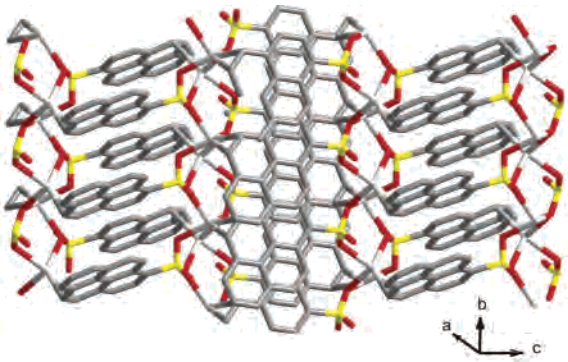


Figure 11. View down onto a single layer of **4** (almost perpendicular to the view in Figure 10). The π-stacking in the layer as well as the alternating columnar nature are both visible.

increase the perpendicular width of the aryl group to 8.14 Å. The structure of the network is shifted, but a two-dimensional motif is still maintained. In this case, the breadth of the pyrene unit requires tilting of not half but all of the aryl units to form π interactions with the silver ions to satisfy the bonding requirements at the metal centers (Figure 10). The structure can be considered as 1-dimensional ribbons of SO_3-bridged silver(I) ions cross-linked by pyrene units. The pyrene moieties form the inter-ribbon bridges both via sulfonate and π-coordination to the Ag centers. Within a layer, between $AgSO_3$ columns, the orientation of the pyrene units alternates by ~74.5° (Figure 11). There is only one type of Ag center present in the structure. It is five-coordinate with an irregular coordination geometry composed of three sulfonate oxygen atoms and the two olefinic carbons. The three bonds to the oxygen atoms are situated close to 90° apart while the η^2 π interaction completes the coordination sphere. There is only one type of sulfonate group present in the structure which bridges three Ag centers in a κ^1O, κ^2O coordination mode (Ag1−O1 = 2.378(3) Å, Ag1−O2 = 2.298(3) Å, Ag1−O1 = 2.507(2) Å). The noncoordinating oxygen atom has a slightly shorter S−O bond length (1.435(2) Å) relative to the two coordinating O atoms (1.467−1.468(2) Å) indicative of more double bond character. The π interactions between the pyrene ring and the Ag center are on the shorter end of the typical range (Ag1−C5 = 2.378(2) Å, Ag1−C6 = 2.426(3) Å). Face-to face π interactions further stabilize the framework. Within a layer, along the *b*-axis, each pyrene ring forms π-stacking interactions with neighboring pyrene units to both sides. These interactions are of an offset face-to-face nature and involve all four rings of the pyrene unit, two being involved to form the π interaction to each side (perpendicular distance = 3.41 Å). Between layers, only van der Waals contacts exist.

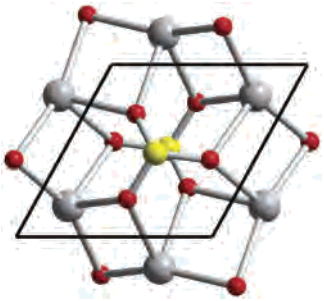
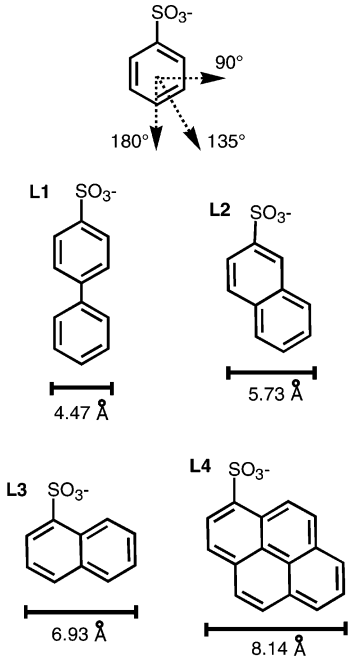


Figure 12. The view onto a single layer of Ag benzenesulfonate.[5c] The rhombus represents the race of the unit cell onto the layer (5.160 × 5.198 Å^2) with an area of 23.45 Å^2. This is taken as an approximation of the minimum area required to accommodate an $AgSO_3$ building unit in the construction of a simple layered solid.

