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Anion influence on co-ordination polymers of Ag(I) with 1,4-dithiacyclohexane †

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The reaction of Ag(I) salts with 1,4-dithiane has produced several interesting co-ordination polymers, the structures of which vary significantly with anion. Compounds with metal : ligand ratios of 2 : 3, 1 : 1 and 2 : 1 have been produced and are discussed in the context of the influence of the anion on structural order. The recurrent topological feature of the three 2 : 3 adducts, [$\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3][BF_4]_2\}_\infty$, $\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3][CF_3SO_3]_2\}_\infty$ and $\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3][NO_3]_2\}_\infty$], is a $\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3]^{2+}\}_\infty$ honeycomb sheet of (6,3) topology. The principal differences between these sheets lie in the size and symmetry of the constituent hexagonal units, the packing of the sheets being governed by the anion. For the polymers with $[BF_4^-]$ and $[CF_3SO_3^-]$ anions, parallel sheets align such that the anions, which complete the four-fold co-ordination of the Ag(I) centres, are located in the hexagonal cavities of adjacent sheets; for the polymers with $[NO_3^-]$ anions, however, the sheets are perpendicularly interpenetrated. The structures of the three 1 : 1 adducts, $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][BF_4]\}_\infty$, $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][SCN]\}_\infty$ and $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][NO_2]\}_\infty$, are all based on the same building block, a $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})]^+\}_\infty$ chain of alternating metal and organic fragments. They differ, however, in the construction of their extended networks, which are anion dependent. All three anions bridge four-co-ordinate Ag(I) centres to form $\{[Ag(\mu\text{-}X)]^-\}_\infty$ chains which criss-cross the $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})]^+\}_\infty$ chains. In the cases where $[BF_4^-]$ and $[SCN^-]$ anions are used, the interlinked chains generate 2-D sheets with (4,4) topology which space fill either by perpendicular two-fold interpenetration to give a 3-D $CdSO_4$ net (for the $[BF_4^-]$ complex) or by parallel stacking (for the $[SCN^-]$ complex). In contrast, when $[NO_2^-]$ acts as the anion, the interlinked chains give a 3-D diamondoid network. The 2 : 1 polymer, $\{[Ag_2(\mu_4\text{-}1,4\text{-dithiane})][SO_4]\cdot H_2O\}_\infty$, has an unprecedented 3-D architecture in which inorganic pillars brace metal–organic sheets. The metal–organic sheets comprise Ag(I) centres linked by μ_2-S, μ_2-S′ bridging 1,4-dithiane ligands and the inorganic pillars comprise Ag(I) centres connected by μ_1-O (μ_1-O is used in this instance to describe an oxygen atom bound to only one silver atom), μ_1-O′, μ_2-O″-bridging sulfate anions and μ_2-O-bridging H_2O molecules.

Introduction

The design of functional materials through the controlled placement of components in three-dimensional systems is currently of great interest.[1–4] The use of rigid organic linkers to separate metal ions in three-dimensional matrices has led to metal–organic hybrid materials with precise positioning of desired moieties and hence to functional frameworks.[3,5–11] Many factors influence the architectural topology of these co-ordination polymers. Although the roles of metal cation, organic bridging ligand and metal : ligand stoichiometry in co-ordination polymer production are well documented,[1–3,12] those of anion [12–18] and solvent [18–22] are less well understood.

The influence of anion on the network structures formed between Ag(I) centres and either 3,6-bis(pyridin-4-yl)-1,2,4,5-tetrazine (4,4′-pytz),[13] sebaconitrile [$NC(CH_2)_8CN$] (sebn) [14] or 3,3′-dicyanodiphenylethyne (3,3′-dcpa) [16] has been probed using diverse salts. The basic building block of the polymers formed by 4,4′-pytz with Ag(I) salts is a linear chain of alternating metal and organic connecting units.[13] With $AgBF_4$ and $AgPF_6$, the elaboration of the structure involves the creation of a double-chain arrangement. With $AgNO_3$, however, the extended structure adopts a helical staircase motif. Thus, whereas $[BF_4^-]$ and $[PF_6^-]$ act as weakly co-ordinating unidentate ligands (Ag–F 3.02 and 2.87 Å, respectively), $[NO_3^-]$ acts a weakly co-ordinating bridging bidentate ligand (Ag–O 2.79 Å), its D_{3h} symmetry conferring a trigonal symmetry to the network construction in which the chains are aligned at an angle of 60° with respect to each other to generate the helical staircase.[13] The reactions of sebn with various Ag(I) salts afford [14] either the polymers $\{[Ag(\mu_2\text{-sebn})_2][X]\}_\infty$ incorporating eight-fold interpenetrated diamondoid-type ($X = [BF_4^-]$ or $[ClO_4^-]$), four-fold interpenetrated $SrAl_2$-type ($X = [PF_6^-]$ or $[AsF_6^-]$) or infinitely catenated 2-D sheets ($X = [SbF_6^-]$ or $[CF_3SO_3^-]$) or the polymers $\{[Ag(\mu_2\text{-sebn})][X]\}_\infty$ having 1-D chain structures. In all the complexes of sebn, the anions are considered to be non-co-ordinating and their size is the key factor in the control over network structure. Treatment of Ag(I) salts with 3,3′-dcpa yields polymers, the structures of which are influenced by both the co-ordinating ability and the size of the anion.[16] Of the five anions studied, $[CF_3SO_3^-]$, $[EF_6^-]$ (E = P, As or Sb) and $[ClO_4^-]$, only $[CF_3SO_3^-]$ co-ordinates the Ag(I) centres and the others remain non-co-ordinating. In the triflate products, $\{[Ag(\mu_2\text{-}3,3'\text{-dcpa})(CF_3SO_3)]\}_\infty$ and $\{[Ag_2(3,3'\text{-dcpa})(CF_3SO_3)_2]\}_\infty$, both anion and 3,3′-dcpa bridge Ag(I) centres

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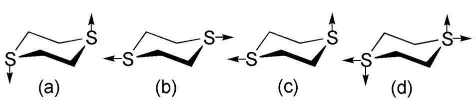
† Electronic supplementary information (ESI) available: selected interatomic distances and angles for polymers **2**, **3** and **7**–**9**; diagrammatic representations of the Ag(I) centres in **1**–**4**, **7** and **8**. See http://www.rsc.org/suppdata/dt/b1/b100635p/

to give 2-D sheet structures. In the other polymers, $\{[Ag(3,3'\text{-dcpa})_2][EF_6]\}_\infty$ and $\{[Ag(\mu_2\text{-}3,3'\text{-dcpa})_2][ClO_4]\cdot H_2O\}_\infty$, the extended structures – for $[EF_6^-]$ two-fold interpenetrated sheets and for $[ClO_4^-]$ eight-fold interpenetrated diamondoid networks – are propagated by Ag(I)–3,3′-dcpa contacts only. The difference in behaviour between $[EF_6^-]$ and $[ClO_4^-]$ may be attributed to anion symmetry.

We report herein the results of a systematic study of the role of the anion in the construction of co-ordination polymers of Ag(I) with 1,4-dithiacyclohexane (1,4-dithiane). 1,4-Dithiane is a versatile *S*-donor ligand, the co-ordination chemistry of which can be compared with that of the *N*-donor ligands, pyrazine [23,24] and piperazine.[24] The versatility of 1,4-dithiane can be ascribed to three key features. Firstly, the saturated six-membered ring can adopt either a chair or boat conformation. Secondly, each of the two sulfur atoms has two lone pairs, giving the possibility of one-, two-, three- or four-fold connectivity. Thirdly, by utilising different combinations of axially and equatorially located metal centres, the two- and three-fold connectivities can have different stereochemical arrangements.

