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FULL PAPER

Bridging mode flexibility of 1,3-dithiacyclohexane in silver(I) co-ordination polymers†

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Co-ordination polymers with Ag:1,3-dithiane molar ratios of 1:1, $\{[Ag_2(1,3\text{-dithiane})_2][X][Y]\}_\infty$ ($X = Y = NO_3$, **1**; $X = Y = PF_6$, **2**; $X = Y = BF_4$, **3**; $X = BF_4$, $Y = Cl$, **4**; $X = Y = NO_2$, **5**, and 2:1, $\{[Ag_2(1,3\text{-dithiane})(SO_4)(H_2O)_2]\cdot H_2O\}_\infty$ **6**, the extended structures of which are 1-D chains and 2-D sheets, respectively, have been synthesised and structurally characterised. The recurrent structural motif is the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cationic dimer in which two chair-conformation 1,3-dithiane molecules act as two-connecting units to bridge two Ag(I) centres. In **1**, **2**, and **6**, the dimers are linked into near-linear chains by pairs of bridging anions *via* formation of an Ag_2X_2 rhomboid dimer. In **3**, instead of forming the Ag_2X_2 ($X = F$) rhomboid dimer, two $[BF_4^-]$ anions form μ_2-F,F′-bridges which support weak Ag–S interactions between cations to give a saw-tooth chain structure. This extra Ag–S contact makes the 1,3-dithiane a three-connecting unit. In **4** and **5**, the Ag(I) centres of the cationic dimer are bridged not only by two 1,3-dithiane molecules but also by a Cl^- or NO_2^- anion, respectively, to give $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2(\mu_2\text{-}Cl)]^+$ (**4**) and $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2(\mu_2\text{-}O,O'\text{-}NO_2)]^+$ (**5**). In **4**, the Cl^- anion acts as a μ_4-bridge to link three $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ moieties and generate a zig-zag chain. In **5**, one oxygen of the bridging NO_2^- anions acts as a μ_2-bridge to link two $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ dimers and generate a saw-tooth chain. Although the chains in **1**, **2**, **3** and **5** are uncharged, that in **4** is cationic and that in **6** is anionic. Charge balance in **4** is maintained by a non-co-ordinated $[BF_4^-]$ anion; that in **5** is maintained by '$Ag(H_2O)_2^+$', the co-ordination polyhedron of which is completed by sulfur donors from separate 1,3-dithiane molecules, which thus act as four-connecting units, and by two oxygens of separate SO_4^{2-} anions to give a two-dimensional sheet structure.

Introduction

The use of *N*-donor organic linkers to bridge metal ions in multi-dimensional matrices has led to a multitude of metal–organic hybrid materials.[1–5] The topologies of these co-ordination polymers can be controlled by judicious choice of metal centre, bridging organic ligand and metal:ligand stoichiometry[1–3] leading to the design and construction of functional frameworks.[3,6–12] The roles of anion[2b,3–18] and solvent[18–22] are also of significance.

Recently, we have reported studies of co-ordination polymer construction using *S*-donor ligands including dithiacyclohexanes,[23] tetramethylhexathiaadamantane[24] and larger thioether macrocycles.[25] Dithiacyclohexanes are attractive bridging ligands due to their versatility which results from (i) the flexibility of their saturated six-membered rings which permits both chair and boat conformations, (ii) the presence of two lone pairs of electrons on each sulfur atom giving the possibility of one-, two-, three- or four-fold connectivity, and (iii) the different stereochemical arrangements which can be achieved by utilising different combinations of axially- and equatorially-located metal centres.

The reaction of 1,4-dithiacyclohexane (1,4-dithiane) with Ag(I) salts has produced several interesting co-ordination polymers with metal:ligand ratios of 2:3,[23,26] 1:1[23,26,27] and 2:1.[23] The recurrent structural feature of the 2:3 adducts, $\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3][X]_2\}_\infty$ ($X = BF_4$, CF_3SO_3 and NO_3), is a $\{[Ag_2(\mu_2\text{-}1,4\text{-dithiane})_3]^{2+}\}_\infty$ honeycomb sheet of (6,3) topology, with the sheets differing primarily in the size of the constituent hexagonal units. By adopting different bridging modes, 1,4-dithiane can generate a range of Ag ··· Ag separations. Thus, axial–axial [ax–ax; Scheme 1(a)] and equatorial–equatorial [eq–eq; Scheme 1(b)] two-fold connectivities give Ag ··· Ag separations in the ranges 6.37–6.72 Å and 7.77–7.87 Å, respectively. In the 2:3 adducts, the ax–ax arrangement is the more common, the eq–eq mode only being adopted when it is necessary to generate larger cavities to accommodate bulkier anions. The structures of the 1:1 adducts, $\{[Ag(\mu_2\text{-}1,4\text{-dithiane})][X]\}_\infty$ ($X = BF_4$, SCN, NO_2 or CF_3CO_2), 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 in the way the chains are linked by the various anions to form 2-D and 3-D networks. Again, the ax–ax arrangement is the more common, the eq–eq mode only being adopted by the $[BF_4^-]$ polymer which

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† Electronic supplementary information (ESI) available: views of asymmetric units of, and numbering schemes for, compounds **1**–**6**; comparison of the molecular structures of the cations in **1**, **4** and **6**; 2-, 3- and 4-fold connectivity of 1,3-dithiane in **1**, **3** and **6**. See http://www.rsc.org/suppdata/dt/b2/b205278b/

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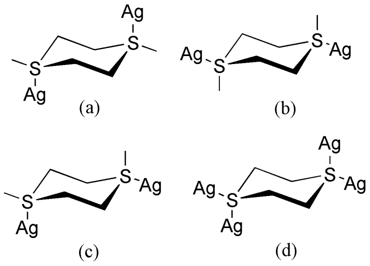
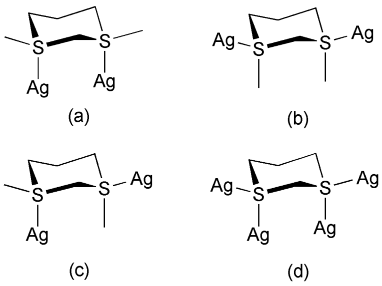


Scheme 1 Two-connecting (a) axial–axial [ax–ax], (b) equatorial–equatorial [eq–eq], (c) axial–equatorial [ax–eq], and four-connecting (d) bridging modes of 1,4-dithiane.

forms a perpendicularly interpenetrated CdSO$_4$-type structure. The 2:1 polymer {[Ag$_2$(μ-1,4-dithiane)](SO$_4$)·H$_2$O}$_\infty$ is unique in that the 1,4-dithiane bridge has four-fold connectivity [Scheme 1(d)]. Although the tetradentate1,4-dithiane molecules in this polymer do have axial–equatorial (ax–eq) connectivities, no polymers have yet been observed in which *bidentate* bridging 1,4-dithiane molecules adopt the ax–eq arrangement [Scheme 1(c)].

We report herein the results of a structural study of the construction of co-ordination polymers of Ag(I) with 1,3-dithiacyclohexane (1,3-dithiane). By analogy with 1,4-dithiane, 1,3-dithiane can be expected to adopt the chair configuration and act as either a bidentate bridging ligand utilising either ax–ax [Scheme 2(a)] or eq–eq [Scheme 2(b)] stereochemical arrangements or as a four-fold connecting unit [Scheme 2(d)]. When the ax–ax co-ordination mode is adopted, the formation of secondary building blocks[10] in the form of [Ag$_2$(μ$_2$-1,3-dithiane)$_2$]$^{2+}$ dinuclear cations can be envisaged. Secondary building blocks give the potential for control of the local environment of an extended co-ordination polymer, a feature which is absent for 1,4-dithiane which can act solely as a simple bridge.