Structural Constraints and Considerations in Layered Silver Sulfonates. To determine structural constraints for a family of solids, it is first necessary to define an ideal framework upon which to draw comparisons. For this purpose, Ag benzenesulfonate[5c] has been chosen. This structure shows a nearly perfect hexagonal arrangement of Ag centers with each face of a hexagon being capped by a SO_3 group in a μ^6 coordination mode. The crystal symmetry is triclinic, but this is due to the vertically aligned phenyl group, with 2-fold symmetry, not being able to match the higher symmetry of the SO_3-bridged silver ions. The parameters of the unit cell for this compound traced onto the inorganic layer correspond to a 5.160 × 5.198 Å^2 rhombus with an interaxis angle of 61.00° (Figure 12); this corresponds to an area of 23.45 Å^2. This encompasses a sulfonate group on each side of the layer and the associated two silver ions. This can be viewed as the approximate area in a plane required for a sulfonate group to coordinate to silver(I) ions for a simple layered motif to be sustained.

For compounds **1**−**4**, it is necessary to examine the geometrical constraints imposed by this ~23.5 Å value. The sulfonate group itself has a breadth of 3.66 Å (taking the mean S−O bond length to be 1.47 Å and the covalent radius of oxygen to be 0.73 Å). This is sufficient to accommodate the thickness of an aryl ring. Thus, with respect to the aryl group, there must exist a critical lateral breadth which, if exceeded, would preclude the formation of a simple SO_3-bridged layered solid. An approximate value for this can be derived from comparison to the $AgPhSO_3$ ideal structure. The area required in this compound for the minimal structural unit was 23.45 Å. Dividing this value by 3.66 Å, required for the perpendicular width of the sulfonated aryl group, would allow an aryl group with a lateral breadth of 6.41 Å to be accommodated while maintaining a lamellar structure. This is not meant to be a quantitatively predictive calculation but simply an approximation of how much space is afforded in the interlayer by a network of SO_3-bridged silver(I) ions.

Scheme 1



For compounds **1**−**4**, whose lateral breadths are given in Scheme 1, the approximation is accurate as only compounds **1** and **2**, with biphenyl and 2-naphthyl appendages, respectively, form simple layered solids. For the 1-naphthyl appendage used in compounds **3** and **3a**, which exceeds the critical breadth by a relatively small amount (6.93 Å versus 6.41 Å), the Ag sulfonate backbone is displaced to allow the incorporation of a water molecule or, under anhydrous conditions, shifts to allow the formation of π interactions with half of the naphthyl groups. For compound **4**, the 1-pyrene appendage significantly exceeds the critical breadth which allows a continuum of SO_3-bridged Ag ions (8.14 Å versus 6.41 Å). In this case, the structure adapts to a greater extent by forming cation−π interaction between silver(I) centers and all the aromatic moieties.

Another notable consideration affecting each structure is the noncovalent interactions between pendant organic groups. The presence of significant aryl−aryl interactions serves to further stabilize the solid, and in the above compounds, with the exception of **1**, the observed structures incorporate contributions from these as well as the Lewis acid/base interactions. In compound **2**, these interactions are prominent as, with neighboring groups in a layer, the 2-naphthyl groups pack in the classic herringbone motif analogous to naphthalene itself.[15] In compound **3a**, a herringbone motif in the π-stacking is also observed, but it runs perpendicular to the 1,4,5,8-positions of the naphthyl ring as opposed to perpendicular to the 2,3,6,7-positions in **3** and naphthalene. In compounds **3** and **4**, intralayer π interactions also exist but not in a herringbone motif. These solids arrange to form offset face-to-face π stacking interactions.

