Self-assembly of a three-dimensional network from two-dimensional layers via metallic spacers: the (3,4)-connected frame of [Ag₃(hmt)₂][ClO₄]₃·2H₂O  
(hmt = hexamethylenetetramine)

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AgClO₄ reacts with hexamethylenetetramine (hmt) in ethanol–CH₂Cl₂ in the ratio 1:1 to yield the two-dimensional polymer [Ag(hmt)] ClO₄, consisting of hexagonal meshed layers, while a twofold excess of AgClO₄ produces [Ag₃(hmt)₂ClO₄]·2H₂O, in which Ag⁺ ions intercalate between the sheets of the two-dimensional polymer, joining them as spacers to give a three-dimensional (3,4)-connected open network of uncommon topological type.

The recent efforts in the field of crystal engineering of networked materials based on polymeric coordination compounds¹,² have been devoted to the use of novel polydentate ligands. In contrast to the more common frameworks based on metal centres and bidentate organic rods, the presence of polyhapto bases also introduces organic centres in addition to the metallic ones, which can give rise to new and varied topological types. Very interesting frames have been assembled with large trihapto trigonal ligands, such as 2,4,6-tris(4-pyridyl)-1,3,5-triazine,³ 1,3,5-tris(4-ethynylbenzonitrile)benzene⁴ and tricyanomelamine.⁵ With polydentate bases L (of hapticity greater than two) the topology of the array may also be entirely determined by the ligands, when the metals (such as diagonal Ag⁺ and Cu⁺) do not occupy nodes of the net, but work as simple spacers (L–M–L metallic synthons).† In this concern a potentially tetridentate ligand such as hexamethylenetetramine (hmt) seems quite suitable for the preparation of supertetrahedral networks with metallic synthons (see Scheme 1), paralleling the supramolecular organic chemistry of adamantyl templates with different synthons,⁶ well exemplified by the fivefold interpenetrated frame of the adamantane-1,3,5,7-tetracarboxylic acid.⁷

Working on these lines we have reacted hmt with different Ag⁺ salts of non-coordinating anions and we have recently described the polymeric [Ag(hmt)][PF₆]·H₂O,⁸ containing a three-dimensional triconnected frame topologically related to the prototypal SrSi₂. We report here that hmt reacts with AgClO₄ in the ratio 1:1 to yield the two-dimensional polymer [Ag(hmt)] ClO₄, 1, while a twofold excess of AgClO₄ gives [Ag₃(hmt)₂] [ClO₄]·2H₂O 2, in which metal ions (with their counter-ions and water molecules) intercalate between sheets like those of 1, joining them (as spacers) to give a three-dimensional (3,4)-connected network of uncommon topological type.

Compound 1 can be obtained in large yields, as needle shaped colourless crystals, on layering over a CH₂Cl₂ solution of hmt an ethanolic solution of AgClO₄ (molar ratio 1:1). The crystal structure of 1 consists of two-dimensional infinite layers of hexagonal meshes formed by alternate triconnected silver ions and hmt molecules [Fig. 1(a)]. These layers are similar to those present in the polymeric [Ag(hmt)]NO₃), 9 the main difference being the stronger Ag···O(NOₓ⁻) interactions, 2.593(8) and 2.62(1) Å, vs. the Ag···O(ClO₄²⁻) ones in 1, 2.796(5) Å. It is noteworthy that the rings in the sheets present a rare conformation of the boat type [see Fig. 2(a)], instead of the usual chair conformation (grey arsenic-like or black phosphorus-like layers).