Scheme 2 Two-connecting (a) axial–axial [ax–ax], (b) equatorial–equatorial [eq–eq], (c) axial–equatorial [ax–eq], and four-connecting (d) bridging modes of 1,3-dithiane.

Thus far, the structures of only two transition metal compounds containing bidentate bridging 1,3-dithiane, {[Hg$_2$(μ$_2$-1,3-dithiane)][NO$_3$]$_2$}$_\infty$[28] and [Ru$_4$H$_4$(CO)$_{10}$(μ$_2$-1,3-dithiane)],[29] have been reported. Although the 1,3-dithiane molecules in these compounds both adopt the chair conformation, they differ in their co-ordination modes. Thus, whereas in {[Hg$_2$(μ$_2$-1,3-dithiane)][NO$_3$]$_2$}$_\infty$,[28] the 1,3-dithiane molecules bridge Hg$_2$$^{2+}$ cations in an eq–eq fashion [Scheme 2(b); Hg ··· Hg 6.78 Å] to form a one-dimensional polymer of alternating metal and organic fragments {[Hg$_2$(μ$_2$-1,3-dithiane)]$^{2+}$}$_\infty$, in [Ru$_4$H$_4$(CO)$_{10}$(μ$_2$-1,3-dithiane)][29] they bridge Ru(I) centres in an ax–ax fashion [Scheme 2(a); Ru ··· Ru 3.00 Å] to generate a molecular complex.

A more complete insight into the co-ordination potential of 1,3-dithiane can be obtained by consideration of 1,3,5-trithiacyclohexane (trithiane) complexes. Although trithiane normally uses all three sulfur atoms to bind metal centres, either in an all equatorial fashion to form a two dimensional sheet of (6,3) topology[30] or in an all axial fashion to cap three metal centres,[31] a limited number of compounds have been structurally characterised in which it acts as a bidentate ligand in a similar fashion to 1,3-dithiane.[27,32–35] In {[(MCl$_2$)(μ$_2$-trithiane)]}$_\infty$ (M = Cu[32] or Hg[33]) the trithiane molecules bridge MCl$_2$ moieties in an eq–eq fashion [*cf.* Scheme 2(b); Cu ··· Cu 7.03 Å; Hg ··· Hg 6.81 Å] to form a one-dimensional chain. One-dimensional chains are also found in {[Ag(trithiane)$_2$]-[X]}$_\infty$ (X = AsF$_6$,[34] NO$_3$[35] or CF$_3$SO$_3$[27]) and {[Ag(trithiane)]-[NO$_3$]}$_\infty$.[36] In the 1:2 Ag:trithiane complexes, the chains comprise Ag(I) centres with pendant monodentate trithiane molecules linked by bidentate trithiane molecules in an ax–eq fashion [*cf.* Scheme 2(c)]. Although the AsF$_6$$^-$ anions are not co-ordinated, the NO$_3$$^-$ and CF$_3$SO$_3$$^-$ anions do form weak contacts to the Ag(I) centres [Ag ··· O(nitrate) 2.71(5) Å;[35] Ag ··· O(triflate) 2.960(3) Å[27]]. A similar chain is formed in the 1:1 Ag:trithiane complex {[Ag(trithiane)][NO$_3$]}$_\infty$.[36] In this case, however, the pendant trithiane molecules are tridentate, the other two sulfur atoms bridging symmetry-related Ag(NO$_3$) moieties. In all four chains, the μ$_2$-trithiane molecules bridge in an ax–eq fashion [*cf.* Scheme 2(c)]. This arrangement is clearly very flexible as the Ag ··· Ag separations vary from 5.30 Å (in {[Ag(trithiane)$_2$][AsF$_6$]}$_\infty$[34]) through 5.72 Å (in {[Ag(trithiane)$_2$][CF$_3$SO$_3$]}$_\infty$[27]) and 5.83 Å (in {[Ag(trithiane)]-[NO$_3$]}$_\infty$.[36]) to 6.44 Å (in {[Ag(trithiane)$_2$][NO$_3$]}$_\infty$[35]). The only other structurally characterised complex in which trithiane acts as a bidentate bridging ligand is the binuclear complex [Ag$_2$(trithiane)$_5$][AsF$_6$]·SO$_2$[37] in which two Ag(trithiane)$_2$ moieties are bridged by a bidentate trithiane molecule in an ax–eq fashion [*cf.* Scheme 2(c); Ag ··· Ag 6.05 Å].

Diverse silver salts with anions of varying size and co-ordination ability (AgBF$_4$, AgPF$_6$, AgNO$_3$, AgNO$_2$ and Ag$_2$SO$_4$) have been considered in this work. Co-ordination polymers with Ag:1,3-dithiane molar ratios of 1:1, {[Ag$_2$(1,3-dithiane)$_2$][X][Y]}$_\infty$ (X = Y = NO$_3$, **1**; X = Y = PF$_6$, **2**; X = Y = BF$_4$, **3**; X = BF$_4$, Y = Cl, **4**; X = Y = NO$_2$, **5**, and of 2:1, {[Ag$_2$(1,3-dithiane)(SO$_4$)(H$_2$O)$_2$]·H$_2$O}$_\infty$, **6**, have been synthesised and structurally characterised.

Results and discussion

Single crystal (or microcrystalline powder) samples of composition {[Ag$_2$(μ-1,3-dithiane)$_2$]X$_2$}$_\infty$ (**1**, X = NO$_3$; **2**, X = PF$_6$; **3**, X = BF$_4$) were obtained by layering (or mixing) of AgNO$_3$, AgPF$_6$, or AgBF$_4$ in MeOH with 1,3-dithiane in CH$_2$Cl$_2$. Single crystals of **1** were also obtained when CH$_2$Cl$_2$ was replaced by CH$_3$CN in the preparation. The powders were characterised by elemental (C H N) analysis, infrared spectroscopy and powder X-ray diffraction. In one instance, attempts to prepare **3** under the conditions described above led to single crystals of {[Ag$_2$(μ-1,3-dithiane)$_2$][BF$_4$]Cl}$_\infty$, **4**.

Treatment of AgNO$_2$ in H$_2$O with 1,3-dithiane in CH$_2$Cl$_2$ gave a white insoluble powder of composition {[Ag$_2$(μ-1,3-dithiane)$_2$][NO$_2$]$_2$}$_\infty$ **5**; the solvent system was modified to allow for the poor solubility of AgNO$_2$ in MeOH.[23] The powder was characterised by elemental (C H N) analysis, infrared spectroscopy and powder X-ray diffraction. Colourless crystals of **5** were grown by layered solvent diffusion using the same solvents as those used for bulk sample preparation. Although attempts to produce a complex between Ag$_2$SO$_4$ and 1,3-dithiane using an analogous method to that used for the preparation of a powder sample of **5** were unsuccessful, crystals of {[Ag$_2$(μ-1,3-dithiane)(SO$_4$)(H$_2$O)$_2$]·H$_2$O}$_\infty$ **6** were obtained by the slow layered diffusion between solutions of Ag$_2$SO$_4$ in H$_2$O and 1,3-dithiane in Me$_2$CO.

Single crystal X-ray diffraction studies confirmed the identities of **1**–**6** and revealed their extended structures. Selected structural data (interatomic distances and angles) are given in Table 1. For compounds **1**–**3** and **5**, powder X-ray methods were used to confirm that the single crystals were representative of the bulk samples.

