Structural studies of molecular-based nanoporous materials. Novel networks of silver(I) cations assembled with the polydentate N-donor bases hexamethylenetetramine and 1,3,5-triazine

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Novel polymeric materials have been isolated from the reactions of silver(I) salts of poorly coordinating anions with the polydentate bases hexamethylenetetramine (hmt) and 1,3,5-triazine (trz), the one-dimensional polymer[Ag(hmt)] $SbF_6 \cdot H_2O$ **1**, and the three-dimensional networked compounds $[Ag_{11}(hmt)_6][PF_6]_{11} \cdot 14H_2O$ **2** and $[Ag_6(trz)_8][BF_4]_6 \cdot H_2O$ **3**, characterized by single-crystal X-ray analysis. Compound **1** is monoclinic, space group $P2_1/n$, $a = 14.252(4)$, $b = 11.061(8)$, $c = 16.450(8)$ Å, b = 90.17(3)°. The structure contains a novel type of ribbon formed by hexagonal meshes of alternate Ag^I ions and hmt molecules. The water molecules coordinated to the silver ions form hydrogen bonds which generate a three-dimensional network of unprecedented topology. Crystals of **2** are monoclinic, space group $I2$, $a = 19.552(6)$, $b = 10.856(6)$, $c = 25.749(11)$ Å, b = 92.83(3)°. It consists of an open three-dimensional network of complex topology with all the hmt molecules tetraconnected. Out of the eleven independent Ag^I ions per formula unit, nine are biconnnected and two triconnected to the hmt bases. The large channels in the network contain many water molecules. Compound **3** is monoclinic, space group $P2_1/c$, $a = 12.535(8)$, $b = 29.517(8)$, $c = 14.704(6)$ Å, b = 93.95(4)°. The structure contains six independent Ag ions and eight independent triazine molecules, which display varied connectivities to give a puzzling three-dimensional network.

The design of new nanoporous materials consisting of two- and three-dimensional networks from the assembly of metal ions and suitable polydentate ligands is of great current interest.[1] Hoskins and Robson[2] have suggested useful criteria for the self-assembly of metallic centres of different coordination geometries and molecular rods of variated nature and length. Many examples of three-dimensional super-diamond nets are presently known,[3] exhibiting up to nine-fold interpenetration,[4] and networked coordination polymers related to other topological archetypes, such as simple cubic a-polonium,[5] PtS,[6] quartz,[7] rutile,[8] $SrSi_2$ [9] and a-$ThSi_2$[10] are also known. Some studies on the exchange ability of guest molecules[11] and on the catalytic properties[12] of this type of materials have recently appeared.

Different synthetic strategies can be employed in the assembly of these species, leading to frameworks containing nodes of different nature, *i.e.*, (*i*) using bidentate ligands, nets containing only metallic nodes are obtained, while (*ii*) polydentate ligands can give nets with alternate metallic and organic centres. Moreover, another class of polymers could be obtained, in principle, from suitable polydentate molecules and metallic connectors, represented by simple ions [such as digonal Ag^I or Cu^I] or metal complexes with two *transoid* sites available for coordination, acting only as spacers (ligand , metal , ligand synthons), [13] with the geometry of the supramolecular array driven by the organic units.

We have recently reported some examples of three-dimensional coordination polymers derived from the self-assembly of Ag^I ions and different bidentate N-donor rigid ligands. Networks topologically related to the prototypal frames of diamond,[14] a-polonium,[15] and the triconnected $SrSi_2$ [(10^3)-a type][16] and a-$ThSi_2$ [(10^3)-b type][17] have been discovered (see Fig. 1). In these species interpenetration of the nets is a very common feature, an interesting phenomenon from the structural point of view, but to be avoided, or at least reduced, in order to obtain larger channels and internal cages.

We are now reacting silver(I) and copper(I) salts of poorly coordinating anions with different polydentate N-donor bases, in particular with the potentially tetradentate tetrahedral hexamethylenetetramine (hmt) and with the potentially tridentate trigonal 1,3,5-triazine (trz). We have already described a three-dimensional polymer from $AgPF_6$ and hmt, namely [Ag(hmt)] $PF_6 \cdot H_2O$, containing a (10^3)-a framework.[18] Here, we report on the isolation and characterization of two novel Ag–hmt coordination polymers, namely $[Ag(hmt)]SbF_6 \cdot H_2O$ **1** and $[Ag_{11}(hmt)_6][PF_6]_{11} \cdot 14H_2O$ **2**, and of the triazine derivative $[Ag_6(trz)_8][BF_4]_6 \cdot H_2O$ **3**. The latter two compounds contain three-dimensional coordination networks which represent model examples of molecular-based nanoporous materials.

