A layered silver sulfonate incorporating nine-coordinate Ag^I in a hexagonal grid

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Silver benzenesulfonate is an example of a layered 'inorgano–organic' solid where the inorganic component is comprised of sulfonate-bridged silver(I) centers and the organic moiety is a phenyl group; the resulting network of silver ions forms a planar hexagonal array incorporating a previously unobserved six-fold metal-bridging mode for the sulfonate ion.

Currently, there are numerous well studied examples of 'inorgano–organic' lamellar solids.[1] This term is used to describe layered solids containing a planar backbone, comprised solely of inorganic elements, which also incorporate organic moieties as covalently bound pendant groups. Organic derivatization of inorganic layers couples the skeletal rigidity of the inorganic lamellae with the structural diversity inherent to organic functionalization. The result can be a new compound with markedly different properties (solubility, intercalation, exfoliation) from the parent inorganic backbone. The principal sub-groups of complexes in this class include metal phosphonates,[2] and perovskite halides.[3] Whereas examples of lamellar networks with phosphonate groups abound,[2] lamellar 'inorgano–organic' systems employing sulfonates are virtually unknown.[4,5] Silver benzenesulfonate is a two-dimensional network from which the phenyl groups protrude from both sides. The resulting phenyl–silver(sulfonate)–phenyl trilayer then assembles by dispersive forces between the phenyl groups. The network of Ag–Ag bonds forms a nearly perfect hexagonal grid. Each Ag^I in the structure has nine atoms at less than van der Waals contact distances and each SO$_3$ group caps six different Ag^I centers. The observed η^6-coordination mode of the sulfonate group to metals is unprecedented.

Silver benzenesulfonate **1** may be generated by the addition of aqueous sodium benzenesulfonate to a solution of AgNO$_3$ in water. Concentration of this solution results in the precipitation of **1**, in very good yields, as a light gray solid.‡ Elemental analyses confirmed a 1:1 stoichiometry of Ag^I to benzenesulfonate. Diffusion of isopropyl ether into a MeOH solution of **1** resulted in the growth of extremely thin plate-like crystals suitable for an X-ray diffraction analysis.§

Silver benzenesulfonate forms a two-dimensional infinite array wherein the Ag^I centers are bridged by SO$_3$ groups to form layers and the phenyl moieties of the sulfonates protrude into the interlayer region (Fig. 1).[6] The asymmetric unit contains a single disordered silver benzenesulfonate unit. The interlayer distance, defined as the perpendicular distance between the layers of Ag^I ions, is 15.23(2) Å. The thickness of an individual lamella, defined as the region containing solely the Ag, S and O atoms, is 3.87(2) Å. The difference between these two values, 11.36(2) Å, constitutes the gallery height in the complex. Adjacent layers in the complex are slightly offset by 1.32(2) Å in a direction between the *a* and *b* axes. The benzenesulfonate has its major axis oriented *ca.* 14° off the normal to the plane containing the silver atoms. The interlayer phenyl group is

disordered between two positions situated 81° apart about the major axis of the ring. NMR shows that at room temperature this disorder is dynamic.[7] The nearest distance between phenyl groups is 5.20(1) Å.[8] The structure is representative of the bulk phase as PXRD data was indexed to the same unit cell.[9]

