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# *Communications to the Editor*

## A Three-Dimensional, Three-Connected Cubic Network of the $SrSi_2$ Topological Type in Coordination Polymer Chemistry: $[Ag(hmt)](PF_6)\cdot H_2O$ (hmt = Hexamethylenetetraamine)

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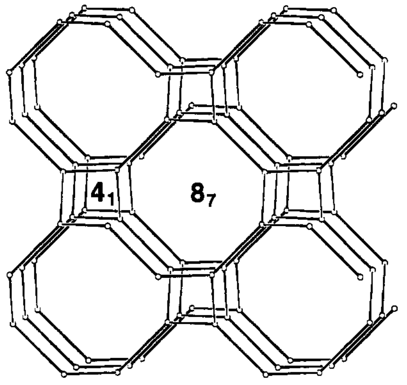
The recent development of crystal engineering in coordination polymer chemistry has shown that molecular-based frameworks related to prototypal structural types, of potential utility as novel materials, can be assembled using proper metallic centers and suitable polydentate ligands.[1] Examples of networks related to the archetypes diamond,[2] α-polonium,[3] α-$ThSi_2$,[4] rutile,[5] PtS,[6] and quartz[7] have been reported.

We have already described silver(I) polymeric complexes with bidentate N,N′-donor ligands, which exhibit frameworks topologically related to diamond,[8] α-$ThSi_2$,[9] and simple cubic α-polonium;[10] these structures have shown the great versatility of the silver ions, assuming coordination geometries ranging from trigonal, to tetrahedral, and even to octahedral. We report here on a silver polymer with the potentially tetradentate hexamethylenetetraamine (hmt), $[Ag(hmt)](PF_6)\cdot H_2O$ (**1**), which contains a molecular-based framework topologically related to the three-dimensional, three-connected (3-D, 3-C) net of highest symmetry (cubic, space group $I4_132$; see **I**, Chart 1),[11] exemplified (in a less symmetrical configuration, *i.e.*, space group $P4_132$) by the prototypal $SrSi_2$.[12] Only one other coordination polymer with this topology is presently known, *i.e.*, the anionic $Fe^{II}$−oxalate frame in $[Fe^{II}(2,2'\text{-bipy})_3][Fe^{II}_2(ox)_3]$.[13] Moreover, **1** is the first example of a 3-D network bridged by hmt only.

**Chart 1**



**I**

Compound **1** was obtained by 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). The solid product contains mainly tetrahedral or octahedral crystals of **1** (~80%),[14] together with a minor amount of other microcrystalline materials, which are presently under investigation. Compound **1** is air and light stable, and its nature has been established by single-crystal X-ray analysis.[15]

The crystal structure of **1**, shown in Figure 1, consists of an infinite cationic array of trigonal silver ions (lying on 3-fold axes) bridged by tridentate hmt ligands. Each $Ag^I$ is surrounded by six nearest-neighbor silvers, with an Ag···Ag separation of 6.479(2) Å. The tridentate hmt ligands also lie on 3-fold axes and display a somewhat trigonally flattened coordination of the three N atoms to the silver ions. The cationic frame displays an Ag−(center of hmt) distance of 3.85 Å.[16] A schematic view of this 3-D net is shown in Figure 2. It contains, in contrast to the prototypal frame **I** (as well as to the anionic network of ref 13), two types of alternating centers, so that the original interconnected $4_1$ helical chains become here $2_1$-Ag−hmt−Ag−hmt−helixes. The $PF_6^-$ anions and the guest water molecules occupy the large octagonal channels and, interestingly, form an extended system of (rather long) hydrogen bonds (see Figures 1 and 2), which results in an interpenetrating (anionic) network of the same topological type of the cationic one.

The 3-D, 3-C enantiomorphic network reported here is of interest at the fundamental structural level. Wells describes this topological type as a uniform $10^3$ net, meaning that the shortest complete circuits including any pair of links from any point are 10-gons.[11] It may be regarded as the 3-C analogue of the

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(14) A sample of crystals of **1**, separated mechanically, gave the following analysis. Anal. Calcd for $C_6H_{14}AgF_6N_4OP$: C, 17.53; H, 3.43; N, 13.63. Found: C, 17.41; H, 3.50; N, 13.50.