Results and Discussion

In our recent investigations on the self-assembly of Ag^I cations with different bidendate N-donor bases (*e.g.* pyrazine, 4′,4′-bipyridyl and similar ligands), we have observed some general trends: (*i*) the reactions lead often to mixtures of products and, moreover, on leaving the solutions to stand, the first product

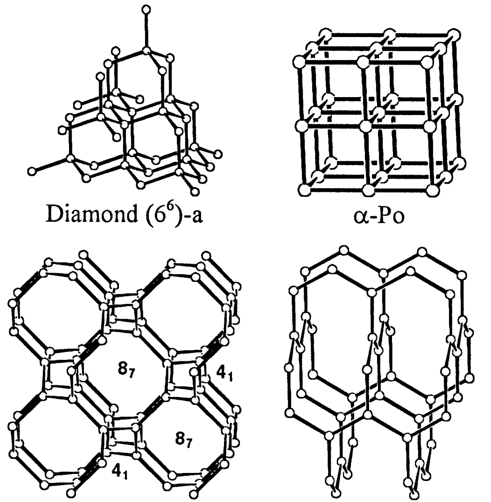


Fig. 1 Prototypal structural types found in some silver(I) polymers with bidentate ligands

formed (favoured by kinetic factors) can give further reactions; (*ii*) the role of counter ions[19] and the solvent system are important in orienting the self-assembly; (*iii*) the silver ions show a great variety of coordination modes. Indeed, the observed geometries with these ligands include, besides the more usual digonal, trigonal and tetrahedral, also T-shaped,[17,20] square-planar,[15] saw-horse,[21,22] square-pyramidal[15] and octahedral[15] stereochemistries. This versatility can represent a problem in the deliberate design of nanoporous materials, but it has offered to us the possibility to characterize frameworks with novel topologies, useful as prototypal models.

On passing to polydentate bases, we have reacted a number of silver(I) salts with hexamethylenetetramine and 1,3,5-triazine, using the methods of slow diffusion for single-crystal growth already employed in our previous works. Polycrystalline samples or materials not suitable for single-crystal X-ray analyses were obtained in many cases. Single crystals were isolated for compounds **1**–**3** described below.

The one-dimensional coordination polymer [Ag(hmt)]$SbF_6 \cdot H_2O$ 1

This species is the dominant product of the reaction of $AgSbF_6$ with hmt in a 1 : 1 molar ratio in ethanol–CH_2Cl_2 and, notably, in spite of sharing the same stoichiometry as [Ag(hmt)]$PF_6 \cdot H_2O$, it has a completely different structure, consisting of ribbons of condensed hexagons of alternating Ag^I ions and hmt molecules, as shown in Fig. 2.

There are two different types of hmt molecules and Ag^I ions: those located in the central part of the ribbons and the external ones. Considering only the Ag–hmt interactions, the internal silver ions and hmt ligands are triconnected [mean Ag(1)—N 2.374 Å], while the external ones are biconnected [mean Ag(2)—N 2.303 Å]. However, each metal ion interacts also with a water molecule (mean Ag—O 2.507 Å), and the external Ag(2) ions show an additional Ag—F(SbF_5) contact of 2.428(6) Å. The resulting coordination geometries are quite distorted tetrahedral for both types of silver ions (Table 1).

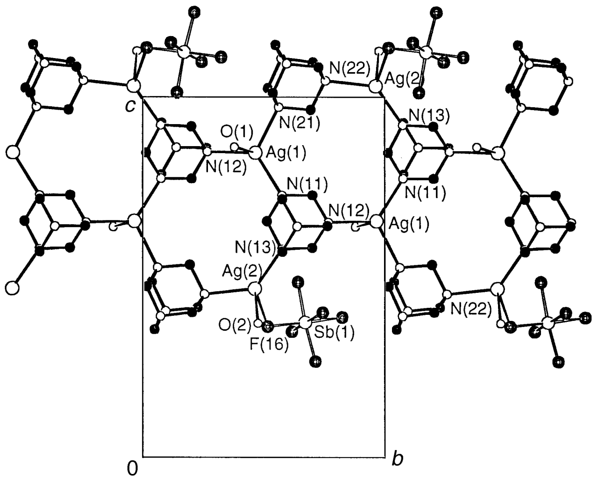


Fig. 2 One-dimensional ribbon in compound **1**

The one-dimensional structural motif observed in **1** is, to our knowledge, unprecedented. It can be described also in terms of a double chain (two *vierer* chains) of vertex sharing tetrahedra (Fig. 3, top), reminiscent of the stuctures of double chain inosilicates, but not related to known species.[23]

Table 1 Main bond lengths (Å) and selected bond angles (degrees) within compounds **1**–**3**