1,4-Dithiane normally adopts the chair conformation and behaves as a bidentate bridging ligand adopting either axial–axial [*ax–ax*; Scheme 1(a)] or equatorial–equatorial [*eq–eq*; Scheme 1(b)] arrangements. The structures of only two extended networks based on 1,4-dithiane have been reported previously.[25,26] Of these, one is the Ag(I) polymer, $[\{Ag(CF_3CO_2)\}(\mu_2\text{-}1,4\text{-dithiane})]_\infty$,[25] and the other is an indium-based polymer, $[\{In(CH_3)_3\}(\mu\text{-}1,4\text{-dithiane})]_\infty$.[26] Whereas 1,4-dithiane links the metal centres in the former through an *ax–ax* co-ordination mode [Scheme 1(a); Ag · · · Ag 6.39 Å], it adopts an *eq–eq* conformation in the latter [Scheme 1(b); In · · · In 8.84 Å]. Two discrete molecular 1,4-dithiane complexes have also been structurally characterised. The first is a Cu(I) dimer, $[\{Cu([9]aneS_3)\}_2(\mu\text{-}1,4\text{-dithiane})][PF_6]_2$, in which the 1,4-dithiane bridge adopts an *ax–ax* co-ordination mode [Scheme 1(a); Cu · · · Cu 6.10 Å].[27] The second is a triosmium cluster $[Os_3(CO)_{10}(1,4\text{-dithiane})]$, with a chelating 1,4-dithiane ligand,[28] in which the 1,4-dithiane molecule adopts the boat conformation. This is the only such example; the chair conformation being adopted by the bridging 1,4-dithiane molecules in the above Ag(I), In(III) and Cu(I) complexes [25–27] and in the free ligand.[29]



Scheme 1

Other six-membered sulfur-containing heterocycles which have been used to promote co-ordination polymer formation are 1,3-dithiane and 1,3,5-trithiane. Whereas there is only one structurally characterised 1,3-dithiane complex, $\{[Hg_2(\mu_2\text{-}1,3\text{-dithiane})][NO_3]_2\}_\infty$,[30] there are several such 1,3,5-trithiane complexes.[25,31,32] Although examples are known in which the 1,3,5-trithiane acts as a tridentate bridge,[31] it more commonly acts as a bidentate bridge.[25,32] In a recent extension to our work, we have described the structures of two series of co-ordination polymers in which thioether macrocycles (*e.g.*, [12]aneS$_4$ and [16]aneS$_4$) are used as bridging ligands to connect either Cu(I) halide motifs [33] or Ag(I) centres.[34] A limited number of Ag(I)–thioether macrocyclic complexes has also been structurally characterised.[35]

Diverse Ag(I) salts with anions of varying size and co-ordination ability ($AgBF_4$, $AgCF_3SO_3$, $AgNO_3$, AgSCN, $AgNO_2$ and Ag_2SO_4) have been considered in this work. Co-ordination polymers with metal : ligand molar ratios of 2 : 3 ($\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3][X]_2\}_\infty$ [X = BF_4^-, **1**; $CF_3SO_3^-$, **2**; NO_3^-, **3**]), 1 : 1 ($\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][X]\}_\infty$ [X = BF_4^-, **4**; $CF_3SO_3^-$, **5**; NO_3^-, **6**; SCN^-, **7**; NO_2^-, **8**]) and of 2 : 1 ($\{[Ag_2(1,4\text{-dithiane})][SO_4]\cdot H_2O\}_\infty$, **9**) have been synthesised and characterised. Structural data have been obtained for compounds **1**–**4** and **7**–**9**. The structures of **1** and **4** have already been communicated.[36] They are included, however, in this more comprehensive report to aid comparison with the other structures discussed here, **2**, **3** and **7**–**9**, and with that of $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][CF_3CO_2]\}_\infty$ **10** described by Kellogg *et al.*[25]

Results and discussion

Treatment of 1,4-dithiane in CH_2Cl_2 with $AgBF_4$ in MeOH gave white insoluble powders of composition $\{[Ag_2(1,4\text{-dithiane})_3][BF_4]_2\}_\infty$ **1** and $\{[Ag(1,4\text{-dithiane})][BF_4]\}_\infty$ **4** depending on reactant stoichiometry. The corresponding reactions of 1,4-dithiane with $AgCF_3SO_3$ and $AgNO_3$ gave similarly insoluble powders of $\{[Ag_2(1,4\text{-dithiane})_3][CF_3SO_3]_2\}_\infty$ **2** and $\{[Ag(1,4\text{-dithiane})][CF_3SO_3]\}_\infty$ **5** and of $\{[Ag_2(1,4\text{-dithiane})_3][NO_3]_2\}_\infty$ **3** and $\{[Ag(1,4\text{-dithiane})][NO_3]\}_\infty$ **6**, respectively.

Owing to the poor solubility of AgSCN, $AgNO_2$ and Ag_2SO_4 in MeOH, it was necessary to use aqueous media for these salts. To provide miscibility with the aqueous solutions, the 1,4-dithiane was dissolved in acetone. Despite the use of a wide range of reagent stoichiometries, all three Ag(I) salts formed only single products: white insoluble powders of composition $\{[Ag(1,4\text{-dithiane})][SCN]\}_\infty$ **7**, $\{[Ag(1,4\text{-dithiane})][NO_2]\}_\infty$ **8** and $\{[Ag_2(1,4\text{-dithiane})][SO_4]\cdot H_2O\}_\infty$ **9**, respectively.

The powders were characterised by elemental (C, H, N) analysis, infrared spectroscopy and powder X-ray diffraction. Where possible (**1**–**4**, **7**–**9**), single crystals were grown by layered solvent diffusion of solutions of the Ag(I) salt and 1,4-dithiane. The same solvents were used for bulk sample preparation and crystal growth. Single-crystal X-ray diffraction studies revealed the extended structures of the co-ordination polymers. Powder X-ray methods were used to confirm that the single crystals were representative of the bulk samples. Selected structural parameters (interatomic distances and angles within the Ag(I) co-ordination spheres in **2**, **3** and **7**–**9**) are quoted in the supplementary data. Diagrammatic representations of the Ag(I) centres in **1**–**4**, **7** and **8** are also included in the supplementary data (ESI).

Structures of the 2 : 3 polymers, 1–3

The structure of **1** has been described in detail in a previous communication;[36] a brief resumé follows. The Ag(I) centre, which is located on a crystallographic three-fold symmetry axis, is co-ordinated by three sulfur atoms from separate 1,4-dithiane ligands [Ag · · · S 2.5027(8) Å] and a fluorine of a $[BF_4^-]$ anion [Ag · · · F 2.637(3) Å] in an approximately tetrahedral manner. The 1,4-dithiane ligands bridge Ag(I) centres to give a two-dimensional sheet of (6,3) topology [Fig. 1(a)]. The three 1,4-dithiane ligands, which are crystallographically equivalent, bridge in an *ax–ax* manner [Scheme 1(a)] to afford a Ag · · · Ag separation of 6.69 Å.

In the structure of **2**, the Ag(I) centre is co-ordinated by three sulfur atoms from separate 1,4-dithiane ligands [Ag · · · S 2.4941(8), 2.4966(8), 2.5112(8) Å] and an oxygen of a $[CF_3SO_3^-]$ anion [Ag · · · O 2.553(2) Å] in an approximately tetrahedral manner. As for **1**, the 1,4-dithiane ligands bridge Ag(I) centres to give a two-dimensional sheet of (6,3) topology [Fig. 1(b)]. In this case, however, there are two crystallographically distinct 1,4-dithiane ligands, one bridging in an *ax–ax* manner [Scheme 1(a)] and the other in an *eq–eq* manner [Scheme 1(b)] with Ag · · · Ag separations of 6.59 Å and 7.84 Å, respectively.

