1-, 2-, and 3-Dimensional Polymeric Frames in the Coordination Chemistry of $AgBF_4$ with Pyrazine. The First Example of Three Interpenetrating 3-Dimensional Triconnected Nets

Lucia Carlucci, Gianfranco Ciani,* Davide M. Proserpio, and Angelo Sironi

Contribution from the Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Via G. Venezian 21, 20133 Milano, Italy

Received November 22, 1994®

Abstract: The reactions of $AgBF_4$ with pyrazine (pyz) in ethanol have led to the isolation of four polymeric coordination products. Using a 1:1 salt/pyz molar ratio, the polymeric species $[Ag(pyz)](BF_4)$(**1**) was obtained, while on performing the reaction with a salt/pyz ratio of 1:2, after the initial precipitation of **1**, a crystalline product formed, having a composition corresponding to $[Ag_2(pyz)_3](BF_4)_2$ (**2**). The crystals of **2** presented two different morphologies: the largely dominant species (**2a**) is air stable, while the other one (**2b**) decomposes when removed from the mother solution. With higher pyz/salt ratios another unstable species was isolated, with composition $[Ag(pyz)_3](BF_4)$ (**3**). Single-crystal X-ray analyses of the four products have been carried out; these have shown that **1** and **3** are 1-D polymers, with linear and zigzag chains, respectively, and have revealed very interesting structural features for the polymorphic **2a** and **2b** species, both containing three-connected Ag^+ ions. The structure of **2a** consists of 2-D 3-C frames formed by six-membered rings of pyz-bridged metal ions in the chair conformation, adjacent pairs of rings being connected in a way reminiscent of the disposition of the rings in *cis*-decaline, thus resulting in markedly undulated layers. More surprisingly, **2b** contains three translationally equivalent interpenetrating 3-D 3-C frameworks, each being topologically similar to the silicon frame in α-$ThSi_2$, an archetypal structure containing one of the three simplest 3-D 3-C nets. The structure of each individual 3-D frame is comprised of layers of parallel -Ag-pyz-Ag-pyz- zigzag chains joined by pyz bridges along the axis normal to the layers; the chains rotate by 55.4° about the normal axis on passing from one layer to the adjacent one and then turn back to the previous direction on further passing to the successive layer (in a *ABAB* sequence). This is, to our knowledge, the first structure presenting three interpenetrating 3-D 3-C frameworks. Compound **1** is orthorhombic, space group *Pmcb* (No. 55), with $a = 7.136(3)$ Å, $b = 7.217(1)$ Å, $c = 14.855(4)$ Å, $Z = 4$, final $R = 0.0266$ $[F_o > 4\sigma(F_o)]$. The crystals of **2a** are monoclinic, space group $P2_1/n$ (No. 14) with $a = 8.385(1)$ Å, $b = 11.785(1)$ Å, $c = 9.797(1)$ Å, $\beta = 102.15(1)°$, $Z = 4$, final $R = 0.0255$ $[F_o > 4\sigma(F_o)]$. Compound **2b** is orthorhombic, space group *Fddd* (No. 70), with $a = 11.579(2)$ Å, $b = 13.272(3)$ Å, $c = 25.304(5)$ Å, $Z = 16$, final $R = 0.0267$ $[F_o > 4\sigma(F_o)]$. Compound **3** gives triclinic crystals, space group $P\bar{1}$ (No. 2), with $a = 7.994(5)$ Å, $b = 10.253(3)$ Å, $c = 10.768(3)$ Å, $\alpha = 90.04(2)°$, $\beta = 102.63(5)°$, $\gamma = 111.47(5)°$, $Z = 2$, final $R = 0.0417$ $[F_o > 4\sigma(F_o)]$. The Ag three-coordination both in **2a** and in **2b** is strictly planar and intermediate between T-shaped and trigonal. In **3** the silver atoms display a distorted tetrahedral geometry, being bonded to two bridging and two unidentate pyz ligands.