compound **1**					
Ag(1)—N(11)	2.360(6)	Ag(1)—O(1)	2.510(6)	Ag(2)—O(2)	2.504(7)
Ag(1)—N(12)	2.408(6)	Ag(2)—N(13)	2.287(6)	Ag(2)—F(16)	2.428(6)
Ag(1)—N(21)	2.355(6)	Ag(2)—N(22)	2.319(6)		
N—Ag(1)—N	114.6(2)–125.7(2)	N(22)—Ag(2)—N(13)	129.9(2)		
N—Ag(1)—O(1)	91.0(2)–94.2(2)	N—Ag(2)—O(2)	92.9(2)–102.6(3)		
compound **2**					
Ag(1)—N(11)	2.36(2)	Ag(3)—N(21)	2.18(2)	Ag(5)—N(32)	2.31(2)
Ag(1)—O(W1)	2.48(7)	Ag(3)—N(34)	2.22(2)	Ag(5)—O(W5)	2.48(4)
Ag(1)—O(W2)	2.54(7)	Ag(4)—N(12)	2.26(2)	Ag(6)—N(14)	2.31(2)
Ag(2)—N(22)	2.28(3)	Ag(4)—N(23)	2.25(3)	Ag(6)—N(31)	2.44(2)
Ag(2)—N(24)	2.22(2)	Ag(4)—F(62)	2.47(7)	Ag(6)—N(33)	2.39(2)
Ag(2)—O(W3)	2.48(4)	Ag(5)—N(13)	2.21(2)	Ag(6)—O(W6)	2.49(3)
Ag(2)—O(W4)	2.45(5)				
N(11)—Ag(1)—N(11)	169.1(11)	N(32)—Ag(5)—N(13)	143.8(8)		
N(22)—Ag(2)—N(24)	140.2(9)	N(14)—Ag(6)—N(33)	120.1(8)		
N(21)—Ag(3)—N(34)	171.2(9)	N(14)—Ag(6)—N(31)	115.4(8)		
N(12)—Ag(4)—N(23)	161.0(8)	N(31)—Ag(6)—N(33)	119.2(8)		
compound **3**					
Ag(1)—N(1A)	2.33(2)	Ag(3)—N(3G)	2.25(2)	Ag(5)—N(5B)	2.30(2)
Ag(1)—N(1B)	2.28(2)	Ag(3)—N(1H)	2.39(2)	Ag(5)—N(5F)	2.39(2)
Ag(1)—N(1C)	2.35(2)	Ag(3)—F(44)	2.67(3)	Ag(5)—O(1A)[a]	2.38(4)
Ag(1)—N(3E)	2.54(2)	Ag(4)—N(3C)	2.35(2)	Ag(5)—O(1B)[a]	2.55(6)
Ag(2)—N(3B)	2.33(2)	Ag(4)—N(3D)	2.77(2)	Ag(6)—N(5D)	2.34(2)
Ag(2)—N(5C)	2.30(2)	Ag(4)—N(5E)	2.43(2)	Ag(6)—N(1E)	2.30(2)
Ag(2)—N(1D)	2.33(2)	Ag(4)—N(1F)	2.30(2)	Ag(6)—N(3F)	2.34(2)
Ag(2)—N(3H)	2.65(2)	Ag(4)—F(62B)	2.57(5)	Ag(6)—N(1G)	2.29(2)
Ag(3)—N(3A)	2.24(2)	Ag(5)—N(5A)	2.67(3)		
N—Ag(1)—N	85.5(7)–128.7(7)	N(5E)—Ag(4)—N	93.7(7)–117.9(7)		
N—Ag(2)—N	85.6(7)–130.1(7)	N(5E)—Ag(4)—F(62B)	79.9(13)		
N(3A)—Ag(3)—N(3G)	147.2(8)	N(5A)—Ag(5)—N(5F)	142.1(8)		
N(1H)—Ag(3)—N	93.5(8)–117.4(7)	N(5B)—Ag(5)—O(1A)	153.7(11)		
N—Ag(3)—F	81.4(8)–98.8(8)	N(5B)—Ag(5)—N	76.0(8)–103.7(7)		
N(3C)—Ag(4)—N(1F)	146.4(7)	N—Ag(6)—N	95.2(7)–123.1(7)		
N(3D)—Ag(4)—F(62B)	158.7(14)				

[a] Water molecule statistically disordered on two close positions.

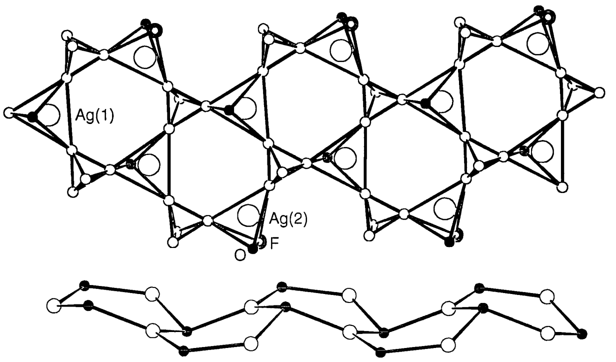


Fig. 3 Two schematic views of the ribbon in **1**: (top) front view showing the double chain of tetrahedral units defined by the N atoms (#) of the hmt ligands and by the coordination spheres of the Ag atoms (#); (bottom) lateral view showing the conformation of the hexagons ($, baricentres of the hmt molecules)

The ribbons are undulated, as schematically shown in Fig. 3 (bottom), and are all disposed parallel to the ***b*** crystallographic axis. However, they are not isolated and display an interesting supramolecular chemistry, in the sense that are cross-linked by hydrogen bonds to give a three-dimensional network. The coordinated water molecules form O—H , N hydrogen bonds with the hmt ligands of adjacent ribbons [O , N 2.837(10), 2.971(10) Å; O—H , N 163.7, 157.8°], as illustrated in Fig. 4.

These interactions generate a three-dimensional net (schematically shown in Fig. 5) of uncommon topological type, based on three-connected (Ag and hmt external in the ribbons) and four-connected (Ag and hmt internal in the ribbons) centres in the ratio 1:1. However, the net is more complex because the water molecules also interact (using the other hydrogen atoms) with the uncoordinated SbF_6^- anion.