The structure of **3** is much less symmetrical than that of either **1** or **2**. The crystallographic asymmetric unit consists of two Ag(I) centres, two $[NO_3^-]$ anions (one of which is disordered) and four 1,4-dithiane ligands (two of which are located on general positions and two on inversion centres). The

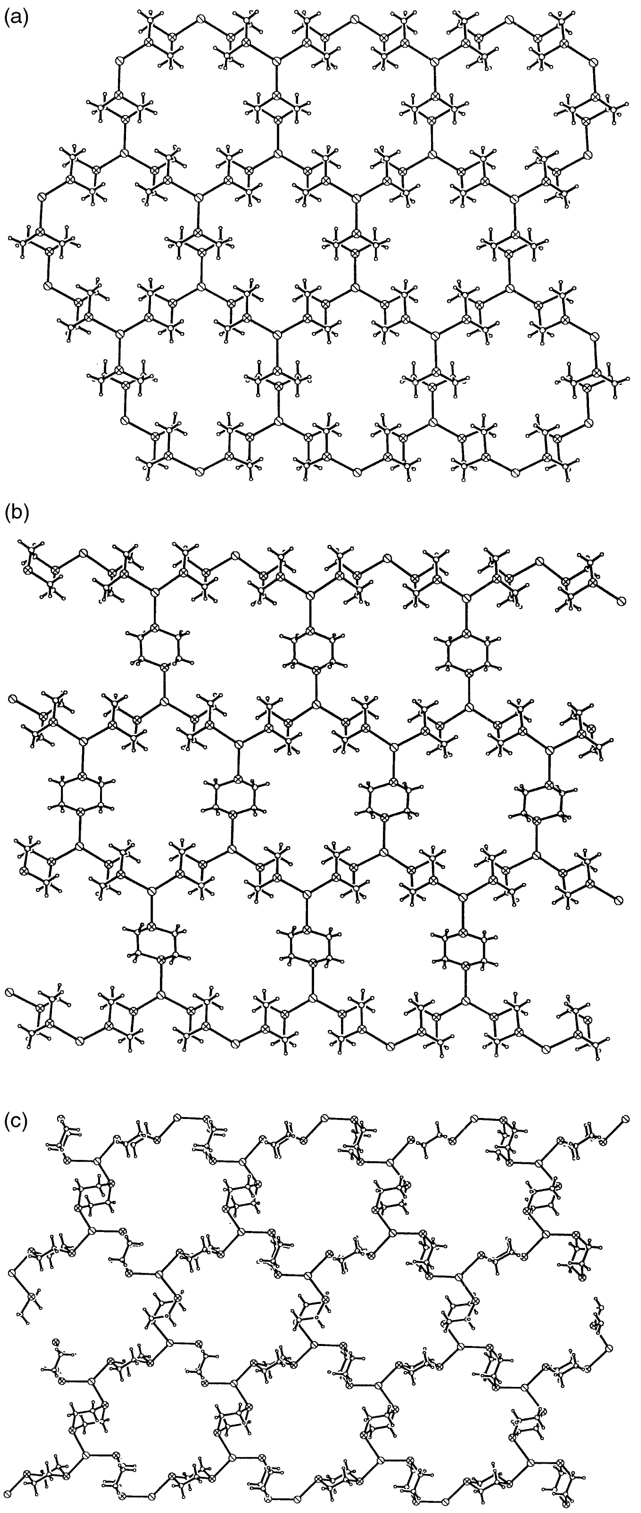


Fig. 1 Projections of the structures of (a) **1**, (b) **2** and (c) **3** showing their (6,3) two-dimensional sheet architectures. (Silver atoms hatched, sulfur cross hatched, carbon shaded. Anions omitted for clarity.)

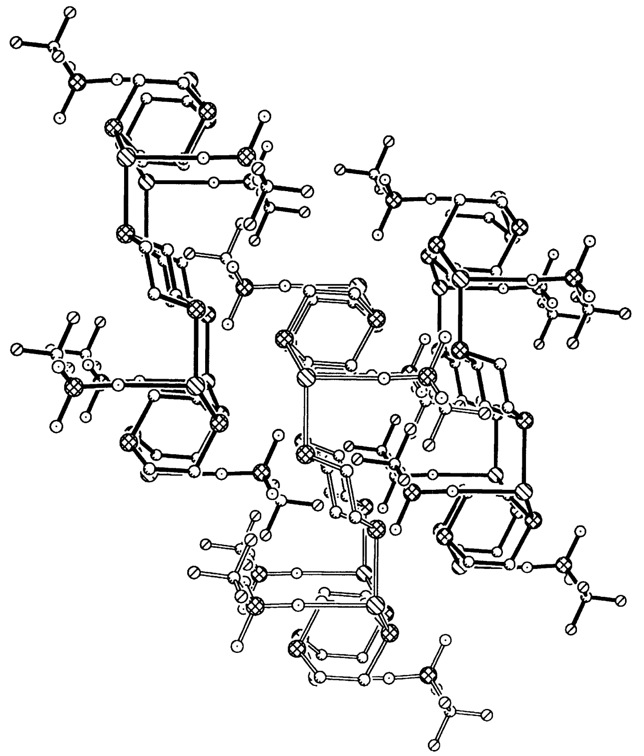


Fig. 2 View of the stacking of adjacent sheets in **2**. Note the interdigitation of $CF_3SO_3^-$ anions into adjacent sheets. The diagram is also representative of the packing in **1**. (Silver atoms left hatched, sulfur cross hatched, oxygen dotted, nitrogen right hatched, carbon shaded.)

first Ag(I) centre, which has an approximately trigonal planar geometry [$\Sigma(\angle SAgS) = 360.0°$], is ligated by three sulfur atoms [Ag···S 2.4829(12), 2.5478(11), 2.5699(11) Å] from separate 1,4-dithiane molecules. An oxygen atom of an otherwise uncoordinated [NO_3^-] is relatively close to the Ag(I) centre [Ag–O 2.661(3) Å] but does not distort the trigonal planar co-ordination geometry of the latter. The second Ag(I) centre is co-ordinated by three sulfur atoms [Ag···S 2.5145(12), 2.5409(11), 2.6302(11) Å] from separate 1,4-dithiane molecules and an oxygen atom [Ag···O 2.527(6) or 2.572(5) Å] of a disordered [NO_3^-] anion in an approximately tetrahedral manner. As for **1** and **2**, 1,4-dithiane ligands bridge Ag(I) centres to give a somewhat unsymmetrical, two-dimensional sheet of (6,3) topology [Fig. 1(c)]. The lack of symmetry arises from the presence of four crystallographically distinct 1,4-dithiane ligands, three of which bridge in an *ax–ax* manner [Scheme 1(a)] and the other in an *eq–eq* manner [Scheme 1(b)] with Ag···Ag separations of 6.54, 6.67, 6.72 Å and 7.82 Å, respectively.

Structural relationships of the (6,3) sheets in the 2 : 3 polymers

The recurrent topological feature of the structures of all three 2 : 3 adducts (**1**, **2** and **3**) is a (6,3) honeycomb sheet. The principal differences between these sheets lie in the size and symmetry of the constituent hexagonal units. In the most symmetrical case, **1**, the hexagons have crystallographic three-fold symmetry and six sides of equal length [Fig. 1(a)]. In **2**, the hexagons have inversion symmetry and four sides of one length and two of another [Fig. 1(b)]. In the least symmetrical case, **3**, there are two different types of hexagon, both of which have a similar arrangement to that in **2**; namely an *ax* : *ax* : *eq* : *ax* : *ax* : *eq* sequence of dithiane bridges [Fig. 1(c)].