Table 1 Interatomic distances (Å) and angles (°) in compounds **1**–**6**

	1 (150 K)	**1** (296 K)	**2**	**4**
Ag ··· Ag^{a}	2.9695(8) [Ag1^{i}]	2.9818(9) [Ag1^{i}]	2.9236(12) [Ag1^{ii}]	2.9659(9) [Ag1^{iii}]
Ag ··· Ag^{b}	3.9101(8) [Ag1^{iv}]	3.9523(9) [Ag1^{iv}]	3.9371(12) [Ag1^{v}]	3.9531(9) [Ag1^{vi}], 4.0214(9) [Ag1^{vii}]
S–Ag–S	175.24(4)	175.41(4)	176.98(6)	141.26(2)
S–Ag ··· Ag–S	180	180	180	141.30(2)
X–Ag–X	81.13(10) [NO_3^-]	80.17(12) [NO_3^-]	96.1(2) [PF_6^-]	—
Ag–X–Ag	98.87(10)	99.83(12)	84.0(2)	94.82(2); 94.50(2) [Cl^-]
Ag–S1	2.4433(9)	2.4427(12)	2.413(2)	2.4972(7) [S2]
Ag–S3	2.4484(9) [S3^{i}]	2.4508(12) [S3^{i}]	2.405(2) [S3^{ii}]	2.4992(7) [S12]
Ag–X1	2.551(3) [O1]	2.565(3) [O1]	2.873(6) [F2]	2.7907(7) [Cl1]
Ag–X1	2.596(3) [O1^{iv}]	2.601(3) [O1^{iv}]	3.011(6) [F2^{v}]	2.6847(7) [Cl1^{vii}]

	3 [Ag(1)]	**3** [Ag(2)]	**5** [Ag(1)]	**5** [Ag(2)]
Ag ··· Ag^{a}	2.9718(12) [Ag2]	—	2.9470(7)	—
Ag ··· Ag^{b}	3.9737(12) [Ag2^{viii}]	—	—	4.4966(8) [Ag2^{ix}]
S–Ag–S	175.58(6)	173.38(6)	129.56(6)	129.53(6)
S–Ag ··· Ag–S	175.2	174.4	134.3	—
Ag–X–Ag	—	—	132.13	—
Ag–S1	2.435(2) [S11]	2.434(2)	2.520(2)	2.525(2) [S13]
Ag–S3	2.452(2)	2.429(2) [S13]	2.539(2) [S11]	2.515(2)
Ag–X	3.034(2) [S13^{viii}]	3.181(2) [S3^{viii}]	2.389(5) [O2]	2.331(5) [O1]
Ag–X	2.761(6) [F1]	2.595(6) [F11]	2.538(6) [O3]	2.588(5) [O1^{ix}]
Ag–X	2.877(6) [F14^{viii}]	3.093(6) [F2^{viii}]	2.652(5) [O4]	—

	6 [Ag(1)]	**6** [Ag(2)]	**6** [Ag(3)]
Ag ··· Ag^{a}	3.0983(5) [Ag2]	3.0983(5) [Ag1]	4.2260(5) [Ag1]
Ag ··· Ag^{b}	3.9119(5) [Ag2^{x}]	3.9119(5) [Ag1^{x}]	4.2296(5) [Ag2]
Ag ··· Ag^{b}	4.2260(5) [Ag3]	4.2296(5) [Ag3]	3.8500(5) [Ag3^{viii}]
S–Ag–S	178.67(4)	—	—
S–Ag ··· Ag–S	180	—	—
O–Ag–O/°	77.83(10) [SO_4^{2-}]	76.88(10) [SO_4^{2-}]	80.34(10) [SO_4^{2-}]
Ag–O–Ag/°	102.64(10) [SO_4^{2-}]	—	99.66(10) [SO_4^{2-}]
Ag–S1	2.4585(7)	—	2.5724(7)
Ag–S3	—	2.4563(7)	2.6281(7) [S3^{x}]
Ag–O [SO_4^{2-}]	2.492(2) [O1]	2.519 [O1^{xi}]	2.533(2) [O2]
Ag–O [SO_4^{2-}]	—	—	2.504(2) [O2^{ii}]
Ag–O [H_2O]	—	—	2.547(3) [O9]
Ag–O [H_2O]	—	—	2.596(3) [O11]

Symmetry transformations used to generate equivalent atoms: i = $-x, -y, -z$; ii = $-x, 1 - y, 1 - z$; iii = $x, 0.5 - y, z$; iv = $1 - x, -y, -z$; v = $1 - x, 1 - y, 1 - z$; vi = $x, 1.5 - y, z$; vii = $-x, 2 - y, 1 - z$; viii = $1 + x, y, z$; ix = $-0.5 + x, 0.5 - y, -z$; x = $x, -1 + y, z$; xi = $x, 1 + y, z$.^{a} Intra-binuclear unit. ^{b} Inter-binuclear unit.

1,3-Dithiane as a two-fold connecting unit

Structures of the 1:1 polymers, {[{Ag_2(μ-1,3-dithiane)$_2$}(μ-NO_3)$_2$]}$_\infty$ 1 and {[{Ag_2(μ-1,3-dithiane)$_2$}(μ-PF_6)$_2$]}$_\infty$ 2. The structures of **1** and **2** comprise [Ag_2(μ-1,3-dithiane)$_2$]$^{2+}$ binuclear cations linked by pairs of NO_3^- or PF_6^- anions to form near-linear 1-D chains, {[Ag_2(μ-1,3-dithiane)$_2$(μ-X)$_2$]}$_\infty$ (X = NO_3 or PF_6) [Figs. 1(a) and 1(b)], with inversion centres lying at the centre of both the cations and the linking [Ag_2(μ-X)$_2$] (X = NO_3 or PF_6) units [Figs. 1(a) and 1(b)]. The asymmetric unit therefore comprises one Ag(I) centre, one 1,3-dithiane molecule and either one NO_3^- or one PF_6^- anion. In the centrosymmetric [Ag_2(μ-1,3-dithiane)$_2$]$^{2+}$ cations, two Ag(I) centres are bridged by two 1,3-dithiane molecules, which adopt the chair conformation and bind in an ax–ax fashion [Scheme 2(a)]. In **1**, the NO_3^- anions of the centrosymmetric [Ag_2(μ-NO_3)$_2$] moiety adopt a μ_2-O bridging mode to give a longer Ag ··· Ag separation [3.910(1) Å] than that in the cation [2.970(1) Å]. Similarly in **2**, the PF_6^- anions of the centrosymmetric [Ag_2(μ-PF_6)$_2$] moiety adopt a μ_2-F bridging mode to give a longer Ag ··· Ag separation [3.937(1) Å] than that in the cation [2.924(1) Å]. The Ag(I) centres are thus co-ordinated by two sulfur atoms from separate 1,3-dithiane ligands and either two oxygen atoms from the NO_3^- anions or two F-donors from the PF_6^- anions in a saw-horse conformation [Figs. 1(a) and 1(b)]. Despite the significant differences in Ag–O [2.551(3), 2.596(3) Å] and Ag ··· F [2.873(6), 3.011(6) Å] interatomic distances, the Ag ··· Ag separations within the [Ag_2(μ-X)$_2$] moieties are very similar (Table 1).

Structures of the 1:1 polymers, {[{Ag_2(μ-1,3-dithiane)$_2$(μ-Cl)}][BF_4]}$_\infty$ 4 and {[{Ag(μ-1,3-dithiane)$_2$}{Ag(NO_2)}(μ-NO_2)]}$_\infty$ 5. The structure of **4** comprises [Ag_2(μ-1,3-dithiane)$_2$]$^{2+}$ cations linked by Cl^- anions to form a 1-D zig-zag chain, {[Ag_2(μ-1,3-dithiane)$_2$]Cl^+}$_\infty$ (Fig. 2), and unco-ordinated BF_4^- anions [shortest Ag ··· F separation is 2.981(3) Å]. The [Ag_2(μ-1,3-dithiane)$_2$]$^{2+}$ cations and BF_4^- anions lie across a crystallographic mirror plane which also includes the Cl^- anion. Thus, the crystallographic asymmetric unit comprises one Ag(I) centre, half a BF_4^- anion, half a Cl^- anion and two halves of different 1,3-dithiane ligands. The [Ag_2(μ-1,3-dithiane)$_2$]$^{2+}$ cation differs from those in **1** and **2** in the positioning of the two 1,3-dithiane bridges, which again adopt the chair conformation and bind in an ax–ax fashion [Scheme 2(a)]. Whereas the two least squares planes containing the two silver atoms and each pair of sulfur atoms of the centrosymmetric [Ag_2(μ-1,3-dithiane)$_2$]$^{2+}$ cation in **1** and **2** are constrained to be coplanar, in **4** they form a roof-shaped arrangement with the Ag(I) centres on the gable. This difference can be quantified by the