(15) Crystal data: $C_6H_{14}AgF_6N_4OP$, fw 411.05, cubic, $P2_13$ (No. 198), $a = 10.578(3)$ Å, $V = 1183.6(6)$ Å$^3$, $Z = 4$, $D_c = 2.307$ Mg m$^{-3}$, Mo Kα radiation ($\lambda = 0.710\,69$ Å), $\mu$(Mo Kα) 1.915 mm$^{-1}$. The data collection was performed at 293 K on an Enraf-Nonius CAD4 diffractometer, by the $\omega$-scan method, within the limits $3 < \theta < 27°$; an empirical absorption correction (based on $\psi$-scans) was applied. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares based on $F^2$ (SHELX93). Anisotropic thermal parameters were assigned to all the non-hydrogen atoms. The two water hydrogen atoms, lying about a 3-fold axis, are disordered with occupancy of 2/3. The final agreement indexes $R$ and w$R^2$ for all 498 independent observed $[F_o > \sigma(F_o)]$ data were 0.0141 and 0.0338, respectively, for the correct enantiomorph. All the diagrams were obtained using SCHAKAL program.

(16) For the ideal network **I**, the relationship between the unit length $d$ and the cell edge is $a = (2)^{3/2}d$, which would give in the present case ($d$ = 3.85 Å) a slightly larger cell edge (10.89 Å) than that observed, the difference being due to the nonplanar coordination of the hmt ligands.

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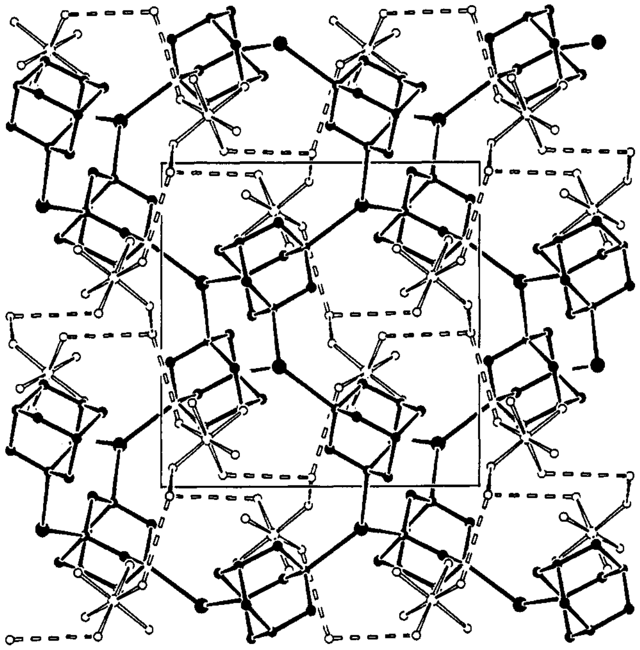

**Figure 1.** Packing of **1**. Dotted lines indicate the hydrogen bond network. The hydrogen atoms of the hmt ligands are omitted for clarity. Relevant bonding parameters: Ag−N 2.362(2) Å, F···O 3.056(3) Å, N−Ag−N 119.52(1)°, Ag−CM−Ag 114.6°, CM−Ag−CM 119.0°, and F···H−O 150(6)°; where CM is the center of mass of the hmt ligand. A weak Ag···O interaction of 2.892(2) Å is also observed.