The spatial arrangement of the sheets is similar for **1** and **2**, but differs markedly for **3**. In **1** and **2** the extended structure comprises layered sheets, laterally displaced to allow interdigitation of the co-ordinated anions in the cavities of the adjacent (6,3) network (Fig. 2). This gives rise to an ABCA . . . sequence of layers similar to that described recently for $\{[(Cu_2(O_2CCH_3)_4)_3(\mu_2\text{-tpt})_2]\cdot 2MeOH\}_\infty$ (tpt = 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine).[37] This stacking arrangement brings Ag(I) centres of adjacent sheets into close proximity. The closest inter-sheet Ag···Ag distances (3.47 Å for **1**; 3.64 Å for **2**) are just outside the value within which the contact can be considered to be a Ag···Ag interaction, the sum of the van der Waals radii for two Ag(I) centres being 3.44 Å.[38] In **3**, the sheets are perpendicularly interpenetrated (Fig. 3).

Consideration of the effect of the anion in **1** and **2** is thus justified. The principal differences between [BF_4^-] and

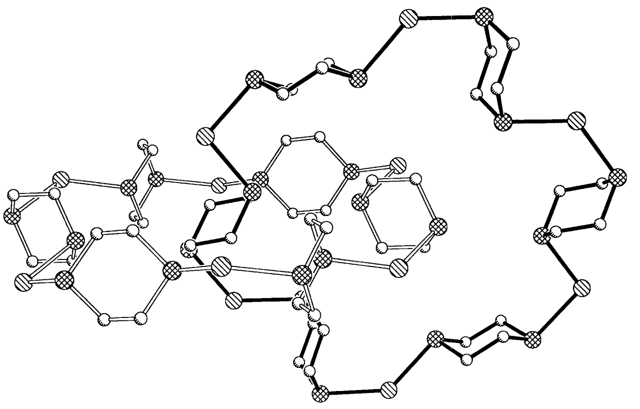


Fig. 3 View of two perpendicularly interpenetrated six-membered rings from independent (6,3) sheets contained within **3**. (Silver atoms hatched, sulfur cross hatched, carbon shaded.)

[$CF_3SO_3^-$] lie in their size (shape) and symmetry. The smaller anion [BF_4^-], which when co-ordinated has local C_{3v} symmetry, fits snugly into a hexagon constructed from six *ax–ax* co-ordinated 1,4-dithiane ligands. The larger, more cylindrical, [$CF_3SO_3^-$] anion dictates that two of the six bridging ligands are *eq–eq* co-ordinated to generate the more appropriate, rectangularly elongated, hexagonal cavity. The reason for the different packing regime in **3** is also ascribed to the size and symmetry of the anion. Although the NO_3^- anion has D_{3h} symmetry, when co-ordinated it adopts C_{2v} local symmetry. Thus, it will not sit comfortably in the hexagonal cavity, and instead, the best packing is achieved by perpendicular interpenetration of the sheets.

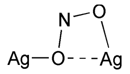
To our knowledge, this is the first time that this subtle control, where similar network structures have their relative packing altered by a change in anion size, has been demonstrated.

Structures of the 1 : 1 polymers, 4, 7 and 8

The structure of **4** has been described in detail in a previous communication;[36] a brief resumé follows. The Ag(I) centre, which is located on a 2/*m* (C_{2h}) special position, is co-ordinated by two sulfur atoms from separate 1,4-dithiane ligands [Ag···S 2.4999(11) Å] and interacts with four fluorines of two [BF_4^-] anions [Ag···F 2.886(2) Å]. If the anions are considered to be point charges, the co-ordination geometry is square-planar. The 1,4-dithiane ligands bridge Ag(I) centres in an *eq–eq* manner (Ag···Ag 7.77 Å) to give a one-dimensional chain of alternating metal and organic fragments. The chains are linked by the [BF_4^-] anions (Ag···Ag 6.94 Å) to give, not a two-dimensional sheet of (4,4) topology, but a three-dimensional architecture of doubly interpenetrated $CdSO_4$-type (Fig. 4). Similar doubly interpenetrated $CdSO_4$-type nets have been reported for {[Cu(μ_2-1,2-bis(4-pyridyl)ethane)$_2$][NO_3]$_2$}$_\infty$[39] and {[Sm(μ_2-4,4′-bipyridine-*N*,*N*′-oxide)$_2$][NO_3]$_3$·0.5H_2O}$_\infty$.[40]

The Ag(I) centre in the structure of **7** is co-ordinated by two 1,4-dithiane ligands [Ag···S 2.6096(9) Å] and two [SCN^-] anions, one *S*-ligated [Ag···S 2.574(2) Å] and the other *N*-ligated [Ag···N 2.251(5) Å], in a distorted tetrahedral arrangement. The crystallographic asymmetric unit comprises an Ag(I) centre and a [SCN^-] anion both of which are located on a mirror plane and a 1,4-dithiane centered on a point of inversion. As for **4**, the 1,4-dithiane ligands bridge Ag(I) centres to give a one-dimensional chain of alternating metal and organic fragments. In this case, however, they bridge in an *ax–ax* manner (Ag···Ag 6.65 Å) [Scheme 1(a)]. The chains are linked by linear [SCN^-] anions (Ag···Ag 6.41 Å) to give an undulating sheet of (4,4) topology (Fig. 5).

The Ag(I) centre in **8** is co-ordinated by two 1,4-dithiane ligands and two [NO_2^-] anions. Although the two 1,4-dithiane ligands, which lie across inversion centres, are crystallographically independent [Ag–S 2.5590(7), 2.5961(7) Å] there is only one crystallographically independent [NO_2^-] anion, which adopts a highly unusual co-ordination mode (Scheme 2).[41]



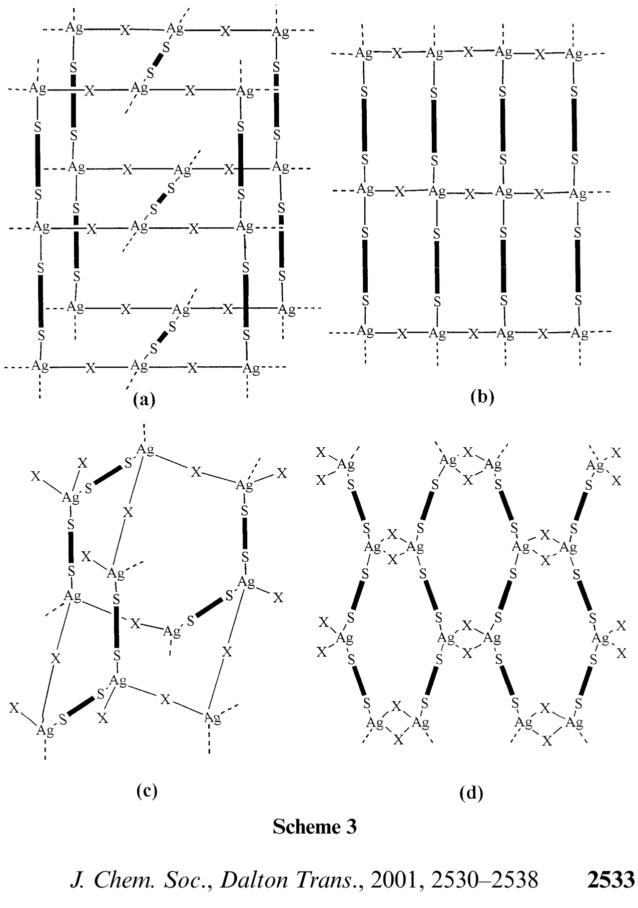
Scheme 2

It bridges two Ag(I) centres, chelating the first [Ag(1)–O(1) 2.381(2); Ag(1)–O(2) 2.615(2) Å] and co-ordinating the second [Ag(1)–O(2) 2.530(2) Å]. If the anions are considered to be point charges, the co-ordination geometry at the Ag(I) centre is therefore distorted tetrahedral. The 1,4-dithiane ligands both exhibit *ax–ax* bridging modes to link the Ag(I) centres (Ag···Ag 6.40, 6.62 Å) and to form a one-dimensional chain of alternating metal and organic fragments, as for **4** and **7**. The chains are linked by [NO_2^-] anions (Ag···Ag 5.03 Å) to give a neutral three-dimensional diamondoid polymer (Fig. 6) in which each Ag(I) centre is connected, in an approximately tetrahedral disposition, to four others by two 1,4-dithiane and two [NO_2^-] bridges.

