# A Novel 3D Three-Connected Cubic Network Containing $[Ag_6(hmt)_6]^{6+}$ Hexagonal Units (hmt = Hexamethylenetetramine)

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The deliberate design of new nanoporous materials based on polymeric coordination compounds requires a careful selection of both the metallic centers and the polydentate ligands.[1] The assembly of these polymers can be attempted by following two main strategies: (i) with linear bidentate ligands, nets containing only metallic nodes are obtained; (ii) using proper polydentate ligands, nets with alternate metallic and organic centers can be recovered. This difference is well exemplified by two very recently reported structures, both topologically related to the 3D triconnected silicon framework of the prototypal $\alpha$-$ThSi_2$, namely $[Ag_2(pyz)_3](BF_4)_2$ (pyz = pyrazine), containing all Ag(I) centers (3-fold interpenetration),[2] and $[Ag(teb)](CF_3SO_3)$ [teb = 1,3,5-tris((4-cyanophenyl)ethynyl)benzene], with alternate Ag(I) and organic centers (6-fold interpenetration).[3] Moreover, a third possibility arises when one considers that digonal coordination is very common for Ag(I) [and Cu(I)]: these metals can play the role of simple spacers, or connectors, for polydentate ligands (ligand···metal···ligand synthons),[4] with the geometry of the supramolecular array driven only by the organic donor units. In this context, it seemed quite appealing to react Ag(I) salts of noncoordinating anions with the potentially tetradentate hexamethylenetetramine (hmt), in order to possibly produce supertetrahedral networks with large interstitial cavities, paralleling the supramolecular chemistry of adamantyl templates with different synthons.[4,5] Our investigations have shown that there are two factors that might conflict with this endeavor: hmt is commonly less than tetradentate in these systems, and Ag(I) often achieves a coordination number higher than 2. Nevertheless, we describe here a novel and interesting polymeric 3D network which exhibits some of the desired features: it contains large hexagonal units of hmt molecules linked by biconnected Ag(I) ions acting as spacers.

We recently reported that when solutions of $AgPF_6$ and hmt in $EtOH/CH_2Cl_2$ were evaporated to dryness, a polymeric species was obtained, namely $[Ag(hmt)](PF_6)\cdot H_2O$,[6] containing a 3D triconnected network topologically related to the prototypal $SrSi_2$ (net $10^3$-a, according to Wells[7]). Since the above reactions led to mixtures of products, we repeated them under slightly different conditions, with the aim of isolating other derivatives. When 1 mL of ethanol and an ethanolic solution (5 mL) of $AgPF_6$ (0.096 g, 0.38 mmol) were over a $CH_2Cl_2$ solution (4 mL) of hmt (0.053 g, 0.38 mmol), the formation of small, beautiful colorless crystals was observed at the interface region after few days. The crystals, mechanically separated from the mixture, revealed the presence of two morphologies: a dominant multifaced type (compound **1**) together with minor amounts of small parallelepipeds (compound **2**). The nature of both species was established by single-crystal X-ray analysis, which revealed that **1** is an oligomeric complex, $[Ag_5(hmt)_6](PF_6)_5\cdot 3CH_2Cl_2$, while **2** is a 3D polymer, $[Ag_4(hmt)_3(H_2O)](PF_6)_4\cdot 3EtOH$.[8]

The structure of compound **1** shows the presence of the large $[Ag_5(hmt)_6]^{5+}$ cation, of idealized $D_{3h}$ symmetry, illustrated in Figure 1. It forms a cage reminiscent of molecules with fused cycles (bicyclic macrocycle).[9] The six hmt ligands are biconnected and are disposed at the corners of a trigonal prism. Two of the Ag(I) ions are triconnected and placed at the centers of the two triangular faces [Ag1−N1 2.35(2) Å, N1−Ag1−N1 116.4(2)°], while the other three metals bridge the lateral (axial) edges [Ag2−N2 2.185(13) Å, N2−Ag2−N2 169.1(7)°]. The center of the cage is empty with distances for the equatorial and apical silver ions of 4.18 and 4.40 Å, respectively. Three $PF_6^-$ anions, weakly coordinated to the equatorial Ag2, direct three fluorine atoms toward the center.