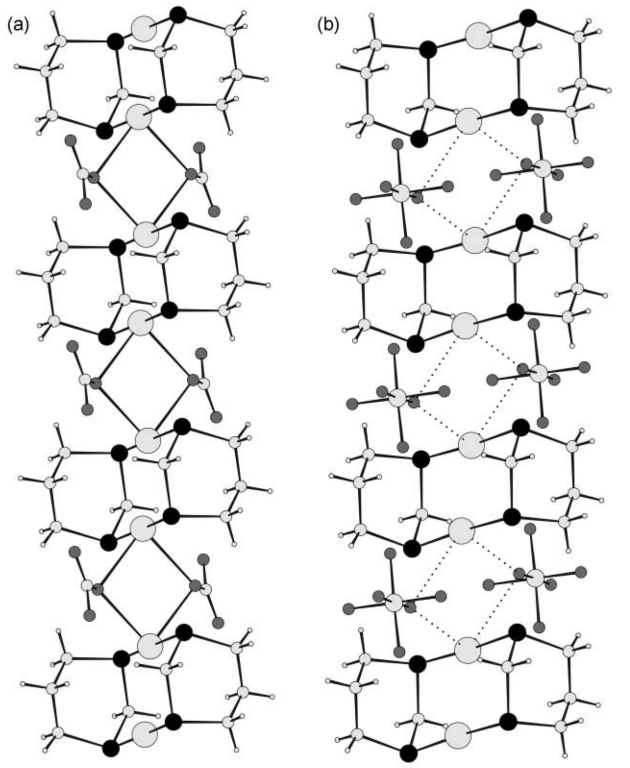


Fig. 1 (a) Portion of the near-linear $\{[\{Ag_2(\mu\text{-}1,3\text{-dithiane})_2\}(\mu\text{-}NO_3)_2]\}_\infty$ chain in **1** showing the linking of the $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations by the nitrate anions (Ag, large open circles; S, intermediate closed circles; O, small shaded circles). (b) Portion of the near-linear $\{[\{Ag_2(\mu\text{-}1,3\text{-dithiane})_2\}(\mu\text{-}PF_6)_2]\}_\infty$ chain in **2** showing the linking of the $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations by the hexafluorophosphate anions (Ag, large open circles; S, intermediate closed circles; P, intermediate open circles; F, small shaded circles).

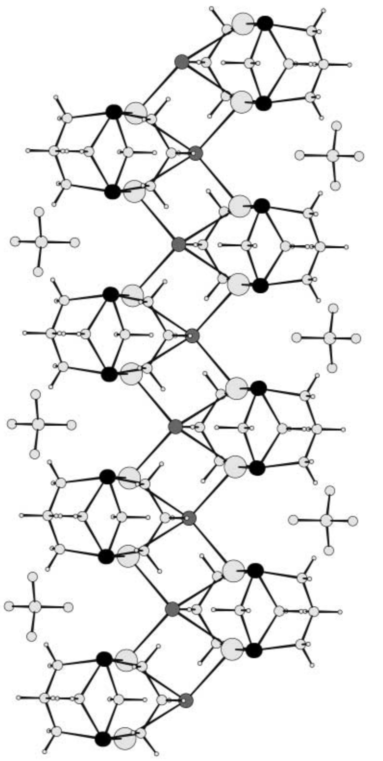


Fig. 2 Portion of the zig-zag $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2(\mu_4\text{-}Cl)]^+\}_\infty$ chain in **4** showing the linking of the $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations by the chloride anions and the disposition of the non-co-ordinated tetrafluoroborate anions (Ag, large open circles; S, intermediate closed circles; Cl, intermediate shaded circles).

S–Ag ··· Ag–S torsion angles (Table 1). The roof-shaped arrangement in **4** allows the Cl^- anion to act as a third bridge between the Ag(I) centres of the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cation [Ag ··· Ag 2.9659(9) Å] and to link to two other $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations and hence generate the $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2(\mu\text{-}Cl)]^+\}_\infty$ zig-zag chain [Ag ··· Ag 3.9531(9), 4.0214(9) Å] giving overall a μ_4-Cl arrangement (Fig. 2). The Ag(I) centre is thus co-ordinated by two sulfur atoms from separate 1,3-dithiane ligands [Ag ··· S 2.4972(7), 2.4992(7) Å] and two Cl^- anions [Ag ··· Cl 2.6847(7), 2.7907(7) Å] in an approximately tetrahedral manner. The zig-zag construction of the chain generates cavities between the cations in which the BF_4^- anions are located and interact with the dithiane ligands *via* a number of weak C–H ··· F hydrogen bonds (H ··· F *ca.* 2.4 Å).

The structure of **5**, which is much less symmetrical than that of either **1** or **2**, comprises $[Ag(\mu\text{-}1,3\text{-dithiane})_2\{Ag(NO_2)\}]^+$ cations linked by $[NO_2^-]$ anions to form a 1-D saw-tooth chain, $\{[Ag(\mu\text{-}1,3\text{-dithiane})_2\{Ag(NO_2)\}(\mu\text{-}NO_2)]\}_\infty$ (Fig. 3). The crystallographic asymmetric unit consists of two Ag(I) centres, two 1,3-dithiane ligands and two NO_2^- anions. The building block in **5**, a binuclear $[Ag(\mu\text{-}1,3\text{-dithiane})_2\{Ag(NO_2)\}]^+$ moiety, differs from those in **1**, **2** and **4** insofar as one of the silver atoms (Ag1) is terminally co-ordinated by a bidentate chelating NO_2^- anion. The arrangement of the bridging 1,3-dithiane ligands in **5** is similar, however, to that in **4**, the two Ag(I) and four sulfur atoms forming a roof-shaped arrangement with the Ag(I) centres on the gable (Table 1). As for **4**, this arrangement allows the second NO_2^- anion (i) to act as a third bridge between the silver centres of the $[Ag(\mu\text{-}1,3\text{-dithiane})_2\{Ag(NO_2)\}]^+$ moiety [Ag ··· Ag 2.9470(7) Å] and (ii) to link to a second cation and hence generate the $\{[Ag(\mu\text{-}1,3\text{-dithiane})_2\{Ag(NO_2)\}(\mu\text{-}NO_2)]\}_\infty$ saw-tooth chain [Ag ··· Ag 4.4966(8) Å] (Fig. 3). The first silver centre, [Ag(1); Fig. 3], is ligated by two sulfur atoms from separate 1,3-dithiane molecules, and three oxygen atoms, one from the bridging NO_2^- anion and two from the terminal NO_2^-

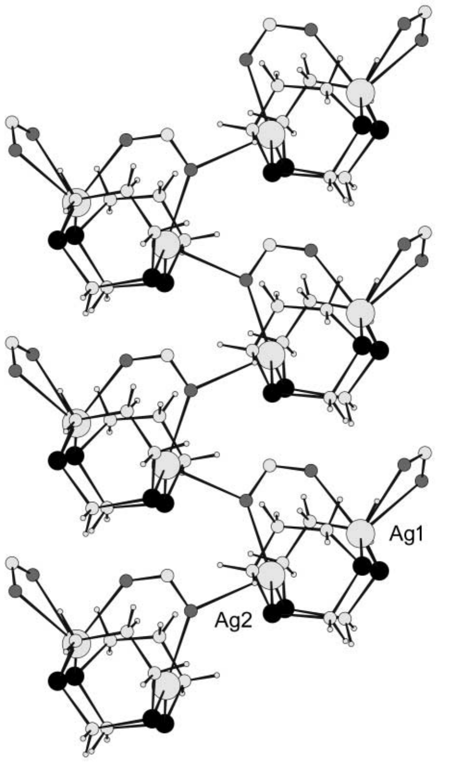


Fig. 3 Portion of the saw-tooth $\{[\{Ag(NO_2)\}(\mu\text{-}1,3\text{-dithiane})_2Ag(\mu_3\text{-}NO_2)]\}_\infty$ chain in **5** showing the linking of the $\{[\{Ag(NO_2)\}(\mu\text{-}1,3\text{-dithiane})_2Ag]^{2+}$ cations by the nitrite anions (Ag, large open circles; S, intermediate closed circles; O, small shaded circles).