The diamondoid structure, seen in **8**, is quite common [1,2] and detailed analyses have considered the effect of ligand length on the degree of interpenetration in these systems.[42] The short ligand lengths of the *ax–ax* 1,4-dithiane linkers (6.40, 6.62 Å) and the nitrite anions (5.03 Å) in **8** prevent interpenetration. Furthermore, solvent and/or guest inclusion is prevented by distortion and compaction of the network.

Structural relationships in the 1 : 1 polymers

Although the extended network structures of the 1 : 1 adducts **4**, **7** and **8** differ markedly, they are all based on the same building block: a chain of alternating metal and organic fragments {[Ag(μ_2-1,4-dithiane)]$^+$}$_\infty$. The differences arise from the role of the anions, which link the chains in diverse ways to give either a $CdSO_4$-type net [**4**; Scheme 3(a)], a sheet structure with



Scheme 3

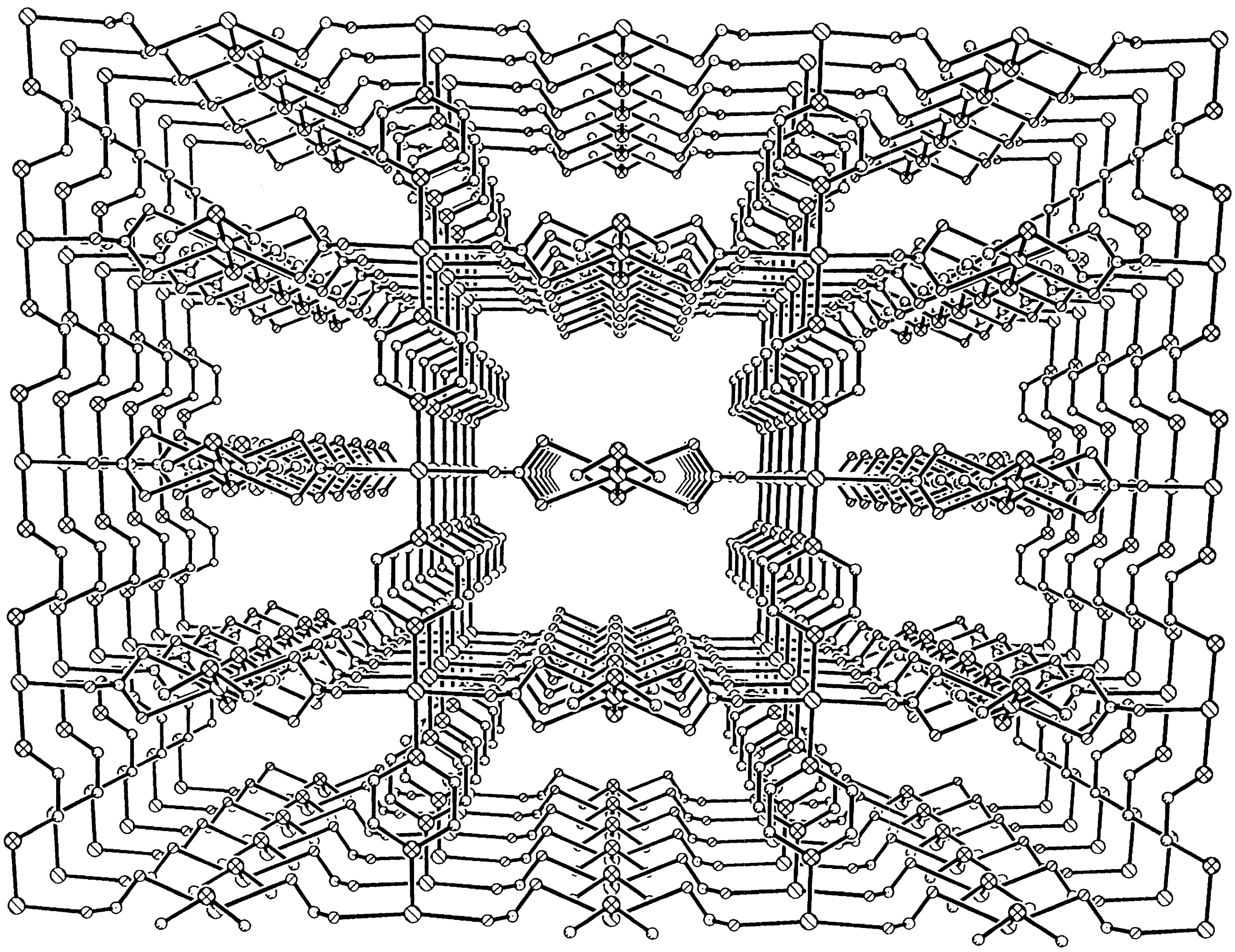


Fig. 4 A view of the doubly interpenetrated $CdSO_4$-type network structure of **4**.[36] (Silver atoms left hatched, sulfur cross hatched, fluorine right hatched, boron dotted, carbon shaded.)

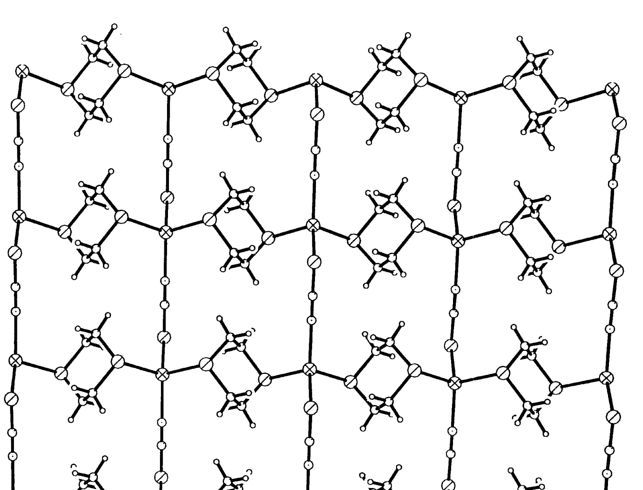


Fig. 5 A projection of the structure of **7** showing its (4,4) two-dimensional sheet architecture. (Silver cross hatched, sulfur hatched, nitrogen dotted, carbon shaded.)

(4,4) topology [**7**: Scheme 3(b)] or a diamondoid network [**8**; Scheme 3(c)].