The structure of **1** is extremely unusual both with respect to the coordination of the Ag^I ions and the mode of coordination of the sulfonate groups to the metals. Each Ag^I ion is nine-coordinate (Fig. 2) with a coordination sphere comprised of six sulfonate oxygen atoms [from six different sulfonate groups, Ag–O distances range from 2.42(1)–2.56(1) Å] and three bonds to other Ag ions [Ag–Ag 2.915(1) Å].[10] The geometry at each Ag^I may be considered as a distorted octahedron of oxygen donors, with three silver donors approaching in a trigonal plane bisecting the octahedron.[11] Congruently, the SO$_3$ groups must form bonds to six different Ag ions, each oxygen coordinating to two silver centres.[12] The six Ag–O distances span a smaller range than observed for the five Ag–O interactions in AgOTs [2.391(6)–2.700(3) Å].[4] Interestingly, the network of Ag–Ag
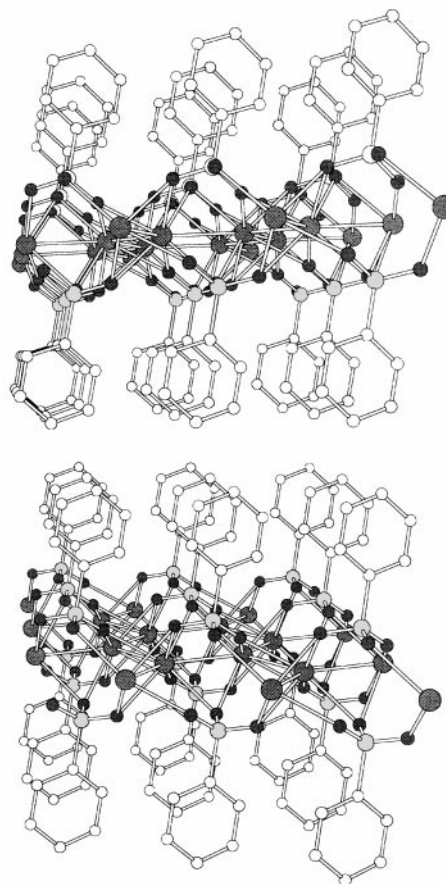

Fig. 1 Structure of **1** showing the overall lamellar network with phenyl groups protruding into the interlayer region. Disorder has been removed for clarity.

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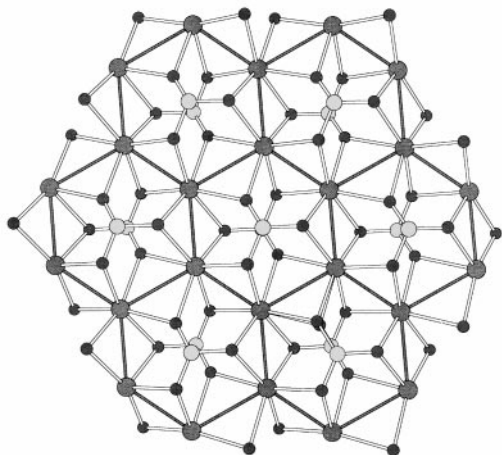
Fig. 2 View down onto a single lamella of the structure of **1** with phenyl rings and disordered oxygen atoms removed for clarity. Silver atoms: large circles, sulfur atoms: medium shaded circles, oxygen atoms: small circles. Note the hexagonal arrangement of the silver(I) centers and the nonavalent coordination mode, and the μ_6-sulfonate groups.

interactions forms a nearly perfect hexagonal grid reminiscent of graphite.[13,14] The hexagons are completely planar with the observed angles around the Ag periphery averaging to 120.0(1)° [the three different angles are 114.83(3), 116.12(3) and 128.79(3)°]. Each Ag hexagon is capped by an SO_3 group and the mean distance across a hexagon is 6.01(30) Å. The solely inorganic component of this structure, the $AgSO_3$ lamellae, possess almost hexagonal symmetry. The phenyl groups, however, cannot adopt this high symmetry necessitating a distortion in the overall structure to a triclinic, albeit pseudo-hexagonal, space group.[15] DSC–TGA analyses of a sample of silver benzenesulfonate revealed the sample to be completely stable to 139.7 °C at which point a reversible endothermic transition was observed in the DSC. A second non-reversible endothermic transition was observed at 198.2 °C followed by an exothermic transition with an onset temperature of 253.4 °C corresponding to loss of 43.9% of sample weight.

Silver(I) is a notoriously pliant ion with respect to its coordination sphere. Coordination numbers ranging from two to four are common[10] but examples of five- and six-coordinate Ag^I have also been observed.[16] Even in this light, the structure of **1** is remarkable. Silver benzenesulfonate possesses a fascinating structure both from the macroscopic viewpoint, the lamellar motif, and from the microscopic perspective, the highly unusual nine-coordinate Ag^I as well as a novel six-fold bridging mode for a coordinating sulfonate. The question of structure-directing effects (Ag–O *versus* Ag–Ag) in the silver sulfonate family will be resolved upon consideration of other derivatives.

Notes and references

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