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Two- and three-dimensional non-interpenetrating open-networks self-assembled by μ$_4$-hexamethylenetetramine (hmt). Syntheses and structures of $[Ag_2(\mu_4\text{-hmt})(SO_4)(H_2O)]\cdot 4H_2O$ and $[Ag_2(\mu_4\text{-hmt})(\mu\text{-}O_2CMe)]MeCO_2\cdot 4.5H_2O$

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Sulfate and acetate complexes comprising two-dimensional grids with square cavities and three-dimensional networks with hexagonal channels, respectively, have been prepared and characterised by X-ray single-crystal structural analysis.

Considerable research effort has recently been focused on the crystal engineering of supramolecular architectures organised by co-ordinate covalent or hydrogen bonding.[1,2] Although supramolecular co-ordination polymers have currently been constructed largely with the use of symmetrically-bridging ligands (such as 2-connectors, trigonal 3-connectors, and tetrahedral or square planar 4-connectors), the use of different synthons[1a,3,4] is one of several strategies that could be employed in the synthesis of frameworks having larger cavities or channels for possible application in separation processes and catalysis. Silver(I) is a good candidate as a simple spacer in L–M–L metallic synthons for the preparation of desired networks, and hexamethylenetetramine (hmt) as a potential tetradendate ligand seems quite suitable for self-assembly of supertetrahedral networks with metallic synthons although no supertetrahedral $[Ag_2(hmt)]$ hypothetical frame has, as yet, been isolated.[5–9] We report here the preparation and crystal structures of two novel two- and three-dimensional non-interpenetrating open-networks organised by μ$_4$-hmt ligand with simple spacers: $[Ag_2(\mu_4\text{-hmt})(SO_4)(H_2O)]\cdot 4H_2O$ **1** and $[Ag_2(\mu_4\text{-hmt})(\mu\text{-}O_2CMe)]MeCO_2\cdot 4.5H_2O$ **2**.

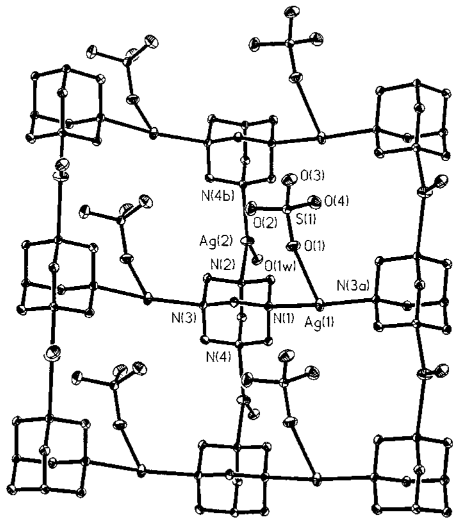
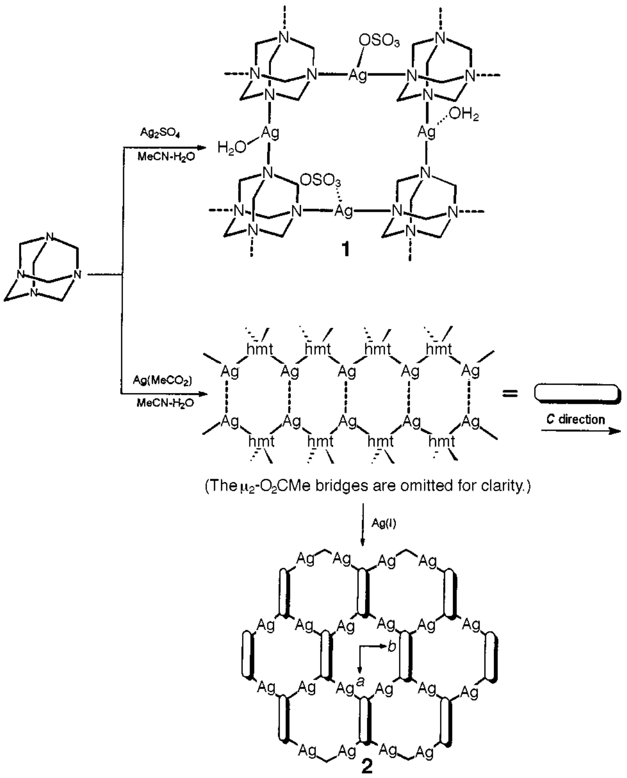


Fig. 1 ORTEP view showing the layer in **1** viewed along the *b* direction. Small open balls represent centres of mass of the hmt ligands. Relevant bonding parameters: Ag(1)–N(1) 2.292(4), Ag(1)–N(3a) 2.279(4), Ag(1)–O(1) 2.571(5), Ag(2)–N(2) 2.347(4), Ag(2)–N(4b) 2.311(4), Ag(2)–O(1w) 2.303(4) Å; N(1)–Ag(1)–N(3a) 172.81(15), N(1)–Ag(1)–O(1) 88.44(16), N(3a)–Ag(1)–O(1) 92.44(15), N(2)–Ag(2)–N(4b) 115.10(14), N(2)–Ag(2)–O(1w) 117.09(15), N(4b)–Ag(2)–O(1w) 127.80(15)°.