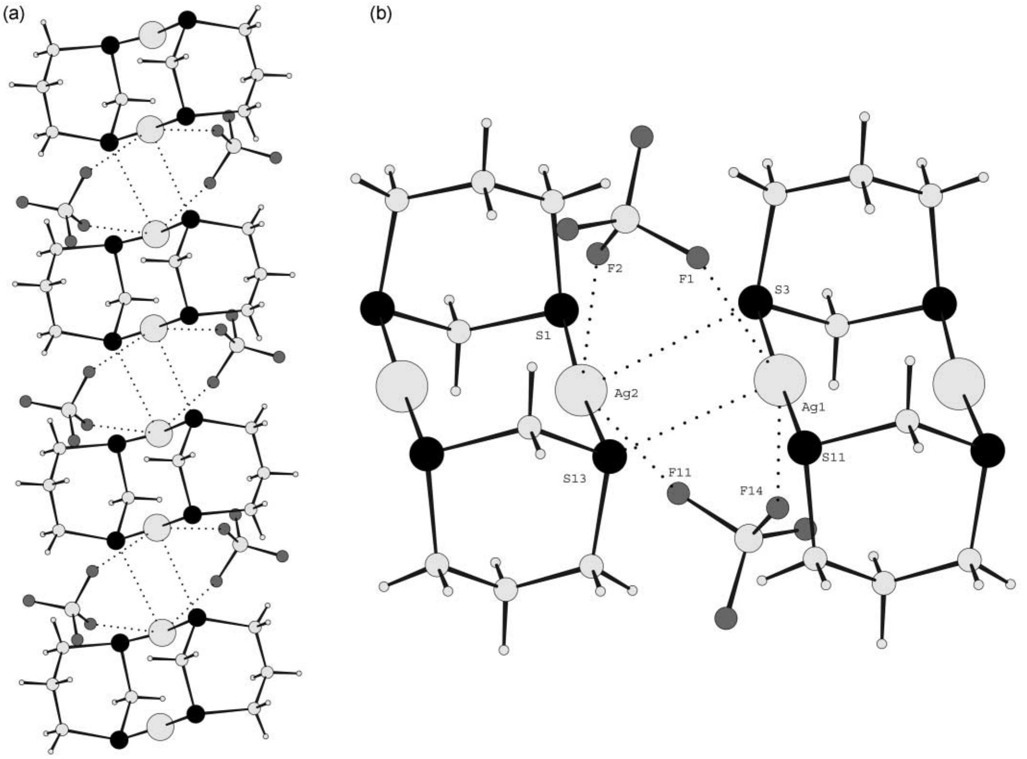
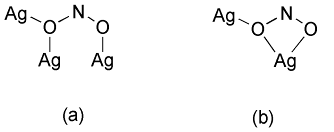


Fig. 4 (a) A portion of the saw-tooth $\{[\{Ag(BF_4)\}_2(\mu\text{-}1,3\text{-dithiane})_2]\}_\infty$ chain in **3**. (b) Detail of the structure showing the long Ag ··· S interactions linking the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations and the supporting μ_2-F,F′-$[BF_4]^-$ bridges (Ag, large open circles; S, intermediate closed circles; F, small shaded circles).

anion. The second silver centre, [Ag(2); Fig. 3], is ligated by two sulfur atoms from different 1,3-dithiane molecules and two oxygen atoms from different bridging NO_2^- anions. The ligating properties of the bridging NO_2^- anion are highly unusual,[23] since the anion co-ordinates to three different Ag(I) centres in a μ_2-O,O′ and a μ_2-O mode [Scheme 3(a)]. An analogous arrangement is seen in the $\{[Ag_2(1,4\text{-dithiane})_2][NO_2]_2\}_\infty$ polymer[23] in which two Ag(I) centres are linked by a single NO_2^- anion which chelates one Ag(I) centre and links to the other using a μ_2-O bridging mode [Scheme 3(b)].



Scheme 3 Nitrite bridging modes in (a) $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2][NO_2]_2\}_n$, and (b) $\{[Ag(\mu\text{-}1,4\text{-dithiane})][NO_2]\}_n$.

1,3-Dithiane as a three-fold connecting unit

Structure of the 1:1 polymer, $\{[\{Ag(BF_4)\}_2(\mu\text{-}1,3\text{-dithiane})_2]\}_\infty$ 3. The structure of **3** comprises $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]$ binuclear cations linked by weak Ag ··· S contacts to form near-linear 1-D chains, $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]\}_\infty$, [Fig. 4(a)]. Each binuclear moiety is built up of two Ag(I) centres bridged by two 1,3-dithiane molecules, both of which adopt the chair conformation and bind in an ax–ax fashion [Scheme 2(a)]. The inter-cation Ag ··· S contacts are quite weak as illustrated by the relatively long Ag ··· S interatomic distances [3.034(2), 3.181(2) Å]. They are supported, however, by two μ_2-F,F′-bridging BF_4^- anions. These contacts are also very weak as illustrated by the relatively long Ag ··· F interatomic distances [2.595(3), 2.761(3), 2.877(3) and 3.093(3) Å]. Thus, the Ag(I) centres are surrounded by three sulfur atoms from separate 1,3-dithiane ligands and two fluorine atoms from the BF_4^- anion in a square pyramidal configuration as shown in Fig. 4(b). The Ag ··· Ag separations within and between the binuclear moieties [2.972(1), 3.974(1) Å] are similar to those in **1** and **2** (Table 1). Although this observation is not surprising for the intra-binuclear unit separation, it is noteworthy for the inter-binuclear unit separation in view of the totally different bridging contacts [Figs. 1(a), 1(b), 4(b)].

1,3-Dithiane as a four-fold connecting unit

Structure of the 2:1 polymer, $\{[\{Ag_2(\mu\text{-}1,3\text{-dithiane})_2\}(\mu\text{-}SO_4)_2\{Ag(H_2O)_2\}_2]\cdot 2H_2O\}_\infty$ 6. The structure of **6** comprises $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ and $[Ag(H_2O)_2]^+$ cations linked by SO_4^{2-} anions to generate a complex 2-D polymeric network (Fig. 5). As the Ag(I) centres of the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations lie on a crystallographic mirror plane, the asymmetric unit consists of these two silver centres [Ag(1), Ag(2)] and their associated 1,3-dithiane ligand, a third silver(I) centre [Ag(3)] and its two associated water molecules, one SO_4^{2-} anion and an unco-ordinated water molecule. The $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cations are bridged by pairs of SO_4^{2-} anions to form near-linear 1-D chains, $\{([Ag_2(\mu\text{-}1,3\text{-dithiane})_2][SO_4]_2)^{2-}\}_\infty$ [Fig. 5; Scheme 4(a)], reminiscent of the $\{[Ag_2(1,3\text{-dithiane})_2]X_2\}_\infty$ chains found in **1** [X = NO_3; Fig. 1(a)] and in **2** [X = PF_6; Fig. 1(b)] insofar as (i) the two silver and four sulfur atoms of the $[Ag_2(1,3\text{-dithiane})_2]^{2+}$ moieties are coplanar (Fig. 5; Table 1), (ii) the Ag(I) centres [Ag(1), Ag(2)] adopt saw-horse co-ordination geometries comprising two sulfur atoms from separate 1,3-dithiane molecules, and two oxygen atoms from separate SO_4^{2-} anions, and (iii) the Ag ··· Ag separations are similar [**1**; 3.910(1) Å, **2**; 3.937(1) Å, **6**; 3.912(1) Å]. The chain in **6** differs from those in **1** and **2** in that the former one is anionic whereas the latter two are neutral. To balance the negative charge in **6**, additional Ag(I) centres [Ag(3)], which serve to link the chains into 2-D sheets, are incorporated into the structure of **6**. Each Ag(3) centre is co-ordinated by two S-donors from 1,3-dithiane molecules in different $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ moieties, by two O-donors from SO_4^{2-} anions in different chains and by two O-donors from water molecules in an approximately octahedral geometry [Scheme 4(b)]. Two of these Ag(I) centres are bridged by the sulfate O-donors to form a centrosymmetric binuclear