Introduction

The ability of pyrazine (pyz) and substituted pyrazines to act as *exo*-bidentate ligands, thus giving rise to the formation of oligomeric and polymeric metal complexes, is well-established.[1] Particular attention has been devoted recently to the development of rational synthetic routes to polymeric coordination complexes of these and related ligands, because they are of interest in connection with materials science, for their potential properties such as electrical conductivity [for instance, in (phtalocyaninato)metal–pyrazine polymers],[2] magnetism (particularly in low-dimensional 1-D or 2-D solids),[1a,3] and photomechanical behavior.[4] Unusual properties were also discovered, as the acoustic emission detected in the preparation of polymeric $ZnCl_2$–pyrazine species.[5] Moreover, Hoskins and Robson[6] have recently proposed a strategy in the design of new 3-D phases, indicated as "scaffolding-like materials", which are assembled by using suitable metal centers and molecular rods of different nature and length and have potential utility in ion-exchange and catalysis. This *rationale* also has been fruitfully applied recently in the case of Cu(I)–pyrazine polymeric systems, leading to a diamondoid framework,[7] and to an interwoven honeycomb architecture.[8]

The known examples of polymeric complexes of pyrazine, substituted pyrazines and related bases, like quinoxaline and

---

® Abstract published in *Advance ACS Abstracts,* April 1, 1995.

[1] (a) Inoue, M.; Kubo, M. *Coord. Chem. Rev.* **1976**, *21*, 1. (b) Steel, P. J. *Coord. Chem. Rev.* **1990**, *106*, 227.

[2] See, *e.g.*: Kobel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103.

[3] (a) Blake, A. B.; Hatfield, W. E. *J. Chem. Soc., Dalton Trans.* **1978**, 868 and references therein. (b) Real, J. A.; De Munno, G.; Munoz, M. C.; Julve, M. *Inorg. Chem.* **1991**, *30*, 2701 and references therein. (c) Kawata, S.; Kitagawa, S.; Kondo, M.; Furuchi, I.; Munakata, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1759.

[4] Jung, O.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 2229.

[5] van Ooijen, J. A. C.; van Tooren, E.; Reedijk, J. *J. Am. Chem. Soc.* **1978**, *100*, 5569.

[6] (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B.F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19.

[7] Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Inorg. Chem.* **1993**, *32*, 1607.

[8] MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325.