The same building block is the basis of the structure of $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][CF_3CO_2]\}_\infty$, **10**, reported previously by Kellogg *et al.*[25] However, the extended network in **10** is different again. Chains of alternating Ag(I) centres and *ax–ax* co-

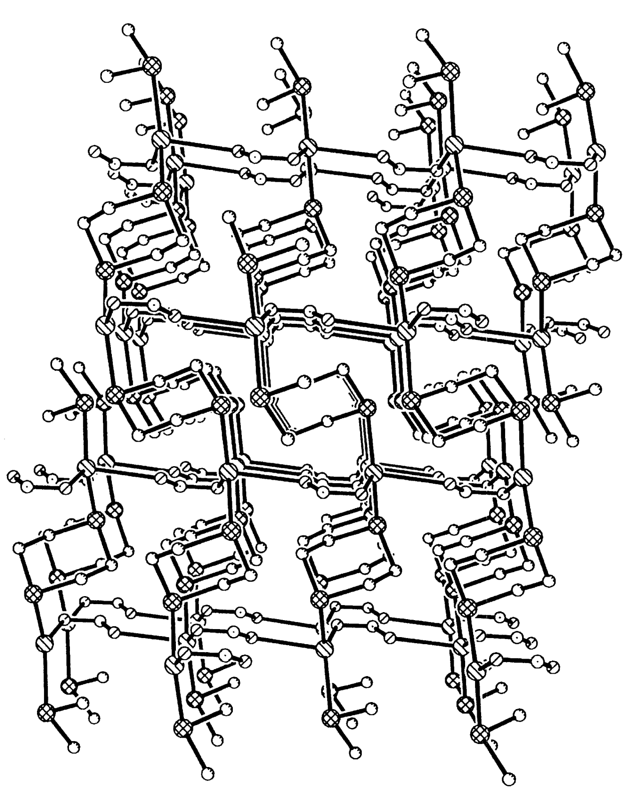


Fig. 6 The neutral diamondoid three-dimensional network of **8**. (Silver atoms left hatched, sulfur cross hatched, oxygen dotted, nitrogen right hatched, carbon shaded.)

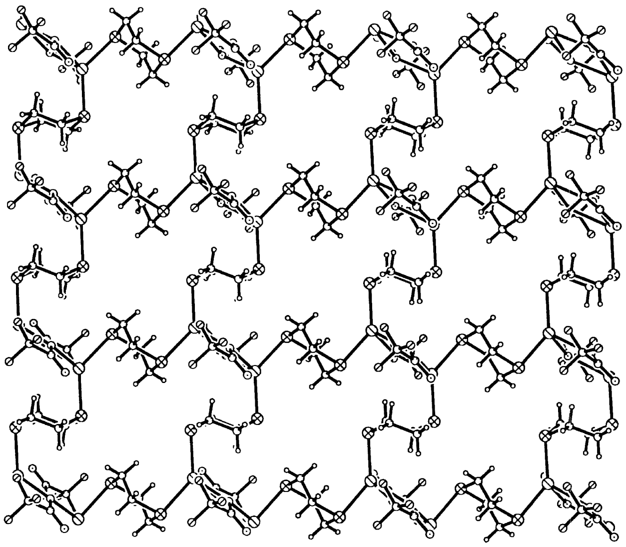


Fig. 7 A projection of the structure of **10** showing its (6,3) two-dimensional sheet architecture. (Silver left hatched, sulfur cross hatched, oxygen dotted, fluorine right hatched, carbon shaded.)

ordinated 1,4-dithiane molecules in **10** (Ag···Ag 6.38, 6.39 Å) are linked by pairs of [CF$_3$CO$_2^-$] anions to form three-connected Ag(I) centres (Ag···Ag 3.84 Å), and hence generate a distorted honeycomb sheet of (6,3) topology [Scheme 3(d); Fig. 7].

It can be seen, therefore, that the role of the anion in the construction of the co-ordination polymer is of utmost importance. In compounds **4**, **7** and **8**, the anions link tetrahedral Ag(I) centres to form {[Ag(μ-X)]$^-$}$_\infty$ chains which criss-cross {[Ag(μ$_2$-1,4-dithiane)]$^+$}$_\infty$ chains. The tetrahedral [BF$_4^-$] and linear [SCN$^-$] anions generate 2-D sheets with (4,4) topology which space-fill either by perpendicular two-fold interpenetration (to give a 3-D CdSO$_4$ net; **4**) or by parallel stacking (**7**). However, the angular [NO$_2^-$] anions link the tetrahedral Ag(I) centres to give a 3-D diamondoid network. Because of the doubly-bridging nature of the [CF$_3$CO$_2^-$] anion in **10** {[Ag(μ-X)]$^-$}$_\infty$ chains are not formed. Instead, each {[Ag(μ$_2$-1,4-dithiane)]$^+$}$_\infty$ chain is linked by an [Ag$_2$(μ-X)$_2$] bridge. Space filling is achieved by parallel stacking.

The rigid architectures of **4**, **7**, **8** and **10** have no charge. Such neutral networks are of interest because any cavities formed within the material will be free of anion and wholly available for guest inclusion. We have investigated previously this phenomenon using copper(I) halides[12,43] and pseudohalides[44] with bridging bi- and tri-dentate *N*-donor ligands. While in **7**, **8** and **10** close packing results in no guest inclusion, in **4** there is room to include a symmetry-related network and two-fold interpenetration occurs.

Structural correlation between the 2 : 3 and 1 : 1 polymers

The basic building block of the 1 : 1 polymers also occurs in the structures of **1**–**3**. Thus, **1**–**3** can be considered to comprise chains of alternating Ag(I) centres and 1,4-dithiane bridges linked by 1,4-dithiane molecules which co-ordinate in either an *ax*–*ax* [**1**; Scheme 1(a)] or an *eq*–*eq* manner [**2**, **3**; Scheme 1(b)] to generate the sheet structures.

1,4-Dithiane co-ordination to Ag(I) centres in an *ax*–*ax* manner [Scheme 1(a)] generates relatively short Ag···Ag separations (*ca.* 6.5 Å; Table 1). The alternative *eq*–*eq* bridging mode [Scheme 1(b)] gives somewhat longer Ag···Ag separations (*ca.* 7.7 Å; Table 1) and a more open structure. The more frequent occurrence of the *ax*–*ax* bridging mode might suggest that it is energetically more favourable than the *eq*–*eq* bridging mode. Indeed, the occurrence of the latter in **2**, **3** and **4** can be attributed to the fact that long Ag···Ag separations are

Table 1 Ag···Ag separations (Å) generated in compounds **1**–**4** and **7**–**10**

	Ag···Ag distances		
Compound	axial–axial	equatorial–equatorial	anion
1[a]	6.69	—	—
2	6.59	7.84	—
3	6.54, 6.67, 6.72	7.82	—
4[a]	—	7.77	6.94
7	6.65	—	6.41
8	6.40, 6.62	—	5.03
9	6.37	7.87	—
10[b]	6.38, 6.39	—	3.84

[a] Ref. 36. [b] Ref. 25.

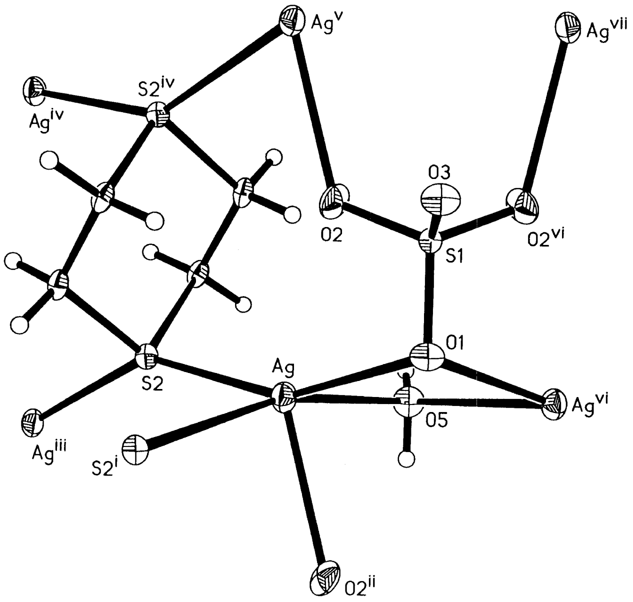


Fig. 8 Co-ordination geometries of the Ag(I) centres in **9**. (Displacement ellipsoids shown at the 50% probability level. Symmetry codes: i 1.5 − *x*, 1 − *y*, 0.5 + *z*; ii 0.5 + *x*, *y*, 0.5 − *z*; iii 1.5 − *x*, 1 − *y*, −0.5 + *z*; iv 1 − *x*, 1 − *y*, −*z*; v −0.5 + *x*, *y*, 0.5 − *z*; vi *x*, 1.5 − *y*, *z*; vii −0.5 + *x*, 1.5 − *y*, 0.5 − *z*.)

required to accommodate the [CF$_3$SO$_3^-$] anion in the hexagonal cavities of **2**, and to permit the formation of perpendicularly-interpenetrated structures in **3** and **4**.