Compound **2** consists of an infinite cationic array composed of almost planar hexagonal units of six hmt molecules linked by biconnected Ag(I) ions [Ag2−N 2.217(12) and 2.228(12) Å, N−Ag2−N 170.1(5)°], as shown in Figure 2. Folded hexagonal meshes were previously observed in the 2D polymer $[Ag(hmt)](NO_3)$,[10] but were formed by three alternate hmt and Ag(I) ions, both triconnected. The large hexagons form bonds to six Ag(I) ions, which are oriented alternately three above and three below the hexagonal plane. These metal ions (Ag1) are triconnected to hmt and join the hexagonal units to give the

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(8) Crystallographic details are as follows. $[Ag_5(hmt)_6](PF_6)_5\cdot 3CH_2Cl_2$ (**1**): $C_{39}H_{78}Ag_5Cl_6F_{30}N_{24}P_5$, fw 2360.15, hexagonal, $P6_3/m$ (No. 176), $a = 16.395(2)$ Å, $c = 16.030(2)$ Å, $V = 3731.5(8)$ Å$^3$, $Z = 2$, $D_c = 2.101$ Mg m$^{-3}$, Mo K$\alpha$ radiation ($\lambda = 0.710\,69$ Å), $\mu$(Mo K$\alpha$) = 1.738 mm$^{-1}$. The data collection was performed at 293 K on an Enraf-Nonius CAD4 diffractometer, by the $\omega$-scan method, within the limits $3 < \theta < 25°$; an empirical absorption correction was applied. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares (SHELX93). Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The final agreement indices $R$ and $R_w$ for all 1220 independent observed [$F_o > 4\sigma(F_o)$] data were 0.0549 and 0.1035, respectively. All the diagrams were obtained using the SCHAKAL program. $[Ag_4(hmt)_3(H_2O)](PF_6)_4\cdot 3EtOH$ (**2**): $C_{24}H_{56}Ag_4F_{24}N_{12}O_4P_4$, fw 1588.17, cubic, $Pa\bar{3}$ (No. 205), $a = 21.850(5)$ Å, $V = 10432(4)$ Å$^3$, $Z = 8$, $D_c = 2.022$ Mg m$^{-3}$, $\mu$(Mo K$\alpha$) 1.733 mm$^{-1}$. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, except the disordered solvated ethanol molecules. The final values of the agreement indices $R$ and $R_w$ for the 1356 independent observed [$F_o > 4\sigma(F_o)$] data were 0.0718 and 0.1714, respectively. Other experimental features are as in **1**.

(9) The cage has the topology of bicyclo[2.2.2]octane, as occurs in lonsdaleite or wurtzite networks. It is interesting to note that $[NH_4\cdot hmt]BF_4$ has a superwurtzite structure containing cages of the above type. See: Ermer, O.; Eling, A. *J. Chem. Soc., Perkin Trans.* **1994**, 925. We thank a reviewer for these suggestions.

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S0020-1669(97)00043-8 CCC: $14.00

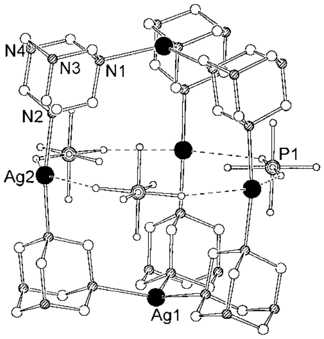

**Figure 1.** Schematic view of the $[Ag_5(hmt)_6]^{5+}$ oligomer of compound **1**. The weak Ag2···F contacts are 2.78(2) and 2.97(3) Å. The hydrogen atoms of the hmt ligands are omitted for clarity.

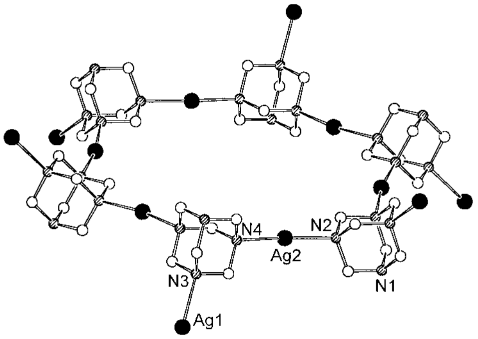

**Figure 2.** The large hexagonal unit of compound **2**. The six silver ions display a deviation from their best plane of ±0.12 Å.The hydrogen atoms of the hmt ligands are omitted for clarity.

infinite 3D network, with a Ag1:hexagon ratio of 2:1 (see Figure 3). The baricenters of the hexagons (not the hexagons themelves) give rise to an fcc lattice. The Ag1 ions (lying on 3-fold axes) also present a bonding interaction with a (terminal) water molecule, which is not relevant to the frame topology. Their coordination geometry is distorted tetrahedral [Ag1−N3 2.355(12) Å, Ag1−O 2.48(3) Å, N3−Ag1−N3 117.9(1)°, N3−Ag1−O 98.3(3)°].