0002-7863/95/1517-4562$09.00/0

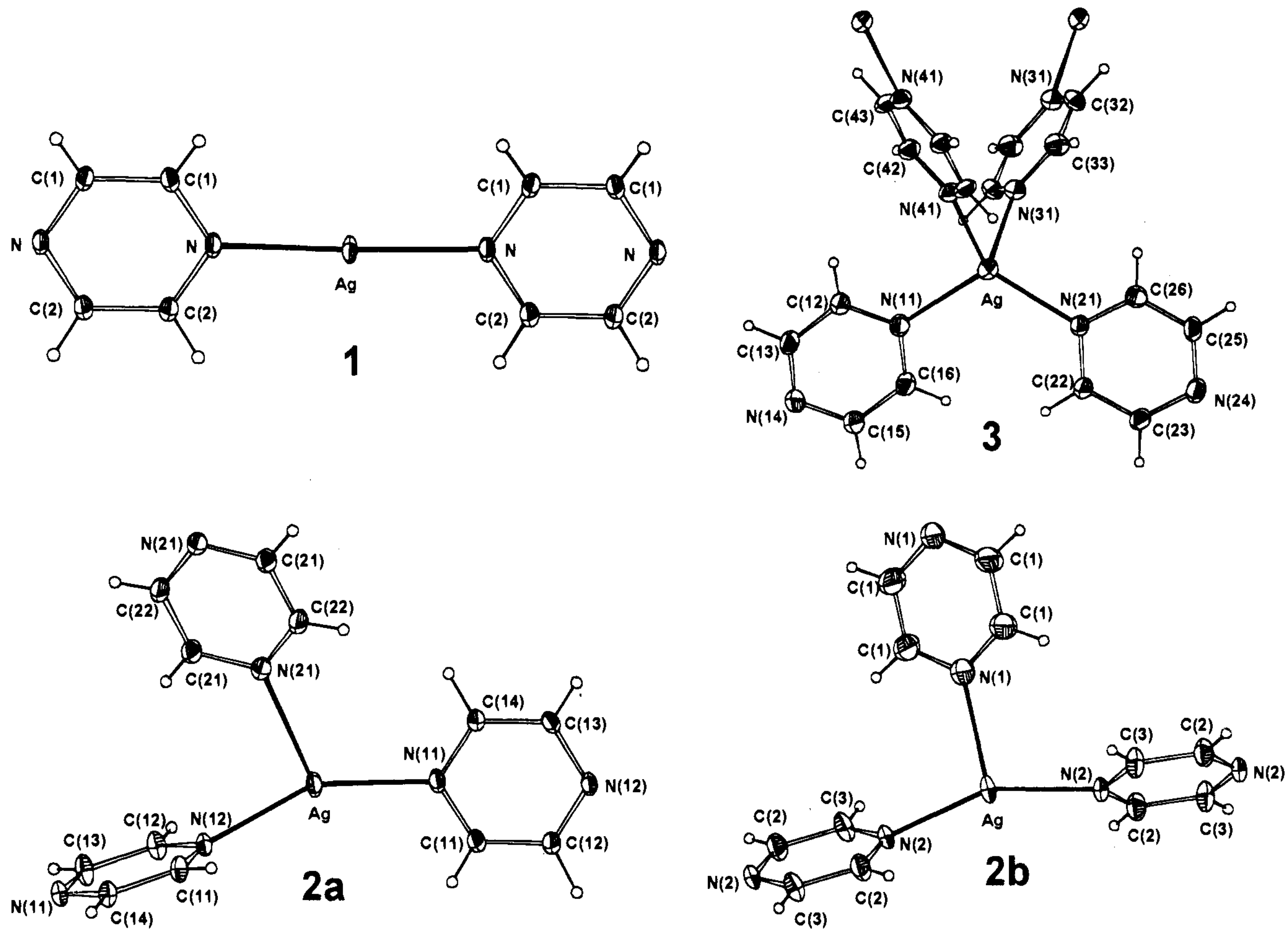

Figure 1. ORTEP drawings of the metal ion coordination for compounds 1–3. Thermal ellipsoids were drawn at the 30% probability level.

phenazine, mainly include 1-D linear chains[9–11] and 2-D planar layers of squares.[3b,12] Linear chains cross-linked by the anions have been described,[13] as well as systems of alternatively perpendicular, instead than parallel, linear chains.[4] A limited number of zigzag 1-D polymers have also been reported.[14,15] More recently novel geometries have been discovered, *i.e.* few examples of 2-D nets of six-membered rings[7,8,15,16] and one case of a 3-D net, the diamond-like cationic frame of the polymeric $[Cu(2,5\text{-}Me_2\text{-}pyz)_2](PF_6)$.[7] A 2-D net of six-membered rings of Cu(I) ions linked by quinoxaline bridges, exhibiting interlayer perchlorato bridges, has also been reported.[17]

The chemistry of these systems is, generally speaking, based on the interactions of the four components: the metal, its counterion, the base, and the solvent. The metal centers, with their different coordination geometries, can give rise to different kinds of frames. Ionic charges, obviously, rule the number of counterions to be arranged in the lattice. The role of the counterion principally depends on its donicity: a strong donor anion can prevent or limit the polymerization and/or can give cross-links between chains or layers. The bases are the molecular rods of the frames and mainly control the metal–metal distances, *i.e.* the dimensions of the cages within the net. With pyrazine and related heterocyclic bases, a relevant factor influencing the crystal packing is the possibility of $\pi-\pi$ interactions involving the stacked aromatic rings.[18] Moreover, the steric requirements of both the anion and the base must also be taken into account. The solvent itself can enter into the metal coordination sphere,[15a] play a role in the reaction process, or fill the cavities of the array.[6a] Finally, interpenetration of nets, a sort of "self-inclusion", can also take place.[8] Attempts to plane

---

[9] (a) Vranka, R. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1020. (b) Tsuda, T.; Ohba, S.; Takahashi, M.; Ito, M. *Acta Crystallogr.* **1989**, *C45*, 887. (c) Munakata, M.; Kitagawa, S.; Ujimaru, N.; Nakamura, M.; Maekawa, M.; Matsuda, H. *Inorg. Chem.* **1993**, *32*, 826.

[10] (a) Ayres, F. D.; Pauling, P.; Robertson, G. B. *Inorg. Chem.* **1964**, *3*, 1303. (b) Santoro, A.; Mighell, A. D.; Reimann, C. W. *Acta Crystallogr., Sect. B* **1970**, *26*, 979. (c) Belford, R. C. E.; Fenton, D. E.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1974**, *17*. (d) Kubel, F.; Strahle, J. *Z. Naturforsch. B* **1981**, *36*, 441; **1983**, *39*, 258. (e) Rivarola, E.; Camalli, M.; Caruso, F. *Inorg. Chim. Acta* **1987**, *126*, 1. (f) Fetzer, T.; Jooss, R.; Lentz, A.; Debaerdemaeker, T. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1750.