Structure of the 2 : 1 adduct of Ag$_2$SO$_4$ and 1,4-dithiane, 9

The Ag(I) centre in **9** is co-ordinated by two 1,4-dithiane ligands, two oxygen atoms from different [SO$_4^{2-}$] anions and a water molecule in a penta-co-ordinate arrangement (Fig. 8). The 1,4-dithiane and water molecules, as well as the [SO$_4^{2-}$] anions, all act as bridging ligands to give a three-dimensional architecture of great complexity (Fig. 9). The 1,4-dithiane molecule, which lies across an inversion centre, acts as a four-connecting unit making use of all four lone pairs on the two sulfur atoms [Scheme 1(d)]. Of the four Ag···Ag separations, two (6.37 and 7.87 Å) are typical of the *ax*–*ax* and *eq*–*eq* contacts, respectively, found in **1**–**4** and **7**–**10** (Table 1). The other two, which are both *ax*–*eq* separations one through a single sulfur atom (5.14 Å), the other across the molecule (4.99 Å), have no parallels in **1**–**4** and **7**–**10** and are unprecedented. The [SO$_4^{2-}$] anion, which lies on a mirror plane, also bridges four Ag(I) centres. The two symmetry-equivalent oxygen atoms [O(2)] bind separate Ag(I) centres [Ag···O 2.429(3) Å; Ag···Ag 3.60 Å] whilst one of the two oxygen atoms on the mirror plane [O(1)] bridges another two symmetry-related Ag(I) centre [Ag···O 2.450(3) Å] to give a μ$_1$-O, μ$_1$-O′, μ$_2$-O″

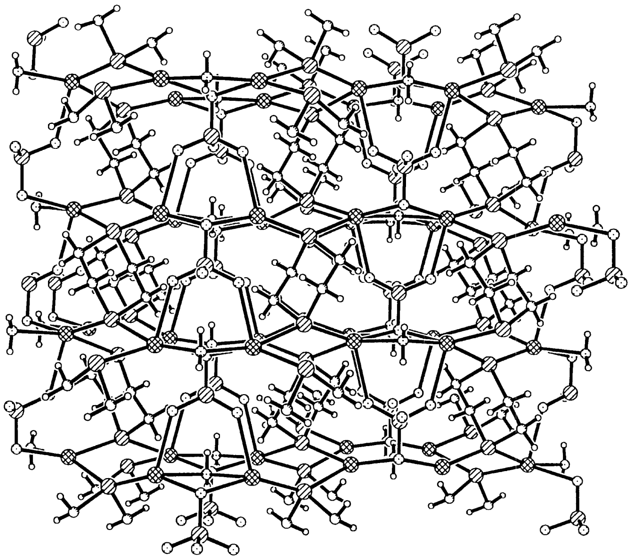


Fig. 9 A view of the three-dimensional architecture of **9**. (Silver cross hatched, sulfur hatched, oxygen dotted, carbon shaded.)

SO_4^{2-} bridging mode (Fig. 8). These latter two Ag(I) centres are also bridged by the oxygen atom [O(5)] of the water molecule. The other sulfate oxygen atom on the mirror plane [O(3)] does not bind to a Ag(I) centre, but acts as a hydrogen-bonding acceptor for two adjacent water molecules [O(5)–H(5A) 0.85 Å; O(5)···O(3) 2.719(6) Å; H(5A)···O(3) 1.89 Å; O(5)–H(5A)···O(3) 164°; O(5)–H(5B) 0.85 Å; O(5)···O(3) 2.820(7) Å; H(5B)···O(3) 2.03 Å; O(5)–H(5B)···O(3) 154°]. To our knowledge, when co-ordinated to Ag(I), the $[SO_4^{2-}]$ anion has not been observed previously to act as a bridging ligand, but simply as a terminal monodentate donor.[45] The intricacy of the extended network is easier to comprehend when considered as a combination of organic and inorganic sections. Removal of the $[SO_4^{2-}]$ anions and water molecules from the structure leaves a two-dimensional sheet of Ag(I) centres bridged by 1,4-dithiane ligands. Similarly, removal of the 1,4-dithiane ligands leaves pillars of Ag(I) centres, $[SO_4^{2-}]$ anions and water molecules. In essence, inorganic pillars brace metal–organic sheets to create the unprecedented three-dimensional architecture shown in Fig. 9.

Conclusions

As a bridging ligand, 1,4-dithiane can be compared to the analogous *N*-donors, pyrazine and piperazine. It is much more flexible and versatile, particularly when compared with pyrazine. Whereas pyrazine can only act as a bidentate linear molecular rod, 1,4-dithiane is able not only to bridge either two or four metal centres but when bridging two metal centres it has a choice of three co-ordination arrangements: *ax–ax*, *ax–eq* or *eq–eq*. Piperazine, which is a bidentate ligand with similar flexibility to 1,4-dithiane in its co-ordination arrangements, has intermediate versatility. Although a significant number of Ag(I)–pyrazine co-ordination polymers have been structurally characterised,[23,24] there is, to the best of our knowledge, only one example of a structurally characterised Ag(I)–piperazine co-ordination polymer.[24] This polymer is noteworthy in that the piperazine bridges are bound in both *eq–eq* and *ax–eq* fashions. The dearth in the number of Ag(I)–piperazine complexes is attributed to the fact that, as a hard base, it does not form particularly stable complexes with Ag(I), a relatively soft acid. Pyrazine and 1,4-dithiane, on the other hand, are much softer bases which can form stable complexes with Ag(I). Within the context of co-ordination polymer design, pyrazine can be used with some certainty when a short molecular rod is required to generate a Ag···Ag separation of *ca.* 6.5 Å. On the other hand, 1,4-dithiane can be used to generate Ag···Ag separations of *ca.* 5.0, 6.5 and 7.7 Å, but the versatility of the ligand means that the choice of separation cannot be guaranteed.

Two factors, co-ordinating ability and size, control the role of the anion in the construction of the Ag(I) co-ordination polymers described herein. Strongly co-ordinating anions ($[SCN^-]$, $[NO_2^-]$ and $[CF_3CO_2^-]$[25]) exclusively form 1 : 1 polymers in which they bridge Ag(I) centres forming extended matrices. The less strongly co-ordinating anions ($[BF_4^-]$, $[CF_3SO_3^-]$, and $[NO_3^-]$) form not only 1 : 1 but also 2 : 3 polymers. In the structurally characterised 1 : 1 polymer containing a weakly co-ordinating anion, the $[BF_4^-]$ anion contributes to the extended network architecture by bridging Ag(I) centres in a similar fashion to the more strongly co-ordinating anions. In the 2 : 3 polymers, however, the elaboration of the extended structure is dependent solely on bridging 1,4-dithiane molecules, which link the Ag(I) centres to form sheets of (6,3) topology. The influence of size and symmetry of the anion is apparent in these systems, in which they act as monodentate ligands. The space required for the anion, which is normally located in the hexagonal cavities of adjacent sheets, dictates the co-ordination mode (*ax–ax* or *eq–eq*) of the bridging 1,4-dithiane molecule and hence the size of the cavity.