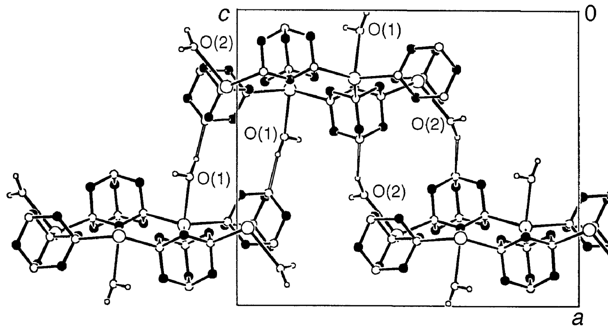


Fig. 4 View of the hydrogen bonds linking the adjacent ribbons in **1**

Attention should be devoted in the near future to the possibility of preparing useful nanoporous materials with the concurrent contribution of different types of interactions to link the units. The results here described are of relevance for the newborn area of crystal engineering concerning the building of networks *via* both coordinative and hydrogen bonds. Investigations based on different strategies are in progress, involving either the self-assembly (direct or mediated by molecular spacers) of suitable mononuclear[24] or polynuclear[3,25] coordination compounds, or the insertion of molecular cross-linkers to join (*via* hydrogen bonds) one-dimensional coordination polymers.[26]

The three-dimensional networked polymer $[Ag_{11}(hmt)_6][PF_6]_{11}\cdot 14H_2O$ 2

Compound **2** has been isolated from the reactions of $AgPF_6$ and hmt in ethanol–CH_2Cl_2, which gave mixtures of polymeric species. Examination under the microscope of samples containing as the dominant product the already described $[Ag(hmt)]PF_6\cdot H_2O$[18] has also revealed the presence of minor amounts of small flat hexagonal crystals of **2**, investigated by single-crystal X-ray analysis.

The structure consists of an open three-dimensional cationic frame, with all the hmt molecules acting as tetradentate ligands, while nine silver cations are biconnected and two are triconnected to hmt molecules per formula unit (note that six Ag and three hmt molecules are crystallographically independent, with one Ag lying on a two-fold axis). From the point of view of the topology of the network, the nine biconnected Ag^I ions are only spacers (metallic synthons).[13] Many interactions of the Ag^I ions with water molecules are also present, which have influence on the coordination geometries of the individual metal ions, but do not change their topological role.

A rationalization of the structure can be achieved considering that it is comprised of layers, as illustrated in Fig. 6, which are normal to the [100] direction, and are joined together only by biconnected silver ions [Ag(1), Ag(3)], to give the overall three-dimensional network. These layers contain the hmt ligands and the other four independent metal ions [Ag(2), Ag(4), Ag(5), Ag(6)], and are unusual, showing two alternate types of one-dimensional structural motifs extending in the [010] direction, *i.e.* ribbons of condensed hexagons and helical —Ag—hmt—Ag—hmt— chains, interconnected by metallic spacers. The ribbons are quite similar to those in compound **1** and contain the biconnected Ag(5) and the triconnected Ag(6) ions (mean Ag—N 2.26 and 2.38 Å, respectively), each

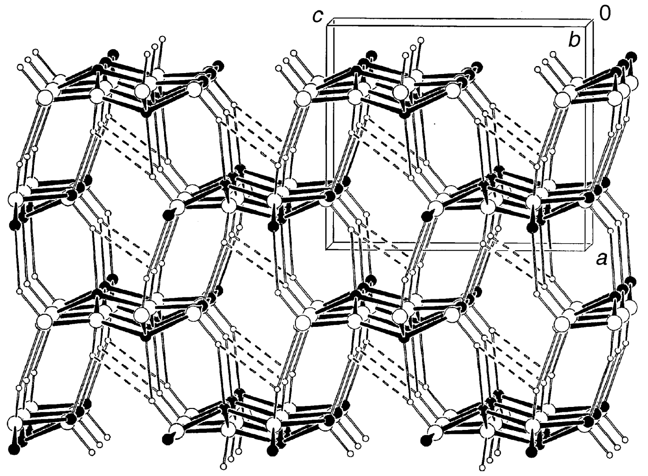


Fig. 5 Schematic view of the three-dimensional net in compound **1** (○, water molecules, other symbols as in Fig. 3). Empty bonds represent the hydrogen bonds, dashed bonds involving the SbF_6^- anions.