[11] (a) Morosin, B.; Hughes, R. C.; Soos, Z. G. *Acta Crystallogr., Sect. B* **1975**, *31*, 762. (b) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 328; **1981**, *20*, 600. (c) Cotton, F. A.; Kim, Y.; Ren, T. *Inorg. Chem.* **1992**, *31*, 2723.

[12] (a) Carreck, P. W.; Goldstein, M.; McPartlin, E. M.; Unsworth, W. D. *J. Chem. Soc., Chem. Commun.* **1971**, 1634. (b) Darriet, J.; Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2679. (c) Haynes, J. S.; Rettig, S. J.; Sams, J. R.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1987**, *65*, 420.

[13] (a) Fetzer, T.; Lentz, A.; Debaerdemaeker, T. Z. *Naturforsch. B* **1989**, *44*, 553. (b) Lindroos, S.; Lumme, P. *Acta Crystallogr.* **1990**, *C46*, 2039. (c) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Sutherland, E. E. *J. Chem. Soc., Chem. Commun.* **1994**, 1049.

[14] (a) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1989**, *67*, 1964. (b) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1990**, *68*, 1901. (c) Cunningham, D.; McArdle, P.; McManus, J.; Higgins, T.; Molloy, K. *J. Chem. Soc., Dalton Trans.* **1988**, 2621.

[15] (a) Kitawaga, S.; Munakata, M.; Tanimura, T. *Inorg. Chem.* **1992**, *31*, 1714. (b) Kitagawa, S.; Kawata, S.; Kondo, M.; Nozaka, Y.; Munakata, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3387.

[16] Turnbull, M. M.; Pon, G.; Willett, R. D. *Polyhedron*, **1991**, *10*, 1835.

[17] Lumme, P.; Lindross, S.; Lindell, E. *Acta Crystallogr.* **1987**, *C43*, 2053.

[18] (a) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101. (b) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

the nature of the products require, therefore, a careful consideration of the above factors.

In spite of the simplicity of the reactions involved within these systems, difficulties arise in the isolation and characterization of the products, since mixtures are often obtained and, what is more problematic, the derivatives are almost insoluble in all the common solvents (unless decomposition takes place) and frequently precipitate as powder materials.

We have undertaken a systematic investigation on a variety of salt/diazine systems, with the principal aim to isolate and structurally characterize coordination polymers exhibiting novel frameworks, and we have already reported on some oligomeric and polymeric pyridazine (1,2-diazine) M^{2+} complexes, investigated by single-crystal X-ray analysis[19] or by *ab-initio* X-ray powder diffraction methods.[20] We describe here the polymeric species obtained from the reactions of pyz with $AgBF_4$ in ethanol. A non-coordinating anion was employed in order to obtain frames with the metal centers bridged only by the diazine. The characterized products include two 1-D, one 2-D, and one 3-D polymers, the last one representing a unique case of three topologically identical interpenetrating 3-D triconnected (3-C) nets.