Both complexes were synthesised by self-assembly of the silver(I) salts with hmt, as shown in Scheme 1. An aqueous solution (5 cm^3) of hmt (0.140 g, 1.0 mmol) was added dropwise to a stirred MeCN solution (5 cm^3) of Ag_2SO_4 (0.156 g, 0.5 mmol) or $Ag(MeCO_2)$ (0.167 g, 1.0 mmol) at 50 °C for 15 min. The resulting colorless solution was allowed to stand in air at room temperature for two weeks, yielding colorless crystals [*ca.* 75% yield based on silver(I)]. Elemental analysis confirmed the formulae of **1** and **2**.† On performing the above reactions with an Ag(I) : hmt ratio of 2 : 1, crystals of **1** or **2** were correspondingly isolated in high yield, suggesting that the Ag(I) ion plays the role of a simple spacer in the self-assembly of **1** and **2**.

X-Ray crystallography‡ has established that **1** is made up of two-dimensional infinite wavy neutral layers of square units and lattice water molecules. As illustrated in Fig. 1, each square unit is organised by four Ag(I) ions in two types of geometries and four hmt molecules each at the midpoint of side and corner, respectively, in which the Ag(2) ion is in a trigonal geometry coordinated by two nitrogen atoms from different hmt ligands and one aqua ligand, while the Ag(1) atom is in a T-shaped geometry ligated by two nitrogen atoms from two hmt ligands and one monodentate SO_4^{2-} anion. Adjacent layers are connected by interlayer hydrogen bonds between the aqua



(The μ$_2$-O$_2$CMe bridges are omitted for clarity.)

(viewed from *c*-axis direction.)

Scheme 1

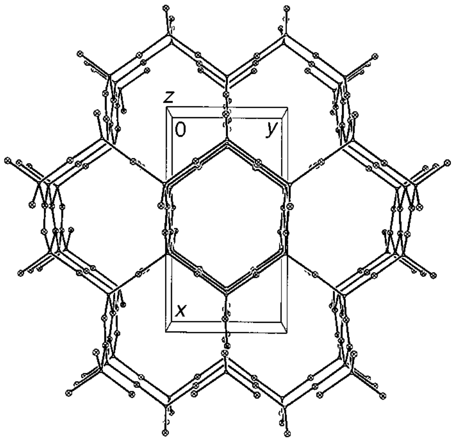


Fig. 2 View of 3-D networks in **2** along the *c*-axis direction. The μ_2-O_2CMe bridges are omitted for clarity. Small open balls represent centres of mass of the hmt ligands.

ligand and SO_4^{2-} anion with an O(1w)···O(SO_4) distance of 2.681–2.691 Å, resulting in a three-dimensional network having irregular pentagonal channels. The lattice water molecules are clathrated in these channels.

The structure of **2** consists of an open three-dimensional cationic network with hexagonal channels, acetate counterions and lattice water molecules. As shown in Scheme 1, the dimeric $Ag_2(MeCO_2)_2$ fragments are bridged by hmt ligands each using two nitrogen atoms into an infinite planar sheet with hexagonal cavities along the *c* direction. These sheets are further joined by the simple Ag(I) spacers through the two remaining nitrogen atoms of hmt ligand into a three-dimensional non-interpenetrating open-network having hexagonal channels along the *c*- and *b*-axis directions (Scheme 1 and Fig. 2). The uncoordinated acetate ions and lattice water molecules are clathrated in the channels.

In the $Ag_2(\mu$-$O_2CMe)_2$ fragments, the Ag(I) atoms are joined by two unusual non-coplanar skew–skew carboxylate bridges[10] with an Ag···Ag distance of 2.9144(8) Å, indicating a relatively strong Ag···Ag interaction;[11] each Ag(I) atom is further ligated by two nitrogen atoms from two different hmt ligands, completing a tetrahedral coordination geometry (Fig. 3).