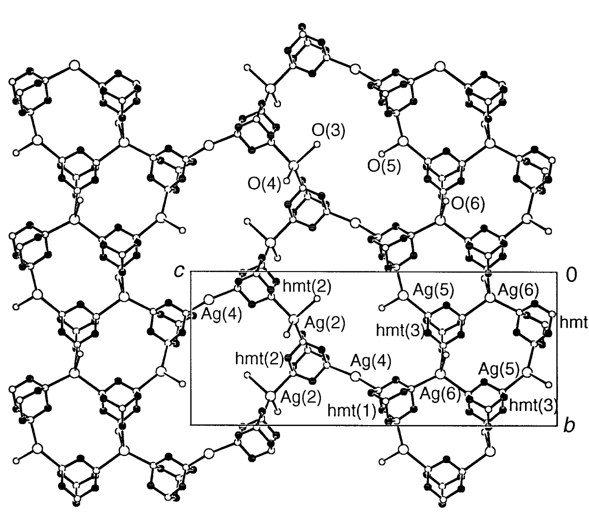


Fig. 6 A two-dimensional layer (down ***a***) contained in compound **2**

interacting also with a water molecule (mean Ag—O 2.48 Å). The helixes involve the Ag(2) ions, which also bear two water molecules [mean Ag(2)—N and Ag(2)—O 2.25 and 2.46 Å, respectively]. The Ag(4) ions, which join the two one-dimensional motifs, interact with the fluorine atom of one anion [mean Ag(4)—N 2.26 Å, Ag(4)—F 2.47(7) Å]. The main bond parameters, illustrating the coordination geometries of the independent metal ions, are collected in Table 1.

The Ag(1) and Ag(3) ions graft the layers of Fig. 6. Two water molecules complete the coordination of Ag(1) (mean Ag—O 2.51 Å), while Ag(3) shows an almost regular digonal coordination. The (3,4)-connected network, schematically shown in Fig. 7 (down ***b***), is comprised of three-connected centres [Ag(6)] and four-connected ones (the hmt ligands) in the ratio 1 : 3; its topological type is complex and quite probably unique, because the four-connected centres are all different. The view in Fig. 7 reveals the presence of two types of parallel channels running down ***b***. These channels host the anions and the 14 water molecules (per formula unit), both coordinated (ten) and the solvated ones (four).

Interestingly, from the results for **1** and **2** we see that the same one-dimensional structural motif (the ribbons of condensed hexagons) can participate in the construction of three-dimensional nets using different kinds of synthons:[13] Ag—O—H , N(hmt) hydrogen bonds and (hmt)N—Ag—N(hmt) bridges, respectively. In reacting hmt and silver salts we had hoped to isolate a supertetrahedral [Ag$_2$(hmt)] net, based on hmt centres only and Ag spacers (Scheme 1, M = metallic synthon), a strict coordination analogue of the extended diamondoid network formed by the interaction of carboxyl groups in pairs in 1,3,5,7-adamantanetetracarboxylic acid.[27] Though we have failed our objective, both the stoichiometry and the nature of the centres in **2** make this species close to what expected for that hypothetical net. However, the presence of the two triconnected silver(I) ions greatly complicates the structure.

The complex three-dimensional network of [Ag$_6$(trz)$_8$][BF$_4$]$_6$·H$_2$O 3

Many attempts were made to obtain polymeric complexes with 1,3,5-triazine (trz) using different silver(I) salts and variated reaction conditions. All were unsuccesful, except for the reaction with AgBF$_4$ in acetone–isopropyl alcohol, leading to compound **3**. The simple potentially tridentate trigonal ligand trz seems particularly attractive for the preparation of two-dimensional graphite-like nets or three-dimensional frames of the (10^3)-a or (10^3)-b type (Fig. 1).

Indeed, very recently the structure of [Ag(trz)]-CF$_3$SO$_3$·H$_2$O, the first coordination polymer assembled with trz, has appeared.[19] It contains an interesting network based on three-connected silver ions and trz ligands, of the (10^3)-d topological type, according to Wells.[28]

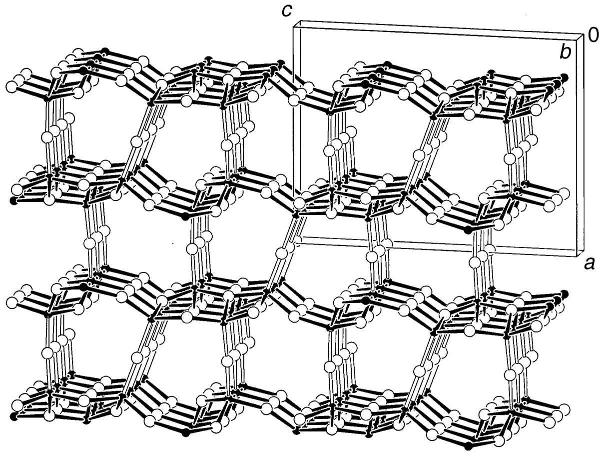
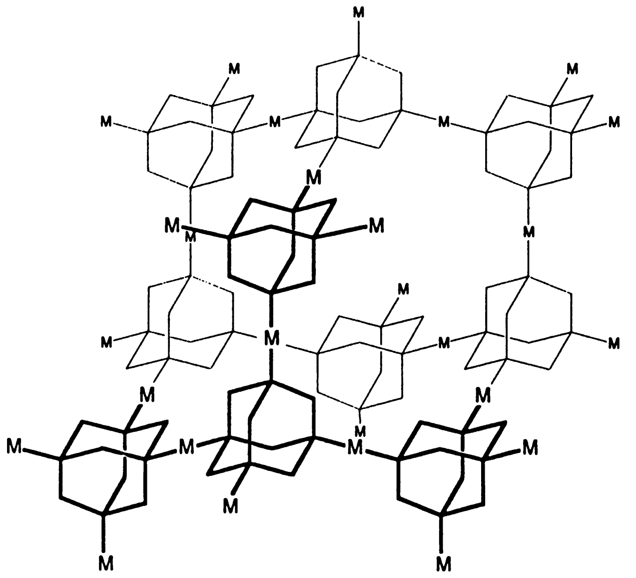


Fig. 7 Schematic view of the three-dimensional net in **2** (down ***b***), with bold bonds within and empty bonds across the layers



Scheme 1

In contrast with the simplicity of this species, compound **3** presents a complicated structure which is difficult to razionalize. This is due to the presence of six Ag^I ions and eight trz ligands which are crystallographically independent and show varied connectivities.

