Triple Interpenetration in [Ag(4,4′-bipyridine)][NO$_3$], a Cationic Polymer with a Three-dimensional Motif Generated by Self-assembly of 'T-shaped' Building Blocks

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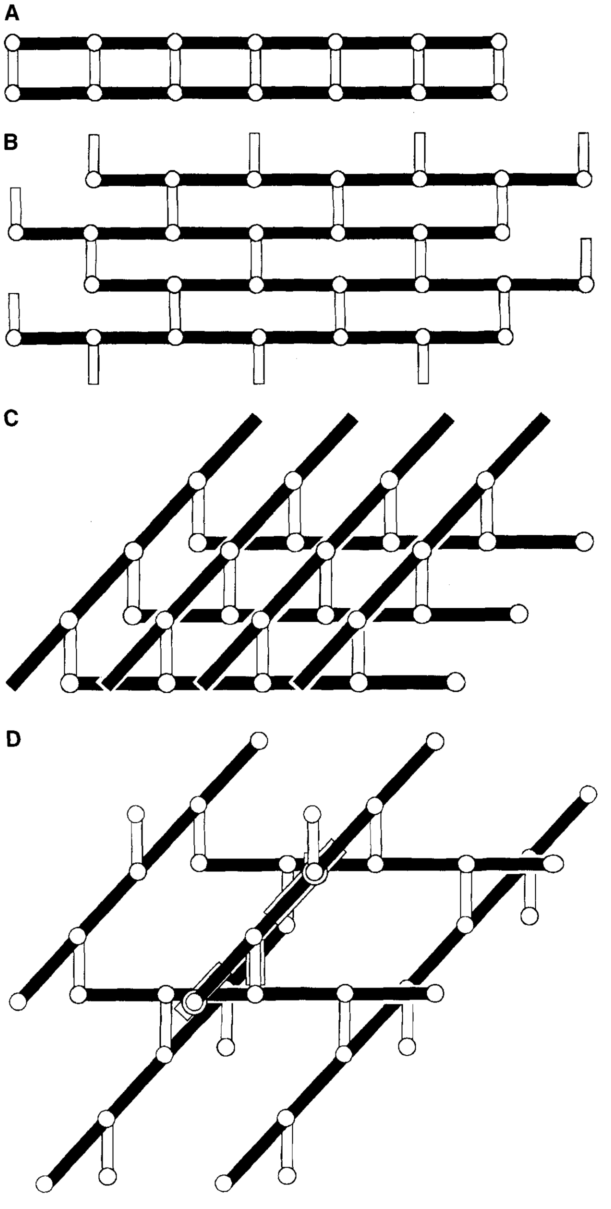
We report the synthesis and single-crystal X-ray structure of a triply interpenetrated cationic framework with a three-dimensional motif that is based upon T-shaped building blocks generated by silver(I) cations and 1 equivalent of 4,4′-bipyridine.

Crystal engineering based upon coordination polymers has evolved rather rapidly in recent years following the outline by Robson and Hoskins[1] of general principles for crystal engineering of three-dimensional coordination compounds. Several groups have recently demonstrated[2–6] that the simple strategy of combining known transition-metal coordination environments with multifunctional exodentate ligands can generate mineralomimetic crystalline architectures with obvious implications for rational design of functional solids. Linear bifunctional 'spacer' or 'rod' ligands have been used to propagate a number of motifs. Diamondoid frameworks that are based upon tetrahedral transition metals or clusters that are capable of sustaining S_4 symmetry represent perhaps the most ubiquitous class yet reported.[7] In such a context, several ligands have been employed as linear exodentate 'spacers' with 4,4′-bipyridine (4,4′-bipy) representing a prototypal example of a rigid 'spacer' ligand. In this communication we report the dramatic effect that 4,4′-bipy can impart on crystalline architecture with even a simple and readily available metal template, Ag^{I}.



Scheme 1 A schematic representation of the four motifs, **A–D**, that are likely to occur from self-assembly of T-shaped moieties. Compound **1** adopts motif **D**, with circles representing Ag cations, filled bars representing 4,4′-bipy molecules and empty bars representing Ag–Ag bonds.