![Scheme 1](image)

**Fig. 1** A SCHAKAL view of the stacking of the two-dimensional layers in compounds **1 (a)** and **2 (b)**. In **2** only one of the two locations of the statistically disordered ClO₄⁻ and H₂O (see text) is shown for clarity.
On performing the above reaction with an AgClO₄:hmt ratio of 2:1 we have observed the initial formation of crystals of 1, but on allowing the solution to concentrate by evaporation the reaction further proceeds giving fine multifaced crystals of 2, investigated by X-ray diffraction analysis.‡

The structure of 2 consists of an open three-dimensional cationic network formed by [Ag(hmt)] hexagonal layers as in 1, joined by biconnected silver ions, which coordinate to the free N atoms of the hmt ligands [Fig. 1(b)]. The Ag–N bond lengths for these spacers, 2.223(5) Å, are shorter than those involving the other silver ions, 2.355(5)–2.396(4) Å [2.326(5)–2.373(4) Å in 1]. On passing from 1 to 2 a relative sliding of the layers takes place, together with a change of the ring conformation from boat (to give black phosphorus-like layers) and, what is particularly interesting, the interlayer separation increases from 7.32 to 9.65 Å. Guest water molecules occupy the large, approximately hexagonal, channels [Fig. 1(b)] and interact with the silver ions of the layers [Ag–O bond lengths of 2.467(10) Å]. Thermal analyses have shown that these water molecules can be reversibly removed from the crystals by thermal activation.§

From the topological point of view the three-dimensional framework of 2 is a (3,4)-connected net, comprised of triconnected (silver ions of the layers) and tetraconnected (hmt molecules) centres in the ratio 1:1 [Fig. 2(b)]. The topological type can be assigned, following the pioneering ideas of Wells,† on considering that the shortest circuits starting and ending on each centre are all three 6-gons for the triconnected silver ions and 6-gons and 8-gons in the ratio 5:1 for the hmt ligands, hence (6)⁵(6,8)-b. Wells has described four nets with this connectivity and has classified that one here reported as (6)⁵(6,8)-b, 10 space group Pmnn (no. 58), a = 6.535(2) Å, b = 10.453(2) Å, c = 19.293(8) Å, \(U = 1317.5(7) \, \text{Å}^3\). The final agreement index \(R = 0.0274\) for 674 independent significant \([I > 3\sigma(I)]\) absorption corrected data. Anisotropic thermal factors were assigned to all the non-hydrogen atoms.

2: orthorhombic, Pmn2₁ (no. 34), a = 6.1593(5) Å, b = 10.433(2) Å, c = 19.293(8) Å, \(U = 1317.5(7) \, \text{Å}^3\). The structure was solved by direct methods and refined by full-matrix least-squares analysis. One of the perchlorato anions and the solvated water molecule, which is hydrogen bonded to it, form a pair statistically disordered about a mirror plane. The final agreement index \(R = 0.0453\) for 1158 independent significant \([I > 3\sigma(I)]\) absorption corrected data. Other experimental features are as in 1.

We have not isolated the supertetrahedral [Ag₄(hmt)] hypothethical frame of Scheme 1, but compound 2 represents at least a step in that direction. Factors such as, inter alia, the tendency of the metal ions to achieve coordination numbers higher than two and that of hmt to be less than tetradentate, as in 1 and in [Ag(hmt)I]PF₆·H₂O, can operate against the desired goal. Nevertheless, interesting networks joined exclusively via metallic synthons will probably assume some relevance in the near future.

Footnotes
† We call metallic synthon, extending the term used for the supramolecular interactions in organic systems by Desiraju, the interaction of two polydentate organic bases mediated by a metal ion (or complex) which, dedicating only two coordination sites to the net, does not influence its topology. Hoskins and Robson have previously considered this kind of interaction.‡ Nevertheless, the networks exclusively based on organic molecules (as centres) and metallic synthons are quite rare.
‡ Crystal data: 1: orthorhombic, Pmnn (no. 62), a = 6.6484(2) Å, b = 10.636(3) Å, c = 14.651(3) Å, \(U = 1010.45(5) \, \text{Å}^3\). The final agreement index \(R = 0.0274\) for 674 independent significant \([I > 3\sigma(I)]\) absorption corrected data. Anisotropic thermal factors were assigned to all the non-hydrogen atoms.
§ Differential scanning calorimetry (DSC) shows an endothermic peak at 140 °C and left in air for a few hours display again the same DSC peak.

References

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Fig. 2 A schematic view, approximately down the a axis, of the two-dimensional layers in 1 (a) and of the three-dimensional network (6)⁵(6,8)-b in 2 (b). Filled spheres = Ag⁺ open spheres = baricentres of the hmt molecules.