Formation of Silver-π Aryl Complexes. Complexes of neutral arene donors with silver(I) are often polymeric, where the counteranion, usually perchlorate, triflate, or nitrate, and the arene molecule bridge metal centers to form the extended structure.[16] The bonding in these systems has been the subject of a number of discussions[17] and has been unified by Kochi and co-workers with a study which defined common features between Ag−arene complexes.[18,19]

With regards to the formation of extended solids with Ag−π interactions, Munakata and co-workers have described numerous polymeric structures containing various arenes and counteranions.[16a,20] Solids derived from these building blocks have structural features, especially when polycyclic aromatic hydrocarbons are employed, that makes them desirable for electronically oriented devices such as conductors or photoactive switches. The reason for this lies in the ability to align the π faces of arenes in one direction in the solid state. Arenes themselves have the tendency to form π−π interactions which do not orient π faces into an optimal stacking arrangement. Consequently, in Ag^I polymers, there exists the potential for arene p-orbitals to overlap and develop a band structure. One exemplary material in this respect by Munakata and co-workers is the assembly between silver(I) cations, 1,2-benzenetriphenylene, and perchlorate ions.[21] This one-dimensional framework is held together by interactions between Ag^I, the arene, and perchlorate. Organizing the aromatic stacking into a columnar structure causes the compound to become electronically conductive at room

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(19) Kochi defined a series of parameters (d, Δ, and β) which describe the relative positioning of the Ag center and the arene ring in a series of structures. In structure **3**, the values of d, Δ, and β measure 2.51 Å, 1.44 Å, and 29.89°, consistent for the most part with other structures, fitting with the median values from Kochi's examination, with the exception of d, which falls close to the longer end of the measurement. Of particular interest in **3** is the relative symmetry of the two Ag−C interactions (Ag2−C7 = 2.506(2) Å, Ag2−C8 = 2.552(3) Å), suggesting that this bonding is close to an ideal η^2 mode. For **4**, the values for d, Δ, and β measure 2.215 Å, 1.93 Å, and 41.71°, respectively. These interrelated values are all at the limits of (or slightly beyond) those of other compounds discussed by Kochi. In essence, the silver ion is situated less above the arene ring than in other complexes, most likely due to the other intermolecular stacking and silver sulfonate bonding effects present, while maintaining comparable Ag−C bond distances.

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temperature, while 1,2-benzenetriphenylene itself is nonconductive. This compound is also EPR active, attributable to the formation of aromatic radicals.

In comparison, compounds **3** and **4** are not conductive; however, they are the first examples of extended structures involving Ag−π interactions assembled from a two component system. Other reported structures are three component systems consisting of an arene, silver(I), counteranion, and possibly an additional ancillary ligand. Given the results above, it is feasible to envisage, with a sulfonate with a sufficiently wide aromatic group, the formation of a coordination network stitched solely by Ag−π coordinate bonds with the sulfonate as a noncoordinating entity. This would facilitate the formation of more efficiently stacked arene arrays in a twofold manner. First, as the SO_3 group itself is small enough to allow for the formation of stacked arene arrays, this would provide steric advantages relative to larger anions such as CF_3SO_3. Second, the anionic moiety is anchored off the π face, perpendicular to the direction of stacking. This would also allow greater prediction of the ultimate packing.

Adaptability of Silver(I) Sulfonates. Examples of extended inorganic frameworks which display considerable dynamic behavior are increasingly being reported.[6,22] Silver(I) sulfonates are excellent candidates to exhibit this feature owing to the many possible binding modes of the SO_3 group as well as the versatile d^{10} coordination sphere of the metal ion itself. In this regard, the present study examines the extent of the adaptability of the inorganic framework. In systems where ligating components have more strictly defined bonding preferences, if the steric or geometrical properties of the organic spacer do not mesh, extensive bonding between metal and ligand is often not observed, or if there is, a loss of order in the assembly is associated. For an extended solid, this would simply result in either the observation of soluble species, as those smaller aggregates which would form would remain partially solvated, or the formation of an amorphous material.