The coordination geometries of the six independent silver ions are shown in Fig. 8. The environments of the Ag(1), Ag(2) and Ag(6) ions are distorted tetrahedral, each being connected to four N atoms of trz ligands. Also Ag(3) and Ag(5) are tetracoordinated: Ag(3) is bound to three trz ligands and to a BF$_4^-$ anion in a saw-horse like geometry, while Ag(4) is coordinated to three trz ligands and a water molecule (disordered on two close positions), in a flattened tetrahedral fashion. Finally, Ag(4) shows a distorted square-pyramidal coordination, involving four trz ligands and one equatorial anion. A list of the relevant bond lengths and angles is given in Table 1.

As usual with networked compounds, it is convenient for topological purposes to ignore atoms and groups which are

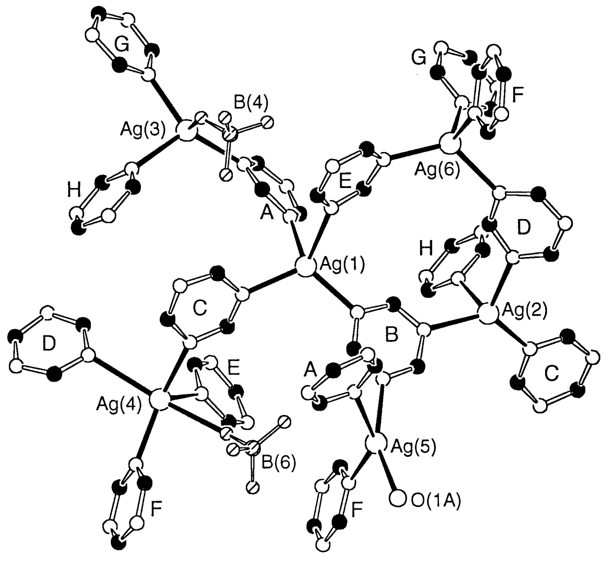


Fig. 8 Coordination geometries of the six independent silver ions in **3**. The triazine rings are labelled A–H.

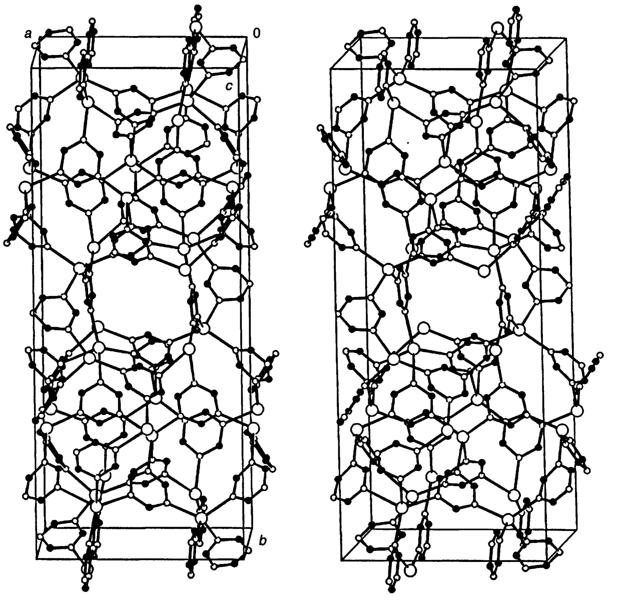


Fig. 9 A stereoview of the network in compound **3** (down ***c***). The BF_4^- anions and the water molecules are omitted for clarity.

simple appendages of the net (dead ends). Considering, therefore, only the Ag–trz interactions we have four tetraconnected [Ag(1), Ag(2), Ag(4), Ag(6)] and two triconnected [Ag(3), Ag(5)] silver ions. All the trz ligands are triconnected but two (G and H), which are simple spacers.

A stereoview of the cell content (without the anions and the water molecules) is shown in Fig. 9. The shortest circuits are six-membered rings of alternate Ag and trz centres, like that in Fig. 8, involving Ag(1), Ag(2) and Ag(6) and the B, D and E rings.

This puzzling (3,4)-connected net (with a 2:1 ratio of the two types of centres) shows also large channels, extending down ***c***. A topological rationalization and classification is fraught with difficulty and is of little practical interest.