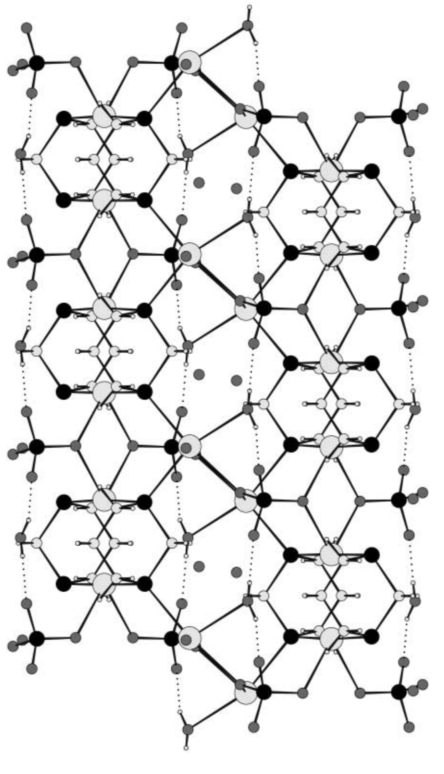
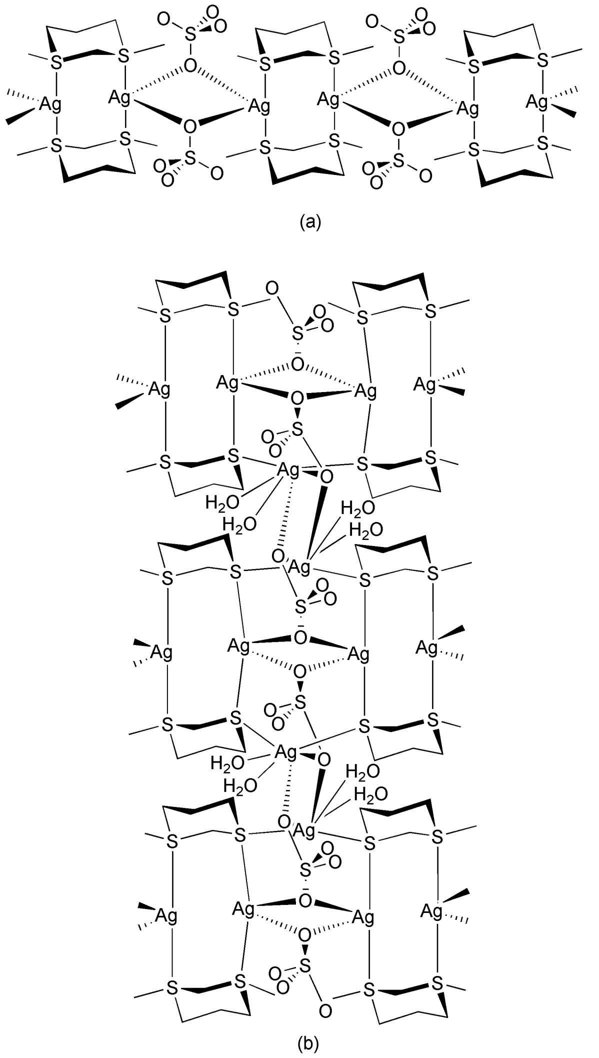


Fig. 5 Section of the sheet structure of $\{[\{Ag_2(\mu\text{-}1,3\text{-dithiane})_2\}(\mu\text{-}SO_4)_2\{Ag(H_2O)_2\}_2]\cdot 2H_2O\}_\infty$ **6** showing the linear $\{[Ag_2(\mu\text{-}1,3\text{-dithiane})_2(\mu\text{-}SO_4)_2]^{2-}\}_\infty$ chains and the linking '$Ag(H_2O)_2{}^{+}$' moieties (Ag, large open circles; S, intermediate closed circles; O, small shaded circles).

unit with an Ag_2O_2 core [Scheme 4(b)]. Thus the $SO_4{}^{2-}$ anion uses two of its oxygen atoms in a μ_2-O, μ_2-O′ fashion to bridge two pairs of Ag(I) centres [Scheme 4(b)] giving two very similar Ag_2O_2 centrosymmetric cores. The 1,3-dithiane molecules act as four-connecting units [Scheme 2(d)] linking the two Ag(I) centres of the $[Ag_2(1,3\text{-dithiane})_2]^{2+}$ cations to four separate $[Ag(H_2O)_2]^{+}$ cations [Scheme 4(b)]. This is the first time that 1,3-dithiane has been seen to behave in this manner. It is interesting to note that the only compound in which 1,4-dithiane is known to exhibit four-connectivity [Scheme 1(d)] is also an Ag_2SO_4 derivative, $\{[Ag_2(\mu\text{-}1,4\text{-dithiane})][SO_4]\cdot H_2O\}_\infty$.[23]

Comparison of the structures

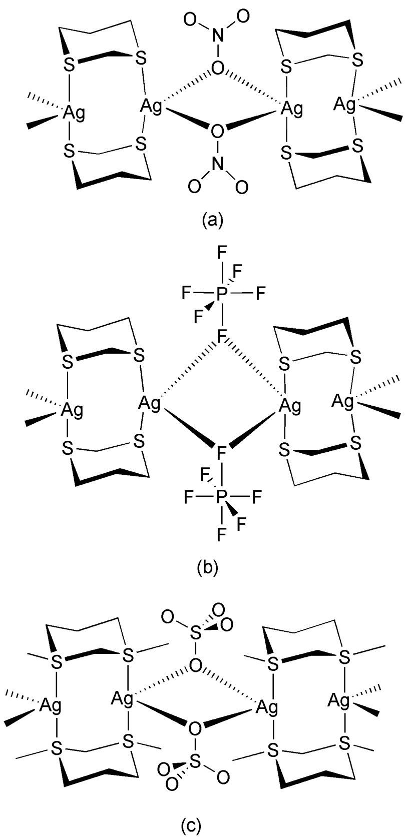
The recurrent structural motif in **1**–**6** is the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ secondary building block. In **1**, **2**, **3** and **6** the bridging 1,3-dithiane molecules are *trans*-located in the Ag(I) co-ordination spheres, giving effectively planar arrangements of the two silver and four co-ordinating sulfur atoms. In **4** and **5** the Ag(I) centres are bridged not only by the two 1,3-dithiane molecules but also by an anion to give $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2(\mu_2\text{-}Cl)]^{+}$ (**4**) and $[Ag(\mu\text{-}1,3\text{-dithiane})_2\{Ag(NO_2)\}(\mu_2\text{-}O,O'\text{-}NO_2)]$ (**5**). As a result, the two silver and four sulfur atoms of the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cationic unit adopt a roof-shaped arrangement with the Ag(I) centres located on the gable. The different behaviour of Cl^{-} and $NO_2{}^{-}$ to that of $NO_3{}^{-}$, $PF_6{}^{-}$, $BF_4{}^{-}$ and $SO_4{}^{2-}$ can be attributed to their more effective co-ordinating ability. Despite the presence of the bridging anion, the Ag ··· Ag separations in **4** [2.9659(9) Å] and **5** [2.9470(7) Å] fall into the range observed in **1**–**3** and **6** [2.9236(12)–3.0983(5) Å].