We and others have recently described infinite diamondoid,[8] honeycomb[5,8] and octahedral[9] frameworks, based upon tetrahedral, trigonal and octahedral metal templates, respectively, linked to 4,4′-bipy or pyrazines. Silver(I) is known to exist in several coordination environments, especially linear and tetrahedral.[10] We therefore anticipated that reaction of AgNO$_3$ with 4,4′-bipy would afford either a linear or a diamondoid framework, depending upon the ratio of 4,4′-bipy to Ag, 1 : 1 or 2 : 1, respectively. However, the spontaneous reaction product of AgNO$_3$ with either 1 or 2 molar equivalents of 4,4′-bipy in MeCN, [Ag(4,4′-bipy)][NO$_3$] **1**, is a manifestation of an unusual geometry for Ag^{I}, three-coordinate 'T-shape' (an Ag–Ag bond occupies the third coordination site).† As illustrated in Scheme 1, self-assembly of T-shaped moieties would reasonably be expected to generate one of four possible motifs. Indeed, two of the four motifs, the one-dimensional 'ladder', **A**, and the two-dimensional 'brick', **B**, were recently reported for what could be called a pseudo 'T-shaped' complex of square-planar Cd^{II} in which one site is occupied by a terminal ligand and the remaining three sites are occupied by linear 'spacer' ligands.[3b] The crystal structure of **1** (Figs. 1 and 2) reveals three independent interpenetrated networks of another of the motifs, the three-dimensional motif, **D**. Each network consists of linear [Ag(4,4′-bipy)]$_\infty$ chains cross-linked by Ag–Ag bonds of 2.970(2) Å.‡ **1** is to our knowledge the first example of a three-dimensional framework that is sustained by self-assembly of T-shaped moieties unless one also considers one of the two forms of [Ag$_2$(pyrazine)$_3$][BF$_4$]$_2$,[4b] which exhibits a similar motif but with a coordination environment around Ag that is intermediate

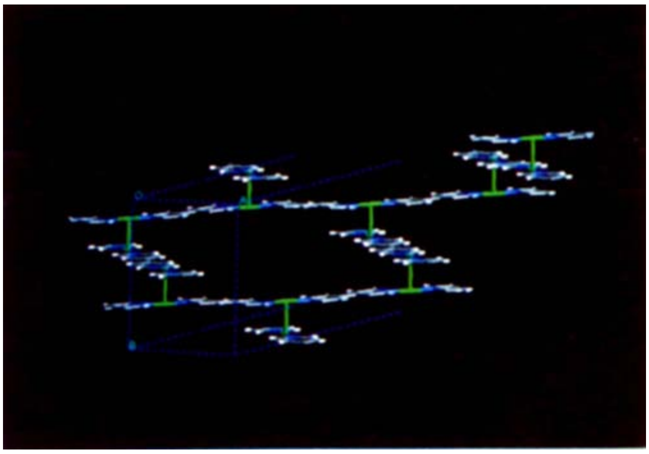


Fig. 1 A single cationic framework of **1**. Ag–N and Ag–Ag distances are 2.163(6) and 2.9696(20) Å, respectively, and the N–Ag–N angles are 173.7(3)°.

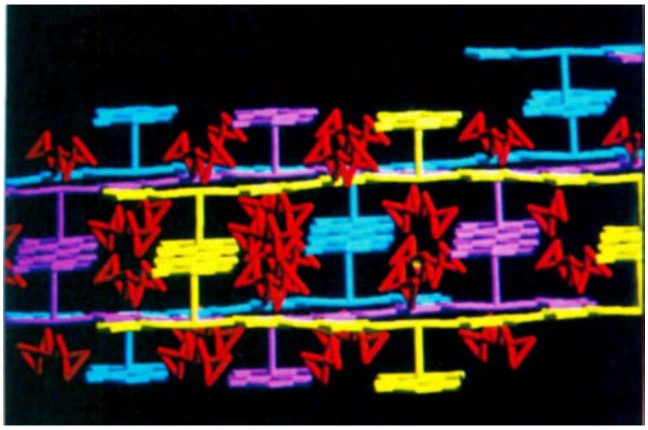


Fig. 2 A view of the three independent frameworks in **1**. The independent networks are coloured magenta, yellow and blue, respectively, and the disordered nitrate anions that occupy channels in the *ac* plane are presented in red.