Experimental

General procedures

All reagents were used as received. Elemental analysis (C, H, N) was performed by the Nottingham University School of Chemistry Microanalytical Service using a Perkin-Elmer 240B instrument. Infra-red spectra were obtained (as KBr pressed pellets) using a Nicolet Avatar 360 FTIR spectrometer. The syntheses of complexes **1** and **4** have been described previously.[36] Bulk samples of **2** and **5**–**9** were prepared by a similar procedure; that for **2** (see below) is typical. Using the same procedure, a pure bulk sample of **3** could not be obtained. Single crystals of **2**, **3** and **7**–**9** suitable for X-ray diffraction studies were grown by slow layered diffusion of solutions of the Ag(I) salt and 1,4-dithiane in the same solvents used for the bulk preparation, in the appropriate stoichiometries. Powder X-ray diffraction studies on the bulk samples of **2** and **7**–**9** revealed that they were micro-crystalline, of single phase and possessed the same structure as the single crystals. Similar studies on the product of the attempted bulk preparation of compound **3** were inconclusive, as were the elemental data. The IR spectra of the bulk samples confirmed the presence of the anions and of the 1,4-dithiane ligands.

Synthesis of 2

To a solution of $AgCF_3SO_3$ (169 mg, 0.67 mmol) in MeOH (10 cm^3) was added a solution of 1,4-dithiane (120 mg, 1.00 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred at room temperature for 1 h, and the resulting white precipitate was filtered, washed with CH_2Cl_2 and dried *in vacuo*. Yield: 260 mg, 90%. Found (calc. for $C_{14}H_{24}Ag_2F_6O_6S_8$) %: C, 19.21 (19.22); H, 2.61 (2.77). IR (KBr disc) ν/cm^{-1}: 2905w, 1406m, 1250vs, 1173s, 1036s, 909s, 901s, 650s, 578w, 519m.

Synthesis of 5

$AgCF_3SO_3$ (170 mg, 0.67 mmol) in MeOH (10 cm^3) and 1,4-dithiane (80 mg, 0.67 mmol) in CH_2Cl_2 (10 cm^3). Yield: 133 mg, 53%. Found (calc. for $C_5H_8AgF_3O_3S_3$) %: C, 16.41 (15.92); H, 2.59 (2.14). IR (KBr disc) ν/cm^{-1}: 3448w, 2891w, 1384s, 1035w, 916m, 825m, 746m.

Synthesis of 6

$AgNO_3$ (114 mg, 0.67 mmol) in MeOH (10 cm^3) and 1,4-dithiane (80 mg, 0.67 mmol) in CH_2Cl_2 (10 cm^3). Yield: 165 mg,

Table 2 Crystallographic data summary for polymers **2**, **3**, **7**, **8** and **9**

Compound	**2**	**3**	**7**	**8**	**9**
Formula	$C_7H_{12}AgF_3O_3S_4$	$C_{12}H_{24}Ag_2N_2O_6S_6$	$C_5H_8AgNS_3$	$C_4H_8AgNO_2S_2$	$C_4H_{10}Ag_2O_5S_3$
M	437.28	700.43	286.17	274.10	450.04
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1/c$	$P2_1/m$	$P2_1/c$	$Pnma$
a/Å	12.874(2)	12.395(3)	5.1248(3)	10.9407(9)	9.655(2)
b/Å	10.994(2)	12.575(2)	13.0696(8)	7.5356(6)	14.749(2)
c/Å	18.687(3)	14.335(2)	6.4077(4)	9.5107(7)	6.9577(13)
β/°	97.801	93.561(4)	106.046(4)	102.229(1)	—
U/Å^3	2619.2(8)	2230.0(7)	412.46(4)	766.3(2)	990.8(3)
Z	8	4	2	4	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
μ(Mo-Kα)/mm^{-1}	2.22	2.35	3.12	3.11	4.57
Reflections collected	8101	13574	4677	4874	1461
Unique reflections, R_{int}	3426, 0.027	5220, 0.047	988, 0.052	1800, 0.040	1009, 0.013
R_1	0.0389 [2986 > $2\sigma(I)$]	0.0320 [3544 > $2\sigma(I)$]	0.0341 [825 > $2\sigma(I)$]	0.0251 [1586 > $2\sigma(I)$]	0.0285 [900 > $2\sigma(I)$]
wR_2 (all data)	0.1082	0.0612	0.0791	0.0612	0.0726

85%. Found (calc. for $C_4H_8AgO_3NS_2$) %: C, 15.97 (16.56); H, 2.56 (2.78); N, 4.87 (4.83). IR (KBr disc) ν/cm^{-1}: 2966w, 2914w, 1438s, 1385s, 1264s, 1154m, 1019m, 899m, 814w, 665w.

Synthesis of 7

AgSCN (110 mg, 0.67 mmol) in aqueous NH_4OH (3 M, 20 cm^3) and 1,4-dithiane (80 mg, 0.67 mmol) in acetone (10 cm^3). Yield: 100 mg, 53%. Found (calc. for $C_5H_8AgNS_3$) %: C, 20.84 (20.98); H, 2.69 (2.82); N, 4.98 (4.90). IR (KBr disc) ν/cm^{-1}: 2895w, 2091s, 1406w, 1156w, 906m.

Synthesis of 8

$AgNO_2$ (103 mg, 0.67 mmol) in water (20 cm^3) and 1,4-dithiane (80 mg, 0.67 mmol) in acetone (10 cm^3). Yield: 159 mg, 87%. Found (calc. for $C_4H_8AgO_2NS_2$) %: C, 17.48 (17.52); H, 2.87 (2.95); N, 5.06 (5.11). IR (KBr disc) ν/cm^{-1}: 2875w, 1406m, 1271s, 1202m, 1155m, 909m, 901m.

Synthesis of 9

Ag_2SO_4 (207 mg, 0.67 mmol) in water (20 cm^3) and 1,4-dithiane (80 mg, 0.67 mmol) in acetone (10 cm^3). Yield: 227 mg, 79%. Found (calc. for $C_4H_{10}AgO_5S_3$) %: C, 10.69 (10.67); H, 2.15 (2.24). IR (KBr disc) ν/cm^{-1}: 3439b, 1406w, 1112s, 901w, 618m.

Crystallography

For compounds **3**, **7**, **8** and **9**, single crystal X-ray diffraction data were collected, using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), on either a Bruker SMART CCD area detector diffractometer (**3** and **8**), a Nonius kappaCCD area detector diffractometer (**7**) or a Stoë Stadi-4 four circle diffractometer (**9**). Single crystal X-ray experiments were undertaken for **2** using a Bruker SMART CCD area detector diffractometer at Station 9.8 of the SRS at Daresbury Laboratory ($\lambda = 0.6891$ Å). All instruments were equipped with Oxford Cryosystems open flow cryostats.[46] Pertinent details of crystal data, data collection and processing are given in Table 2. The structures of all five compounds were solved by direct methods using SHELXS 97[47] and full matrix least squares refinement undertaken using SHELXL 97.[48] All hydrogen atoms were placed in geometrically calculated positions and thereafter refined using a riding model except those of the water molecule [O(5)] in **7** which were found in the difference map and restrained to have a sensible geometry. All non-hydrogen atoms were refined with anisotropic displacement parameters. Structure **3** contains a nitrate anion disordered over two positions related by a rotation about the N(2)–O(6) bond. The refined occupancy of the two components representing the other two oxygen atoms [O(4), O(5)] was found to be 57.8(7) : 44.2(7)%. Structure **7** contains unexplainable residual electron densities of 2.57 e Å^{-3} (1.65 Å from Ag), 1.80 e Å^{-3} (1.62 Å from Ag) and 1.56 e Å^{-3} [2.01 Å from S(1)] which cannot be accounted for by a sensible disorder model and are unlikely to be due to twinning.

CCDC reference numbers 156906–156910.

See http://www.rsc.org/suppdata/dt/b1/b100635p/ for crystallographic data in CIF or other electronic format.

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