Scheme 4 (a) Schematic representation of the $\{([Ag_2(\mu\text{-}1,3\text{-dithiane})_2][SO_4]_2)^{2-}\}_n$ 1-D chain in $[Ag_2(\mu\text{-}1,3\text{-dithiane})(SO_4)(H_2O)_2]\cdot H_2O$. (b) Schematic representation of the use of pairs of $[Ag(H_2O)_2]^{+}$ cations to link the $\{([Ag_2(\mu\text{-}1,3dithiane)_2][SO_4]_2)^{2-}\}_n$ chains in $[Ag_2(\mu\text{-}1,3\text{-dithiane})(SO_4)(H_2O)_2]\cdot(H_2O)$.

With the exception of **3**, the elaboration of the structures containing the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ binuclear cations with near planar Ag_2S_4 units involves the linking of the cations into chains through anions *via* formation of an Ag_2X_2 rhomboid dimer in which two Ag(I) centres are linked by two μ_2-X atoms of bridging $NO_3{}^{-}$ [**1**; Scheme 5(a)], $PF_6{}^{-}$ [**2**; Scheme 5(b)] or $SO_4{}^{2-}$ [**6**; Scheme 5(c)] anions. It is worth noting that the Ag ··· Ag separations within the Ag_2X_2 rhomboid dimers fall into a very restricted range, which extends from 3.9101(8) Å (for **1**) through 3.9119(5) Å (for **6**) to 3.9371(12) Å (for **2**). This observation is surprising in view of the marked differences in the geometries of the anions and in their co-ordination abilities. The reason for the uniformity in the Ag ··· Ag separations, which is maintained by an increase in Ag–X–Ag angles compensating for a decrease in the length of the Ag–X contacts (Table 1), is unclear. In the exception, **3**, the $BF_4{}^{-}$ anion does not form an Ag_2X_2 (X = F) rhomboid dimer similar to those in **1**, **2** and **6**; instead, two anions form μ_2-F,F′-bridges which support direct, but weak, Ag ··· S interactions between cations. The chain so generated is skewed in comparison to those in **1**, **2**, and **6** in order to permit formation of the inter-cation Ag ··· S contacts. This difference is best quantified by the Ag ··· Ag ··· Ag angle which varies from 132.1° in **3** to 171.8, 142.5 and 180° in **1**, **2** and **6**, respectively. The different behaviour of $BF_4{}^{-}$ compared with $PF_6{}^{-}$ is unexpected as they are thought to be anions with similarly weak co-ordinating ability.[38]

In **4** and **5** the construction of the chains depends on the anions not only acting as intra-cation bridges but also as inter-cation links. In **4**, the Cl^{-} anion acts as a μ_4-bridge to link three $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cationic units (Fig. 2) and generate a zig-zag chain. In **5** one $NO_2{}^{-}$ oxygen acts as a μ_2-bridge to link



Scheme 5 Schematic representation of the $[Ag_2(\mu\text{-}X)_2]$ rhomboid dimers linking $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cationic motifs in (a) **1**, (b) **2** and (c) **6**.

two $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cationic units (Fig. 3) and generate a saw-tooth chain; the second NO_2^- oxygen completes the μ_2-O,O′-$[NO_2]$ intra-cation bridge.

Although the chains in **1**, **2**, **3** and **5** are uncharged, that in **4** is cationic and that in **6** is anionic. Charge balance in **4** is maintained by a non-co-ordinated BF_4^- anion and that in **6** is maintained by the presence of a second Ag(I)-containing species, '$[Ag(H_2O)_2]^+$', which acts as a μ_2-Ag-bridge to link pairs of cations through Ag ··· S contacts [2.6281(7)] to give a two-dimensional sheet structure.

The versatility of 1,3-dithiane as a bridging ligand is demonstrated in these complexes in which it exhibits two-connectivity (**1**, **2**, **4**, **5**), three-connectivity (**3**) and four-connectivity (**6**). The Ag–S bonds within the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ cationic units are very similar [**1**; 2.443(1), 2.448(1), **5**; 2.515(2)–2.539(2), **6**; 2.456(1), 2.459(1)] implying similar strength. Ag ··· S bonds linking cationic units to give three-connected 1,3-dithiane [**5**; 3.034(2) 3.181(2)] and four-connected 1,3-dithiane are longer [**6**; 2.5724(7) 2.6281(7), Table 2] suggesting weaker interactions, especially in the case of the three-connected 1,3-dithiane. Although weak, the latter are considered to be structure-determining since the spatial arrangement of the Ag(I) ions around the two-, three- and four-connected 1,3-dithianes is very similar despite the wide variation in Ag ··· S interatomic distances (Fig. 4).

Conclusions

As envisaged, $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ secondary building blocks are found in Ag(I)–1,3-dithiane co-ordination polymers. Indeed, they form the basis of all the structurally characterised Ag(I)–1,3-dithiane co-ordination compounds, giving rise to totally different extended structures from Ag(I) 1,4-dithiane complexes. Although the 1,3-dithiane ligand normally prefers to act simply as a two-connecting unit (**1**, **2**, **4** and **5**), it does act as a three- or four-connecting unit but only when forced to do so, in the presence of either a poorly co-ordinating anion (**3**) or a doubly charged anion (**6**). The increased denticity of the 1,3-dithiane results from the need to complete, in the first case, the co-ordination sphere of the Ag(I) centres comprising the $[Ag_2(\mu\text{-}1,3\text{-dithiane})_2]^{2+}$ dimers and, in the second case, the co-ordination sphere of the additional Ag(I) centres required to balance the extra negative charge associated with the sulfate anion.

Table 2 Interatomic distances and angles associated with the two- (**1**), three- (**3**), and four-connected (**6**) 1,3-dithiane bridging ligands

	Ag ··· S/Å	C2–S ··· Ag/°	C4 (C6)–S ··· Ag/°
1			
Ag–S(1)	2.4433(9)	110.3(2)	103.6(2)
Ag–S(3)	2.4484(9)	107.7(2)	106.9(2)
3			
Ag(1)–S(11)	2.435(2)	107.3(3)	109.8(3)
Ag(1)–S(3)	2.452(2)	108.6(3)	109.9(3)
Ag(2)–S(1)	2.434(2)	106.6(3)	108.6(3)
Ag(2)–S(13)	2.429(2)	107.9(3)	110.5(3)
Ag(1)–S(13)	3.034(2)	120.8(3)	123.6(3)
Ag(2)–S(3)	3.181(2)	120.4(3)	127.2(3)
6			
Ag(1)–S(1)	2.4585(7)	112.7(1)	108.3(1)
Ag(2)–S(3)	2.4563(7)	114.1(1)	108.8(1)
Ag(3)–S(1)	2.5724(7)	106.9(1)	114.0(1)
Ag(3)–S(3)	2.6281(7)	107.3(1)	113.8(1)

Experimental

General procedures

All reagents were used as received. Elemental analyses (C H N) were performed either using a Perkin-Elmer 240B instrument at University of Nottingham or conducted by Schwarzkopf Microanalytical Laboratory, Woodside, New York, USA. Infrared spectra were obtained (as KBr pressed pellets) using a Nicolet Avatar 360 or a Perkin-Elmer 1600 Series FTIR spectrometer.