Conclusions

We have described three novel polymeric silver(I) species with the polydentate bases hmt and trz. The use of these ligands instead of bidentate ones has introduced another variable into the system, related to the possibility of an incomplete and varied employment of the base donor functions, as observed in **1** and in **3**, which can lead to unusual or complex stuctures. Compound **1** has offered to us the interesting opportunity to study a three-dimensional frame with mixed bonding interactions. In compounds **2** and **3** the three-dimensional nets are not interpenetrated, in contrast to what is observed in many previously studied networks with bidentate bases. The tetradentate hmt seems to be more promising than trz in giving networked materials with large channels. Considering the complicated structure of **3** we can perhaps conclude that trz should be better employed with a metal ion having a less variable coordination geometry than silver.

Experimental

All the reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of this University.

Preparation of compounds 1–3

Synthesis of [Ag(hmt)]SbF$_6$·H$_2$O 1. On a solution of hexamethylenetetramine (0.0451g, 0.32 mmol) in CH_2Cl_2 (3 ml) was layered 1 ml of pure ethanol and then a solution of $AgSbF_6$ (0.106 g, 0.31 mmol) in ethanol (3 ml). The solution was left to slowly evaporate for many days in the dark, affording elongated crystals, with small amounts of impurities. The crystals were recovered by filtration, dried in air, and, after having mechanically removed the impurities, submitted to elemental analysis (yield *ca.* 50%). Anal. Found: C, 14.02; H, 2.98; N, 11.30. Calc. for $C_6H_{14}AgF_6N_4OSb$: C, 14.36; H, 2.81; N, 11.17%.

Table 2 Crystallographic data for compounds **1–3**

formula	$C_6H_{14}AgF_6N_4OSb$ **1**	$C_{36}H_{100}Ag_{11}F_{66}N_{24}O_{14}P_{11}$ **2**	$C_{24}H_{24}Ag_6B_6F_{24}N_{24}O$ **3**
formula weight	501.83	3874.64	1832.75
space group (no.)	$P2_1/n$ (14)	$I2$ (5)	$P2_1/c$ (14)
a/Å	14.252(4)	19.552(6)	12.535(8)
b/Å	11.061(8)	10.856(6)	29.517(8)
c/Å	16.450(8)	25.749(11)	14.704(6)
b/degrees	90.17(3)	92.83(3)	93.95(4)
V/Å^3	2593(2)	5459(4)	5428(4)
Z	8	2	4
D_c/g cm^{-3}	2.571	2.357	2.243
absorption coefficient/mm^{-1}	3.664	2.260	2.257
crystal size/mm	0.45 × 0.1 × 0.07	0.20 × 0.15 × 0.05	0.50 × 0.35 × 0.30
scan interval/degrees	1.3 + 0.35 tan h	1.4 + 0.35 tan h	1.1 + 0.35 tan h
max time per reflection/s	60	60	40
h range/degrees	3–25	3–24	3–23
index ranges *hkl*	−16 to 16, 0–13, 0–19	−22 to 22, 0–12, 0–29	−13 to 13, 0–25, 0–16
reflections collected	4773	4489	5317
independent reflections (R_{int})	4514	4489	5137
crystal decay (%)	0	0	9
min., max. transmission	0.76, 1.0	0.55, 1.0	0.85, 1.0
data/restraints/parameters	3870/0/344	2942/631/397	2970/351/387
R indices (observed data)[b]	R_1 0.0335, wR_2 0.0887	R_1 0.0856, wR_2 0.2192	R_1 0.0717, wR_2 0.1752
weighting A,B[c]	0.0605, 8.2507	0.1694, 0.0	0.0827, 77.3044
goodness-of-fit GOF[d]	1.038	1.070	1.081

[a] Details in common: monoclinic, v scans, $R_{int} = 0.0000$, reflections $I > 2s(I)$ considered observed. [b] $R_1 = S||F_o| - |F_c||/S|F_o|$, $wR_2 = [S\ (F_o^2 - F_c^2)^2/S\ wF_o^4]^{1/2}$. [c] Weighting: $w = 1/[s^2(F_o^2) + (AP)^2 + BP]$ where $P = (F_o^2 + 2\ F_c^2)/3$. [d] $GOF = [Sw(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Isolation of $[Ag_{11}(hmt)_6][PF_6]_{11}\cdot 14H_2O$ 2. Compound **2** was isolated as a minor product from the reaction of $AgPF_6$ and hmt in ethanol–CH_2Cl_2, together with the already described $[Ag(hmt)]PF_6\cdot H_2O$.[18] Slow evaporation (almost to dryness) of a system consisting of an ethanolic solution (5 ml) of $AgPF_6$ (0.074 g, 0.29 mmol) layered on a solution of hmt (0.041 g, 0.29 mmol) in CH_2Cl_2 (3 ml) afforded a crystalline product containing mainly tetrahedral or octahedral crystals of $[Ag(hmt)]PF_6\cdot H_2O$ (*ca.* 80%), together with a minor amount of small flat hexagonal crystals of **2**. Both compounds are air- and light-stable and the nature of **2** has been established by single-crystal X-ray analysis.