It is noteworthy that **1** is the first two-dimensional open-network constructed by μ_4-hmt. Of the reported metal–hmt networks, hmt acts rarely in tetradendate coordination mode,[5,6,8,12–14] and only two compounds with μ_4-hmt ligand have been documented.[7,9] Moreover, the topology in **2** is, to the best of our knowledge, unprecedented. In **2**, each hexagon unit viewed from the *c*-axis direction is equivalent, and involves four Ag(I) atoms, two $Ag_2(O_2CMe)_2$ fragments and six hmt ligands, while the hexagonal units viewed from *b*-axis direction is non-equivalent and can be classified into two categories, one involves two $Ag_2(O_2CMe)_2$ fragments and two hmt ligands, another involves four Ag(I) atoms and four hmt ligands. These features are in contrast to those of the reported three-dimensional networks, a 3-D, 3-C enantiomorphic interpenetrating network in $[Ag(hmt)]PF_6\cdot H_2O$,[6] a (3,4)-connected net in $[Ag_3(hmt)_2](ClO_4)_3\cdot 2H_2O$,[7] and a triconnected 3D net in $[Ag_4(hmt)_3(H_2O)](PF_6)_4\cdot 3EtOH$.[8]

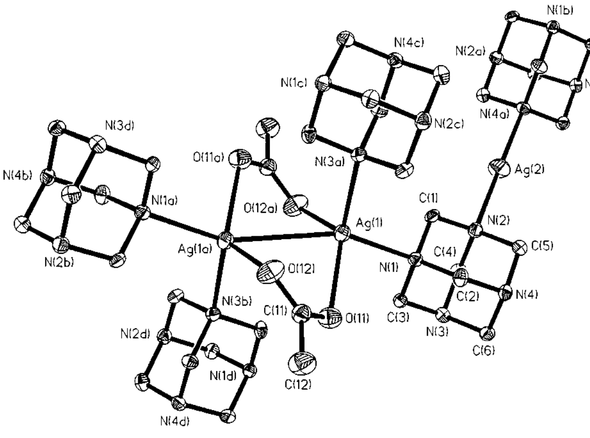


Fig. 3 Coordination environments (at 35% probability level) of the metal atoms in **2**. Relevant bonding parameters: Ag(1)–Ag(la) 2.9144(8), Ag(1)–N(1) 2.405(4), Ag(1)–N(3a) 2.403(4), Ag(2)–N(2) 2.240(4), Ag(2)–N(4a) 2.254(4), Ag(1)–O(11) 2.366(4), Ag(1)–O(12a) 2.391(4) Å; O(11)–Ag(1)–O(12a) 125.84(17), O(12a)–Ag(1)–N(3b) 108.63(14), O(12a)–Ag(1)–N(1), 91.41(15), N(1)–Ag(1)–N(3a) 115.61(14), N(1)–Ag(1)–O(11) 96.64(15), N(3a)–Ag(1)–O(12a) 108.63(14) and N(1)–Ag(2)–N(4a) 178.08(15)°.

As the self-assembly of supramolecular frameworks is highly influenced by factors such as the solvent system,[1a] template[15] and steric requirement of the counter ion,[16] our present work demonstrates that participation of counter ions plays an important role in self-assembly of these frameworks. The isolation of the title complexes and others[11,12] also suggests effective routes to constructing desired frameworks with organic molecules and metallic spacers.

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Notes and references

† Anal. Calc. for $C_6H_{22}N_4O_9SAg_2$ **1**: C, 13.29; H, 4.09; N, 10.34. Found: C, 13.16; H, 4.02; N, 10.22%. Calc. for $C_{10}H_{27}N_4O_{8.5}Ag_2$ **2**: C, 21.64; H, 4.90; N, 10.09. Found: C, 21.48; H, 4.79; N, 10.04%.

‡ *Crystal data*: **1**: $C_6H_{22}N_4O_9SAg_2$, M_r = 542.08, monoclinic, space group *Cc* (no. 9), a = 6.362(6), b = 18.813(13), c = 12.552(4) Å, β = 91.64(6)°, V = 1502(2) Å^3, Z = 4, D_c = 2.398 g cm^{-3}, μ = 27.98 cm^{-1}. **2**: $C_{10}H_{27}N_4O_{8.5}Ag_2$, M_r = 555.10, orthorhombic, space group *Pbcn* (no. 60), a = 22.7015(3), b = 12.1200(2), c = 12.9889(2) Å, V = 3573.79(9) Å^3, Z = 8, D_c = 2.063 g cm^{-3}, μ = 2.240 cm^{-1}. Data collection ($2.17 \leqslant \theta \leqslant 29.06$ for **1** and $1.79 \leqslant \theta \leqslant 25.03$° for **2**) was performed at 293 K on a Siemens R3m diffractometer (Mo-Kα, λ = 0.71073 Å). The structures were solved with direct methods (SHELXS-97)[17] and refined with full-matrix least-squares technique (SHELXL-97),[18] giving for **1** a final R_1 value of 0.0259 for 200 parameters and 2177 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.0663 for all 2177 reflections and for **2** a final R_1 value of 0.0487 for 235 parameters and 2567 unique reflections with $I \geqslant 2\sigma(I)$ and wR_2 of 0.1335 for all 3147 reflections CCDC 182/1176. See http://www.rsc.org/suppdata/cc/1999/561/ for crystallographic files in .cif format.

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