Anion pillaring of layered silver coordination networks

George K. H. Shimizu,*† Gary D. Enright, Chris I. Ratcliffe and John A. Ripmeester

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada. E-mail: gshimizu@ucalgary.ca

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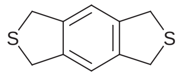
Silver *p*-toluenesulfonate and the dithia ligand, 1 form a layered framework where the sulfonate anion serves to 'pillar' the network, as in clay-like solids, allowing for inclusion of benzene.

The generation of microporous metal-organic networks, patterned after naturally occurring solids, is a burgeoning field of research.[1,2] Relative to their wholly inorganic cousins, these 'mineralomimetic'[3] coordination networks offer the promise of greater functionality, inherent to the incorporation of organic moieties, generally at the cost of the thermal or chemical stability of the framework.

Clays are a family of layered compounds, many of which have reactive sites in the interlayer space suitable for acid catalysis and anion exchange. A common strategy to enhance the efficacy of clays is to 'pillar' the interlayer region with a large ion, thereby offering greater access to the interlayer.[4] We recently reported the self-assembly of $AgBF_4$ and the dithia ligand, **1**, to yield an infinite layered network, structurally analogous to an anionic clay, which swells to different degrees depending on the solvent.[5] As part of our ongoing study of how closely this family resembles clay-like materials, we present a new complex, formed between **1** and silver *p*-toluenesulfonate, AgOTs. This complex maintains the previously observed lamellar motif but also incorporates a coordinating anion to 'pillar' the interlayer region and allow for selective inclusion of benzene.



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AgOTs in MeCN was added to a MeCN solution of **1** in a 1 : 1 molar ratio. Diffusion of benzene into this solution gave colourless, plate-like crystals of $\{Ag(\mathbf{1})OTs\cdot0.5C_6H_6\}_\infty$, **2**, suitable for an X-ray analysis.‡ The structure of **2** (Fig. 1), reveals the formation of an infinite two-dimensional array consisting of cationic Ag(**1**) layers reinforced by a coordinating *p*-toluenesulfonate anion. The geometry at the metal centre is a distorted trigonal monopyramid comprised of three thioether donors, where the Ag–S angles sum to 355°, and a sulfonate oxygen (Ag–S1 = 2.5347(6) Å, Ag–S2a = 2.6077(7) Å, Ag–S2b = 2.5739(6) Å, Ag–O3 = 2.574(2) Å). Each molecule of **1** is asymmetrically ligated to three different silver ions (Fig. 2). That is, the sulfur donor on one side of the ligand coordinates to two silver ions while the sulfur atom on the other side of the ligand bonds to only one, consistent with the Ag(**1**)BF_4 complexes.[5] However, in contrast to the BF_4^- complex, the Ag(**1**) network in **2** does not form perfectly flat layers. In complex **2**, a corrugated motif is adopted (Fig. 2), as necessitated by the distorted trigonal geometry at the Ag^I centre. The dihedral angle formed by the central benzene rings of adjacent molecules of **1** is 48.50(9)°. In **2**, ligand **1** is observed solely in the *anti* conformation, with respect to the orientation of the sulfur donors in the slightly puckered pentagonal rings.

The toluenesulfonate anion is coordinated to the silver ions and orients itself at an angle of 24.2(1)° to the mean lamellar plane. The interlayer distance in **2** is 11.230(1) Å (*cf.* 10.085(1) Å in the BF_4 salt), defined as the perpendicular distance between Ag^I ions. Thus, the anion serves as a pillar to prop the lamellae apart and allow for inclusion of 0.5 molecules of benzene per asymmetric unit. This structure is analogous to that of a pillared anionic clay. The crystals readily lose the benzene upon standing but DSC/TGA reveals the desolvated network to be thermally stable to 190 °C, similar to the BF_4^- complexes.[5]

The ligand–ligand separation, measured perpendicular to the plane of the central benzene ring in **2**, is 3.940(1) Å. The maximum breadth of the *p*-toluenesulfonate ion, taken as the spherical diameter of the SO_3 group, was calculated as 4.92 Å.[6] Although the average spherical diameter of the anion is larger than the inter-ligand distance, the anions are not aligned directly adjacent to each other. For comparison, in the complex, $\{Ag(\mathbf{1})(MeCN)_2(BF_4)\}_\infty$, the inter-ligand distance[5] is 3.826(1) Å and the ionic diameter of a BF_4 ion is 4.79 Å.[6] Thus, in **2**, the lamellae have expanded to incorporate a slightly larger anion.