Synthesis of $[Ag_6(trz)_8][BF_4]_6\cdot H_2O$ 3. A solution of triazine (0.035g; 0.43 mmol) in isopropyl alcohol (7 ml) was layered on a solution of $AgBF_4$ (0.762g, 0.39 mmol) in acetone (6 ml). After several days in the dark a white precipitate together with needle shaped crystals were formed. This material was recovered by filtration, washed with a small amount of isopropyl alcohol and dried in the air (yield *ca.* 70%). The elemental analyses of the precipitate and of the crystals were identical. Anal. Found: C, 15.33; H, 1.68; N, 18.01. Calc. for $C_{24}H_{26}Ag_6B_6F_{24}N_{24}O$: C, 15.71; H, 1.43; N, 18.33%.

Single-crystal X-ray analysis

Colourless crystals of **1–3** were mounted on glass fibres in the air at room temperature, on an Enraf-Nonius CAD4 automated diffractometer, and 25 intense reflections (17° < 2h < 23°) were centred using graphite-monochromated Mo-Ka radiation (0.710 69 Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 2, together with other details associated with data collection and refinement. The diffracted intensities were corrected for Lorentz, polarization and decay effects. An empirical absorption correction based on y-scans was applied to all data. The structures were solved by direct methods with SIR92[29] and refined by full-matrix least-squares on F_o^2. Anisotropic thermal displacements were assigned to all non-hydrogen atoms for compound **1** and only to the heavy atoms Ag, P for **2** and Ag for **3**. All the hydrogen atoms were placed in calculated positions; for **2** and **3** the water hydrogen atoms were ignored. The final difference electron density maps showed no significant features. All calculations were performed using SHELX-93.[30] Compound **1** showed a monoclinic unit cell [b = 90.17(3)°] emulating orthorhombic symmetry, and a considerable improvement of the final agreement factor was obtained with the TWIN refinement directive of SHELX-93 with twin matrix [1 0 0, 0 −1 0, 0 0 −1] and parameter 0.1811(8). The assignement of the absolute structure for compound **2** was confirmed by the statistics and the refinement of the absolute structure parameter to a value of 0.07(13). Some disordered water molecules and anions were refined as 50% over two positions in compounds **2** and **3**. Crystal drawings were produced with SCHAKAL.[31] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/36.

References

1 C. L. Bowes and G. A. Ozin, *Adv. Mater.*, 1996, **8**, 13.

2 (*a*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546. (*b*) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecture*, ACS publications, Washington, DC, 1992, ch. 19.

3 See for example: M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, 283.

4 K. A. Hisch, D. Venkataraman, S. R. Wilson, J. S. Moore and S. Lee, *J. Chem. Soc., Chem. Commun.*, 1995, 2199.

5 See for example: (*a*) S. C. Abrahams, J. L. Bernstein, R. Liminga and E. T. Eisenmann, *J. Chem. Phys.*, 1980, **73**, 4585; (*b*) B. F. Hoskins, R. Robson and N. V. Y Scarlett, *J. Chem. Soc., Chem. Commun.*, 1994, 2025; (*c*) T. Soma, H. Yuge and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1665.

6 B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature* (*London*), 1994, **369**, 727.

7 (*a*) S. C. Abrahams, L. E. Zyontz and J. L. Bernstein, *J. Chem. Phys.*, 1982, **76**, 5485; (*b*) B. F. Hoskins, R. Robson and N. V. Y. Scarlett, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1203.

8 S. R. Batten, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1991, 445.

9 (*a*) S. Decurtins, H. W. Schmalle, P. Schneuwly and H. R. Oswald, *Inorg. Chem.*, 1993, **32**, 1888; (*b*) S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly and A. Hauser, *Inorg. Chem.*, 1996, **35**, 1451.

10 G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature* (*London*), 1995, **374**, 792.

11 (*a*) D. Venkataraman, G. B. Gardner, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 11600; (*b*) G. B. Gardner, Y.-H. Kiang, S. Lee, A. Asgaonkar and D. Venkataraman, *J. Am. Chem. Soc.*, 1996, **118**, 6946.

12 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.

13 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.

14 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755.

15 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895.

16 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393.

17 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.

18 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 12861.

19 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hisch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030.

20 See for example: (*a*) F. Robinson and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1995, 2413; (*b*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295.

21 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Inorg. Chem.*, 1995, **34**, 5698.

22 D. Venkataraman, G. B. Gardner, A. C. Covey, S. Lee and J. S. Moore, *Acta Crystallogr., Sect. C*, 1996, **52**, 2416.

23 F. Liebau, *Structural Chemistry of Silicates*, Springer, Berlin, 1985.

24 See for example: M. M. Chowdhry, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 899.

25 S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1993, 1078.

26 S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo and M. Katada, *Inorg. Chem.*, 1996, **35**, 4449.

27 O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747.

28 (*a*) A. F. Wells, *Acta Crystallogr.*, 1954, **7**, 535; (*b*) *Three-dimensional Nets and Polyhedra,* Wiley, New York, 1977; (*c*) *Further studies of Three-dimensional Nets,* ACS Monogr., No. 8, Pittsburgh, PA, 1979.

29 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

30 G. M. Sheldrick, SHELX-93: program for structure refinement, University of Göttingen, 1994.

31 E. Keller, SCHAKAL 92: a computer program for the graphical representation of crystallographic models, University of Freiburg, 1992.

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