Results and Discussion

Reactions of $AgBF_4$ with pyz. When $AgBF_4$ dissolved in ethanol is reacted at room temperature with an ethanolic pyz solution in a 1:1 molar ratio, the immediate precipitation of a white microcrystalline product is observed, which was shown to be the polymeric 1:1 adduct $[Ag(pyz)](BF_4)$ (**1**). The compound is air stable and insolubile in common organic solvents, except in MeCN, where a reaction takes place. In water it is stable for many hours and then slowly decomposes. On performing the same reaction with a 1:2 salt/pyz molar ratio the immediate precipitation of **1** cannot be avoided. However, on leaving the above solution to stand for 1 day the formation of crystals on the walls of the reaction vessel was observed. After an additional few days an almost complete transformation of the initially formed precipitate of **1** to give the novel crystalline product takes place. This product analyzes as $[Ag_2(pyz)_3](BF_4)_2$ (**2**). Attempts to obtain directly crystals of **2** alone by slow diffusion of two proper solutions (acetone/2-propanol or THF/ethanol) were unsuccessful, leading to unidentified quite unstable derivatives, which are presently under investigation. On carefully layering an ethanolic solution of the base on a solution of $AgBF_4$ in ethanol (molar ratio 2:1) in a test tube the formation of a crystalline crust at the interface was often observed. After 1 day, examination of the test tube under the microscope revealed the presence of needle-shaped crystals of **1** in the bottom and of beautiful colorless crystals of **2** on the walls, which presented two different morphologies. The exceedingly dominant species (**2a**) was present in crystals with a distorted cubical shape, while the crystals of the minor component (**2b**) appeared as compressed rhombohedra. The crystals of **1** and **2a** are stable when the mother liquor is removed, while those of **2b** become opaque and begin slowly to decompose. Crystals of the three products, selected from the same reaction pot, were submitted to single-crystal X-ray analysis under a coating of cyanoacrylate glue in order to prevent decomposition. The formation of crystals of **2b** was not always observed; it seems to be favored by the slow diffusion of the two solutions, which can be achieved also by interposing between them a layer of filter paper or of cotton. Pure **2** can be obtained in high yields upon treatment of **1** suspended in ethanol with an equimolar ethanolic solution of the base and on leaving the reaction mixture to stand for a few days. The product exhibits the same solubility behavior as **1**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**−**3**[a]

Compound **1**			
Ag−N	2.193(3)	Ag−N−C(1)	121.4(3)
		Ag−N−C(2)	122.1(3)
N−Ag−N^{i}	173.6(2)	C(1)−N−C(2)	116.4(4)
^{i}-$x + 1, y, z$			
Compound **2a**			
Ag−N(11)	2.245(2)	Ag−N(11)−C(14)	121.0(2)
Ag−N(12)^{i}	2.280(2)	C(11)−N(11)−C(14)	115.9(3)
Ag−N(21)	2.419(3)	Ag^{ii}−N(12)−C(12)	122.0(2)
		Ag^{ii}−N(12)−C(13)	120.8(2)
N(11)−Ag−N(12)^{i}	152.6(1)	C(12)−N(12)−C(13)	116.2(3)
N(11)−Ag−N(21)	113.8(1)	Ag−N(21)−C(21)	121.9(2)
N(12)^{i}−Ag−N(21)	93.02(9)	Ag−N(21)−C(22)^{iii}	122.3(2)
Ag−N(11)−C(11)	121.9(2)	C(21)−N(21)−C(22)^{iii}	115.3(3)
$^{i}x - {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; $^{ii}x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z - {}^{1}/_{2}$; ^{iii}-$x$, -$y$, -$z + 1$			
Compound **2b**			
Ag−N(1)	2.375(8)	Ag−N(1)−C(1)	122.8(4)
Ag−N(2)	2.239(3)	C(1)−N(1)−C(1)^{i}	114.4(8)
		Ag−N(2)−C(2)	122.2(3)
N(1)−Ag−N(2)	102.4(1)	Ag−N(2)−C(3)^{ii}	121.0(3)
N(2)−Ag−N(2)^{i}	155.2(2)	C(2)−N(2)−C(3)^{ii}	116.0(4)
$^{i}x, -y + {}^{1}/_{4}, -z + {}^{1}/_{4}$; $^{ii}-x + 1, -y + {}^{1}/_{2}, -z + {}^{1}/_{2}$			
Compound **3**			
Ag−N(11)	2.349(5)	Ag−N(11)−C(16)	120.6(4)
Ag−N(21)	2.276(5)	C(12)−N(11)−C(16)	116.1(5)
Ag−N(31)	2.410(5)	Ag−N(21)−C(22)	122.4(4)
Ag−N(41)	2.314(5)	Ag−N(21)−C(26)	121.7(4)
		C(22)−N(21)−C(26)	114.9(5)
N(11)−Ag−N(21)	116.6(2)	Ag−N(31)−C(32)	123.7(4)
N(11)−Ag−N(31)	107.4(2)	Ag−N(31)−C(33)^{i}	121.2(5)
N(11)−Ag−N(41)	106.7(2)	C(32)−N(31)−C(33)^{i}	115.1(5)
N(21)−Ag−N(31)	102.7(2)	Ag−N(41)−C(42)	119.7(5)
N(21)−Ag−N(41)	126.8(2)	Ag−N(41)−C(43)^{ii}	124.5(4)
N(31)−Ag−N(41)	91.8(2)	C(42)−N(41)−C(43)^{ii}	115.8(5)
Ag−N(11)−C(12)	122.9(4)		
^{i}-x, -y, -$z + 1$; ^{ii}-x, -y, -$z + 2$			

[a] Symmetry operations used to generate equivalent atoms are indicated for each compound.