Interestingly, if one compares the metal centres in this structure with the two previously observed Ag(**1**)(solv)BF_4 (solv = $(MeCN)_2$ or PhCN) structures, one observes a different

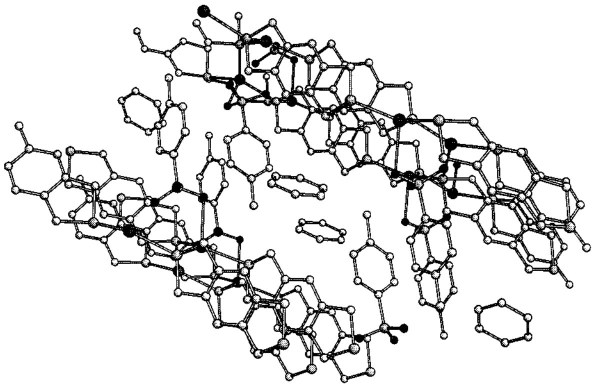

Fig. 1 View of the lamellar network formed by the complex, $\{Ag(\mathbf{1})OTs\cdot0.5C_6H_6\}_\infty$, showing the 'pillaring' effect of the OTs anions and the inclusion of benzene in the resultant void space.

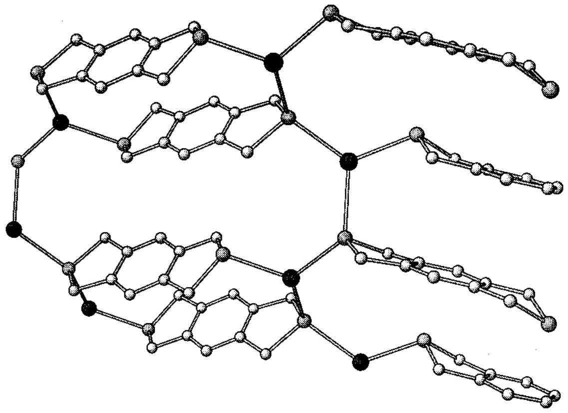

Fig. 2 View of the corrugated structure of the cationic Ag(**1**) layers and the distorted trigonal geometry at Ag^I.

coordination geometry in each case, a distorted trigonal monopyramid in the present case, and trigonal bipyramidal and near perfect trigonal monopyramidal for the MeCN and PhCN adducts of the $AgBF_4$ compounds, respectively. However, in each case, the overall motif adopted is that of a layered network. Silver(I) is well known to have a particularly pliant coordination sphere, as illustrated by these and other examples.[7] A number of studies exist where completely different structures are observed with silver(I) and a given ligand by varying the anion.[8] The tendency of the Ag(**1**)X system, where X is a monovalent anion, to adopt lamellar networks represents the manifestation of a structural constraint built into the dithia ligand, **1**, and the operation of a 'Lamellar Chelate Effect'.[5]

An attempt was made to generate compound **2** *via* anion exchange from the compound $\{Ag(\mathbf{1})(MeCN)_2BF_4\}_\infty$. The BF_4 salt was stirred, as a heterogeneous suspension, in a 0.1 M aqueous solution of sodium *p*-toluenesulfonate for 30 minutes. The solid was filtered off, washed with copious amounts of water, and analyzed by solid-state ^{13}C CP MAS NMR. The spectrum revealed a *ca.* 20% exchange of OTs for BF_4. This process was repeated twice more with the same solution resulting in a *ca.* 40% exchange. A likely scenario, consistent with clay-like behaviour, is that exchange occurs primarily around the periphery of the layered structure thus rendering the core sites inaccessible. Experiments in which exchanges with successively larger anions, also incorporating catalytic amounts of 'swelling' solvents, are in progress.

Notes and references

† Current address: Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4, Canada.

‡ Crystal data for **2**: $C_{20}H_{20}AgS_3O_3$, $M = 512.42$, monoclinic, space group $P2_1/n$, $a = 11.8117(5)$, $b = 7.8813(5)$, $c = 22.3316(10)$ Å, $\beta = 102.245(5)°$, $V = 2031.6(2)$ Å^3, $Z = 4$, $D_c = 1.675$ g cm^{-3}, μ(Mo-Kα) = 1.32 mm^{-1}, crystal size 0.04 × 0.20 × 0.20 mm. Data were collected with a Siemens SMART CCD diffractometer using graphite-monochromatized Mo-Kα radiation. A total of 22941 reflections ($3 < 2\theta/° < 57.4$) were processed of which 5244 were unique and 4171 were considered significant with $I_{net} > 2.5\sigma(I_{net})$. The structure was solved by direct methods and refined using the NRCVAX suite of programs.[9] Final residuals were $R = 0.029$ and $R_w = 0.028$ (GOF = 1.92) for 324 parameters. CCDC 182/1159.

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5 G. K. H. Shimizu, G. E. Enright, C. I. Ratcliffe, J. A. Ripmeester and D. D. M. Wayner, *Angew. Chem.*, 1998, **110**, 1510, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1407. As a control, the monothia derivative of **1** was synthesized and complexation with silver(I) was studied. Without the enhanced stability provided by the layer formation, neither the AgOTs nor $AgBF_4$ salts formed stable complexes; in fact, the $AgBF_4$ salt underwent immediate photolysis and decomposition.

6 A value for the ionic volumes was calculated using Moldraw software. A qualitative value of the ionic diameter was determined by assuming a spherical ion and doubling the value of the radius from $V = \frac{4}{3}\pi r^3$. To obtain the spherical radius of the SO_3 group of the *p*-toluenesulfonate, an SO_4 group was employed.

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