(4-C) diamond net.[11b] Recent theoretical studies on possible new low-energy forms of carbon have considered this topology.[17] However, it is quite rare, the known examples (after Wells[11]) including the silicon frame in $SrSi_2$ at normal conditions, the hydrogen bonded network of $H_2O_2$, and the $Hg_3S_2$ frame in $Hg_3S_2Cl_2$. The same topological type of network can be envisaged also in $Sn_2F_3Cl$[18] and in β-$SnWO_4$.[19]

The possible accommodation in the same volume occupied by frame **I** of a second net, having helixes of opposite chirality and interpenetrating the former one, as the hydrogen-bonded net here described, was also anticipated by Wells on a purely theoretical basis.[11a]

Both silver ions and hmt ligands are able to assume different coordination modes; the role of the anions and the eventual presence of solvated molecules within the frame, are, therefore, of fundamental importance in the assembly of a specific structural motif.[20]

An hypothetical cationic [Ag(hmt)] frame based on tetrahedral $Ag^I$ and tetradentate hmt could assume a super-diamond structure in the presence of counterions of proper dimensions. The network of **1** could be ideally converted into a diamondoid frame by connecting all the silver ions with the noncoordinating N atoms of the facing hmt ligands along the 3-fold crystallographic axes (in the Ag···$H_2O$···N direction). However, the cages would be too small (distance from the center to the four nearest cage nodes, 3.85 Å) to accommodate the $PF_6^-$ anions.

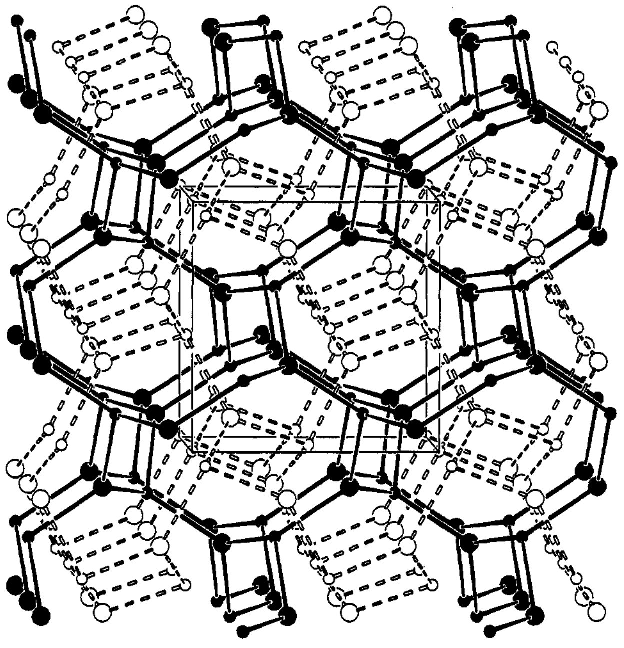

**Figure 2.** Schematic view of the framework in **1**. The cationic net is black (large balls, silver ions; small balls, centers of mass of the hmt ligands), and the hydrogen bond net is white, with dotted lines (large balls, $PF_6^-$ anions; small balls, water molecules). Note that one-third of the hydrogen bonds are lacking, given the hydrogen atoms disorder.[15]

The cationic framework is preserved also after thermal removal of the water molecules. Differential scanning calorimetry (DSC) shows an endothermic peak at 154 °C ($\Delta H \approx 7$ kcal/mol), and thermogravimetric analysis (TGA) gives at that temperature a weight loss corresponding to 1 water molecule per formula unit.[21] Monitoring of the heating process up to 200 °C by X-ray powder diffraction analysis shows that the diffraction pattern remains substantially unchanged although broadening of all peaks occurs, with a small shortening of the cubic cell parameter down to 10.54 Å. The process is reversible, since samples heated to 170 °C and left in air for a few days display again the same DSC peak at 154 °C, and the original cell parameters are restored.

**Supporting Information Available:** Molecular scheme with numbering and tables of crystal data, data collection, structure determination, and refinement details, fractional atomic coordinates and thermal parameters, and bond distances and angles (5 pages); structure factors for **1** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(20) A polymer of similar stoichiometry, [Ag(hmt)]($NO_3$), presents trigonal coordination of the metal ions and tridentate hmt ligands, as in **1**, but adopts a 2-D structure, consisting of infinite sheets of hexagonal meshes: Michelet, A.; Viossat, B.; Khodadad, P.; Rodier, N. *Acta Crystallogr.* **1981**, *B37*, 2171.

(21) The frame is stable up to ~200 °C and begins to decompose after an exothermic peak at 213 °C ($\Delta H \approx -22$ kcal/mol).