The whole frame is, therefore, a triconnected 3D net, composed of two types of centers [hmt and Ag1, in a ratio of 3:1], illustrated in Figure 3. The topological type can be assigned by considering the three shortest circuits starting and ending at each center, *i.e.* hexagons and decagons (ratio 1:2) for the hmt molecules and decagons for the Ag(I) ions, $(6,10^2)_3(10^3)$ according to Wells.[7] The decagonal circuits present the sequence $-(hmt)_2-Ag-(hmt)_2-Ag-(hmt)_3-Ag-$, *i.e.*, the rings involve three silver ions and three hexagons (bonded *ortho*, *ortho*, and *meta*). This topology is, to our knowledge, new, though a related simpler net consisting of directly interconnected hexagons, $(6,10^2)$, was considered by Wells[7] and actually observed in $\beta$-hydroquinone (2-fold interpenetration)[11] and in the hydrogen-bonded frame of water molecules in the clathrate hydrate hmt·6H$_2$O.[12] The network of **2** presents large cavities and channels of the hexagonal sections (see Figure 3, bottom), containing as guests the $PF_6^-$ anions and the solvent molecules.

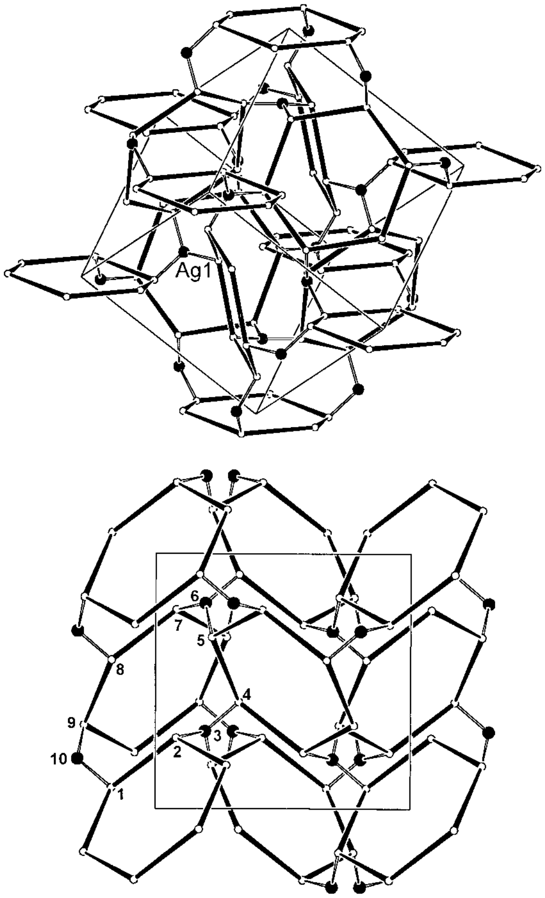

**Figure 3.** Two sketches of the $[Ag_4(hmt)_3]$ cationic framework of **2**, showing the connections of the hexagonal units (formed by the baricenters of hmt) with the Ag1 ions: Top, view with the [111] direction almost vertical; bottom, view down [100], with one of the decagonal circuits (see text) numbered.

The results here described confirm, at least in part, that, with polydentate bases, simple metal ions can play the unusual "*inverted*" role of spacers (metallic synthons) in the assembly of networks.[13] Other studies in this area, involving the use of different anions and/or solvents, are in progress.

**Supporting Information Available:** X-ray crystallographic files, in CIF format, for **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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(13) Also, metal complexes with two *transoid* sites available for coordination are potential spacers for the assembly of networks based on polydentate molecules.[1a] This is the case for an α-ThSi$_2$ type frame recently reported, $[\{Mn(hfac)_2\}_3L_2]$, where L = a complex trinitroxide radical: Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803.