For comparison, there are no complexes of the phosphonate analogues of L3 and L4 known with any metal. Interestingly, for metal phenylphosphonate complexes, type 1 solids are actually quite uncommon and are observed primarily with higher oxidation state metals (Zr^{4+},[23a] U^{4+},[23b]) or, in one case, when prepared solvothermally (Sn^{2+}).[23c] More typical is a type 2 solid where water is coordinated to the metal center (Cu^{2+},[24a] Mn^{2+},[24b] Mg^{2+},[24b] Zn^{2+},[24b] Fe^{2+}[24c]). Some anhydrous complexes have been also observed with monoanionic phenylhydrogenphosphonate ligands (La^{3+},[25a] Pb^{2+},[25b] Ba^{2+},[25b] Ca^{2+},[25c] Sr^{2+}[25c]).

For Ag sulfonates, when the lateral breadth of the aryl appendage exceeds the limit beyond which a simple layered solid is possible, the structure is able to adapt to maintain an extended framework. This adaptation is manifested as the formation of additional Lewis base contacts to the Ag centers, both ancillary solvent and π-bonding to the aryl groups, which necessitate shifts in the Ag−sulfonate bonding interactions. There is no regular geometry associated with the Ag center. In **1**−**4**, the Ag centers are observed as both six-coordinate octahedral and trigonal prismatic, five-coordinate trigonal bipyramidal and square pyramidal, as well as distorted variations of these. More important than the specific geometry is the fact that the geometry of the metal center is adaptable. As a complement, the bridging mode of the sulfonate group is highly varied; it ranges from μ^6 and μ^5 in the type 1 structures (**1** and **2**) to μ^4 in the type 2 structure (**3a**), to μ^3 in the type 3 structures (**3** and **4**). The observation that **3a**, the hemihydrate of the 1-naphthyl derivative, efficiently converts to **3** upon heating affirms the adaptable nature of the silver sulfonate backbone. This structural dynamic has led us to draw an analogy to phosphonate chemistry where, if a phosphonate group could be considered as nailing an organic group to an inorganic layer, the sulfonate group would be attaching the organic moiety with a ball of Velcro.[26] The use of multiple weak bonding interactions allows these solids to reminimize in a facile manner so that the cost of dynamic behavior is not loss of order.

Functional layered solids are known for systems sustained by stronger bonding (e.g., aluminosilicate clays) but equally for those sustained by weaker interactions (e.g., cell membranes). In the latter case, weaker bonding and enhanced dynamic behavior are critical for, rather than an impediment to, the function of the solid (i.e., the fluid mosaic model). Thus, the significance of this class of silver sulfonate (and similar solids) cannot be seen if regarded simply as less stable analogues of metal phosphonates or other rigid frameworks; rather, they should be regarded as complements to these networks which may possess novel functions.

Conclusions

A systematic study of a family of silver sulfonate solids has been presented which shows that there is a critical lateral breadth for a pendant R group (ca. 6.4 Å) beyond which a simple (type 1) layered solid is possible. Beyond this point, the network must adapt by either the incorporation of additional Lewis base (type 2) of by formation of Ag−π interactions with pendant arenes (type 3). The breadth of the sulfonate group itself does not preclude the formation of stacked arene arrays and the role of π interactions in these

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solids has been discussed. A two-component approach to functional solids incorporating π-stacked arene arrays offers potential advantages, with respect to ordering and ultimately design, over more typically employed three component systems.

Importantly, the networks formed are not static and can adapt to retain a stable continuous form. Typically, when one refers to "hybrid" inorganic−organic solids, the nomenclature is meant to depict a rigid inorganic scaffolding to which structural variation may be imparted via organic pendants. In this case, the descriptor is particularly appropriate as, beyond describing the elemental composition, the Ag sulfonate interactions sustaining the framework (mostly 2.3−2.6 Å) are truly intermediate to, for example, metal oxide bonding, in a wholly inorganic solid, and hydrogen bonding, in a wholly organic solid. This enables the framework to be adaptable in structure.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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