between 'T-shaped' and trigonal. Interestingly, this compound also crystallizes in space group *Fddd* with $Z = 16$ and three interpenetrated three-dimensional networks. A single cationic framework of **1** is illustrated in Fig. 1 and reveals an open framework with large interconnected cavities that form stair-like microchannels of approximate cross-section 6 × 23 Å. The Ag^I cations occupy crystallographic twofold positions and the Ag–N bonds are therefore identical [2.163(6) Å]. The NO_3^- counter ions also lie around crystallographic twofold axes that represent two types of microchannel that lie roughly orthogonal to one another in the *ac* plane. The oxygen atoms of the nitrate anions are crystallographically disordered. The shortest Ag···O distances, 2.789(21) Å, are beyond what one would expect for covalent bonding but are consistent with contacts in other nitrate salts of silver(I) complexes.

It is becoming increasingly clear that microporous structures with designable pore sizes that exceed those found in zeolites are in principle achievable *via* a crystal engineering approach. Unfortunately, interpenetration of the type encountered herein frequently occurs in solids with voids that occupy more volume than the network itself, thereby precluding realization of the full potential for porosity.[2–7] Nevertheless, our results indicate that even the simplest and most readily available transition-metal templates can be exploited in order to rationally generate covalent frameworks. Furthermore, although the 'T-shaped' coordination environment is extremely rare, in principle, any square-planar metal moiety should also be capable of forming motifs **A–D** if the coordination sphere contains three 'spacer' ligands and one monofunctional terminal ligand.

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Footnotes

† *Crystal data* for **1**: [Ag(4,4′-bipy)] [NO_3], $M = 326.1$, orthorhombic, space group *Fddd*, $a = 9.9122(10)$, $b = 12.9515(15)$, $c = 34.482(4)$ Å, $U = 4426.7(9)$ Å^3, $Z = 16$, $D_c = 1.96$ mg m^{-3}, $\lambda = 0.70930$ Å, $F(000) = 2560$. 654 absorption corrected reflections (empirical ψ-scan, transmission range 0.85–0.92) with $I_{net} > 3\sigma(I_{net})$ out of the 978 unique reflections measured at 290 K for a crystal of dimensions 0.2 × 0.3 × 0.4 mm on an Enraf-Nonius CAD4 diffractometer using the ω-scan model ($4 < 2\theta < 50°$) on convergence gave final values of $R_f = 0.041$ and $R_w = 0.046$. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were calculated ($d_{C-H} = 1.00$ Å) and fixed with thermal parameters based upon the carbon atom to which they are bonded. The nitrate oxygen atoms were observed to be disordered over two sites and refined at 50% occupancy. All crystallographic calculations were carried out with the PC version of the NRCVAX program package locally implemented on an IBM compatible 80486 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ One could compare this interatomic distance with the following: (*a*) the metallic radius of Ag, 1.44 Å (U. Müller, *Inorganic Structural Chemistry*, p. 32, Wiley, Chichester, 1993). (*b*) Au–Au distances of 2.9947 Å in the T-shaped moieties present in [{[Au(pyridine)$_2$]AuI$_2$}$_2$] (H.-N. Adams, W. Hiller and J. Strahle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 81). (*c*) The Cambridge Structural Database (F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146) contains 18 'T-shaped' Ag^I coordination environments of which all but three are restricted because of chelating ligands. The unrestricted compounds, FUWXIE, SERVIU and JOKWEL, exhibit Ag–Ag distances that range from 3.1796 to 3.3012 Å. Surprisingly, [Ag(pyridine)$_2$] [NO_3]·H_2O, AGPYNO, does not contain Ag–Ag bonds, the closest Ag···Ag contact being >4 Å.

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