Synthesis of 1

To a solution of $AgNO_3$ (114 mg, 0.67 mmol) in MeOH (*ca.* 10 cm^3) was added a solution of 1,3-dithiane (80 mg, 0.67 mmol) in CH_2Cl_2 (*ca.* 10 cm^3). The mixture was stirred at room temperature for *ca.* 1 hour, and the resulting white precipitate was filtered, washed with CH_2Cl_2 and dried *in vacuo*. Yield 161 mg, 0.56 mmol, 83%. Found (calc.) for $C_4H_8AgO_3NS_2$: C, 16.90 (16.55); H, 2.80 (2.80); N, 4.80 (4.85%). IR (KBr disc) ν/cm^{-1}: 1262(s), 1178(m), 1035(m), 904(w), 647(w), 519(w). Colourless crystals of **1** were grown following concentration of the mixture formed by the layered diffusion of a solution of $AgNO_3$ in MeOH and 1,3-dithiane in either CH_2Cl_2 or CH_3CN. Powder patterns for both the bulk powder sample preparation and a ground sample from the single crystal preparation were each found to be consistent with the pattern calculated from the single crystal structure determination.

Synthesis of 2

Colourless crystals of **2** were grown following concentration over two days of the mixture formed by the layered diffusion of a solution of $AgPF_6$ (253 mg, 1.00 mmol) in MeOH (5 cm^3) on 1,3-dithiane (120 mg, 1.0 mmol) in CH_2Cl_2 (5 cm^3). Yield 0.346g, 93%. Found (calc.) for $C_4H_8AgPF_6S_2$: C, 13.15 (12.90); H, 2.20 (2.15%). IR (KBr disc) ν/cm^{-1}: 2927(w), 1740(w), 1418(w), 1387(w), 1311(w), 1151(w), 1076(w), 913(s), 832(s), 744(w), 667(w), 560(s). A powder pattern of the (ground) sample from which the single crystal was obtained confirmed the homogeneity of the sample.

Table 3 Crystallographic data summary for compounds **1**–**6** (data for the determination of the structure of **1** at both 150 and 296 K are included)

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_4H_8AgNO_3S_2'$	$C_4H_8AgF_6PS_2$	$C_4H_8AgBF_4S_2$	$C_8H_{16}Ag_2BClF_4S_4$	$C_4H_8AgNO_2S_2$	$C_4H_{14}Ag_2O_7S_3$
M	290.10	373.06	314.90	578.45	274.10	486.07
T/K	150(2) [296(2)]	296(2)	183(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$Pnma$	$P2_12_12_1$	$C2/c$
a/Å	6.862(1) [6.918(2)]	6.5099(9)	6.3604(3)	14.290(2)	6.5119(10)	22.876(2)
b/Å	7.902(1) [7.963(2)]	18.743(3)	9.2890(5)	6.919(2)	13.135(2)	7.0102(5)
c/Å	15.962(1) [15.994(3)]	8.2518(12)	15.9760(8)	16.189(2)	18.463(3)	16.866(2)
α/°	90	90	85.837(1)	90	90	90
β/°	90.121(1) [90.122(4)]	93.404(2)	84.788(1)	90	90	116.449(2)
γ/°	90	90	83.627(1)	90	90	90
U/Å^3	865.5(1) [881.1(3)]	1005.1(2)	932.31(8)	1600.6(6)	1579.2(4)	2421.6(3)
Z	4	4	4	4	8	8
μ/mm^{-1}	2.769 [2.720]	2.624	2.612	3.159	3.019	3.766
Measured reflections	8776 [12296]	14192	13675	10906	10023	8132
Unique reflections	2066 [2550]	2891	5276	2427	3677	3289
R_{int}	0.031 [0.1040]	0.0739	0.0508	0.025	0.10	0.023
Reflections with [$I > 2\sigma(I)$]	2058 [1961]	2176	3294	2173	2984	2914
R_1 [$I > 2\sigma(I)$]	0.0282 [0.0536]	0.0862	0.0737	0.0369	0.0368	0.0383
wR_2 (on F^2, all data)	0.0717 [0.1430]	0.2211	0.2172	0.0791	0.0723	0.1008

Synthesis of 3

A bulk powder sample of **3** was prepared as for **1** using $AgBF_4$ (130 mg, 0.67 mmol) instead of $AgNO_3$. Yield 120 mg, 0.38 mmol, 57%. Found (calc.) for $C_4H_8AgBF_4S_2$: C, 15.40 (15.25); H, 2.60 (2.55%). IR (KBr disc) ν/cm^{-1}: 2900(w), 1420(w), 1036(vs), 916(w), 885(w), 747(w), 532(w), 521(w). Colourless crystals of **3** were grown following concentration over three days of the mixture formed by the layered diffusion of a solution of $AgBF_4$ (194 mg, 1.0 mmol) in MeOH (5 cm^3) on 1,3-dithiane (120 mg, 1.0 mmol) in CH_2Cl_2 (5 cm^3). Yield 0.305g, 97%. The powder pattern for the bulk powder sample preparation was found to be consistent with the pattern calculated from the single crystal structure determination. However, a ground sample from the single crystal preparation indicated that this sample was not homogeneous but consisted primarily of the same phase as the single crystal determination.

Synthesis of 4

Colourless crystals of **4** were grown in an analogous manner to **3** by the slow layered diffusion of solutions of $AgBF_4$ in MeOH and 1,3-dithiane in CH_2Cl_2. All attempts to prepare bulk powder samples starting from equimolar $AgBF_4$/AgCl mixtures failed.

Synthesis of 5

To an aqueous solution (*ca.* 20 cm^3) of $AgNO_2$ (103 mg, 0.67 mmol) was added a solution of 1,3-dithiane (80 mg, 0.67 mmol) in Me_2CO (*ca.* 10 cm^3). The mixture was stirred at room temperature for *ca.* 1 hour, and the resulting white precipitate was filtered, washed with CH_2Cl_2 and dried *in vacuo*. Yield 88 mg, 0.32 mmol, 48%. Found (calc.) for $C_4H_8AgO_2NS_2$: C, 17.50 (17.55); H, 2.85 (2.95); N, 5.05 (5.10%). IR (KBr disc) ν/cm^{-1}: 3440(s, br), 2900(w), 1410(w), 1275(s), 1205(m), 1160(w), 917(w), 751(w). Colourless crystals of **5** were grown by the slow layered diffusion of solutions of $AgNO_2$ in H_2O and 1,3-dithiane in Me_2CO.

Synthesis of 6

High quality single crystals of **6** were grown by the slow layered diffusion of solutions of Ag_2SO_4 in H_2O and 1,3-dithiane in Me_2CO. All attempts to prepare bulk powder samples failed.

Crystallography

Single crystal X-ray diffraction data were collected using either graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART CCD area detector diffractometer (**1**, **2**, **3** and **5**) or using a Bruker SMART CCD area detector diffractometer at Station 9.8 of the SRS at Daresbury Laboratory (**4**, **6**; λ = 0.6891 Å). Data for **1** and **4**–**6** were obtained at 150 K using instruments equipped with Oxford Cryosystems open flow cryostats.[39] Data for **1** and **2** were obtained at 296 K, while data for **3** were obtained at 183 K using a Bruker LT3 cryostat. Pertinent details of crystal data, data collection and processing are given in Table 3. The structures of all six compounds were solved by direct methods using SHELXS97[40] and full-matrix least squares refinement undertaken using SHELXL97.[41] All hydrogen atoms, except those of the water molecules in **6**, were placed in geometrically calculated positions and thereafter refined using a riding model. The hydrogen atoms on water oxygen O(9) in **6** were located in the difference electron density map and restrained to have a sensible geometry. The hydrogen atoms on water oxygens O(10) and O(11) in **6** could not be located in the difference electron density map and hence were not included in the model. All non-hydrogen atoms were refined with anisotropic displacement parameters. All structure diagrams were generated using the program CAMERON.[42]

CCDC reference numbers 187162–187168.

See http://www.rsc.org/suppdata/dt/b2/b205278b/ for crystallographic data in CIF or other electronic format.

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