Reactions were also carried out using higher pyz/metal molar ratios, up to 4:1. After separation of the bulk initial precipitate of **1**, the solutions were left to stand for several days. The crystalline products formed were essentially **2**. In the case of the reaction performed with a 4:1 molar ratio, few crystals (elongated parallelepipeds) were also obtained, and these were unstable when removed from the mother liquor. This product was shown to have a composition of $[Ag(pyz)_3](BF_4)$ (**3**), on the basis of a single-crystal X-ray analysis performed on a sample coated with cyanoacrylate glue.

IR spectra of the two stable species **1** and **2a** were recorded in Nujol mull. These showed bands attributable to the coordinated pyz molecules, modified with respect to the free ligand, as previously reported for similar complexes,[21] and to the BF_4^- anions.[22]

Thermal Analyses. Compounds **1** and **2a** are stable, without melting, up to *ca.* 250 °C. Preliminary thermal analyses on both species have been carried out. Thermogravimetric analysis (TGA) of **1** shows that decomposition starts at *ca.* 260 °C, evolving in steps to a net peak at 310 °C, with 60.4% weight

---

(19) Carlucci, L.; Ciani, G.; Moret, M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1994**, 2397.

(20) Masciocchi, N.; Cairati, P.; Carlucci, L.; Ciani, G.; Mezza, G.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1994**, 3009.

(21) Ferraro, J. R.; Zipper, J.; Wozniak, W. *J. Appl. Spectrosc.* **1969**, *23*, 160.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York 1986.

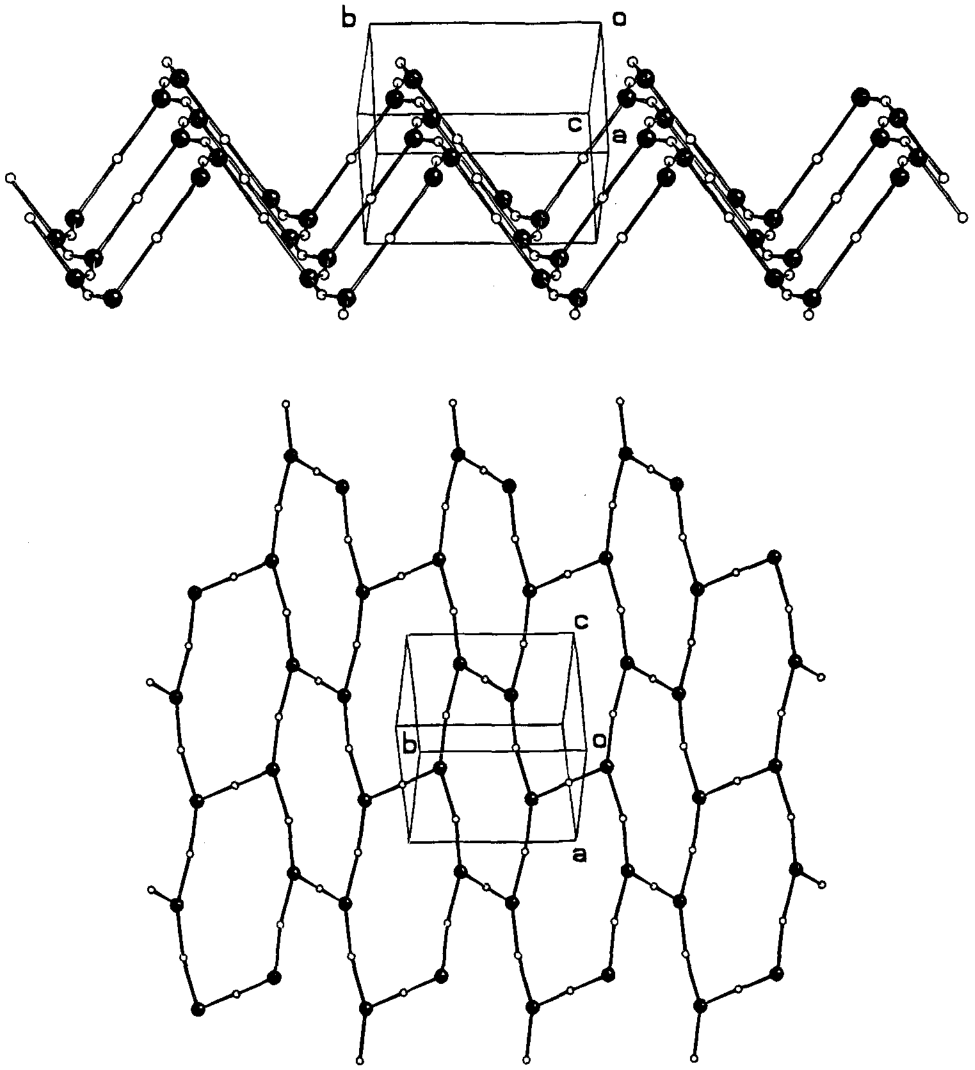

Figure 2. Two views of a schematized single sheet in **2a**, with the pyz ligands replaced by their baricenters (small empty balls).

loss, the residue (38.9%) corresponding to metallic silver. Differential scanning calorimetric analysis (DSC) in the range 50−300 °C reveals the presence of a small endothermic peak (onset at 139.4 °C, $\Delta H = 0.7$ kcal/mol). On cooling the same sample to 50 °C an exothermic peak (onset at 124.0 °C, $\Delta H = -0.9$ kcal/mol) was observed. Repeated cycles of programmed heating and cooling in the range 50−200 °C confirmed the above events, which are attributed to a reversible crystal-to-crystal phase transition. TGA of **2a** shows a peak at 139.8 °C, with a 12.7% weight loss, corresponding to one pyz molecule *per* formula unit. The remaining species has the stoicheiometry of **1**, and the upper part of the thermogram is similar to that obtained from **1**, with a peak at 304 °C (52.0% weight loss), the residue being attributable to metallic silver again. The conversion of **2a** to **1** has been confirmed by X-ray powder diffraction analysis of a sample placed in an oven at 145 °C for 10 h and then cooled at room temperature. DSC analysis of **2a** in the range 50−280 °C shows a broad endothermic peak (onset 125.6 °C), with a ΔH of 9.4 kcal/mol, essentially due to the loss of one pyz molecule *per* formula unit. This ΔH value is somewhat lower than in other pyz complexes (14−22 kcal/mol);[23],[14b] it can be taken as an indication of the presence of a loosely bonded ligand (see below). On cooling the sample to 50 °C and then heating it again to 250 °C the same endothermic peak at *ca.* 139 °C ($\Delta H = 0.7$ kcal/mol) found for **1** was observed.

Molecular Structural Features. The crystal structures of the four new polymeric compounds **1**−**3** consist of extended cationic frames of differently coordinated Ag^+ centers, linked by the linear pyz bridges, with the interstitial holes or channels occupied by the BF_4^- anions. The interactions of the Ag^+ ions with the tetrafluoroborate anions are very weak, the shortest $Ag\cdot\cdot F(BF_4^-)$ contact being 2.714(5) Å in **1**.

The coordination geometries at the metal centers are illustrated in Figure 1 and selected bond distances and angles for all the compounds are collected in Table 1. Few comments are necessary to illustrate the "molecular" structural features of these units. The metal coordination in **1** is linear, with an N−Ag−N angle of 173.6(2)° and an Ag−N bond length of 2.193(3) Å, similar to analogous interactions in linear silver complexes.[9] In **3** the metal ions are bound to two bridging and two terminal pyz ligands [Ag−N 2.276(5)−2.410(5) Å] in a distorted tetrahedral fashion, with rather scattered N−Ag−N angles [91.8(2)−126.8(2)°]. While the two above coordination geometries are usual for silver complexes, less common are the three-coordination modes present in **2a** and **2b**. In both species one Ag−N bond is markedly longer than the other two and the N−Ag−N angle involving the shorter bonds is somewhat larger than the others [152.6(1)° vs 93.0(1)° and 113.8(1)° in **2a**; 155.2(2)° *vs* two equivalent values of 102.4(1)° in **2b**]. The coordination geometries are strictly planar and intermediate between T-shaped and trigonal, a situation observed in other Ag^+ and Cu^+ complexes (see *e.g.* refs 7, 8, 9c, 15b, 16).

---

(23) Beech, G.; Mortimer, C. T. *J. Chem. Soc. A* **1967**, 1115.

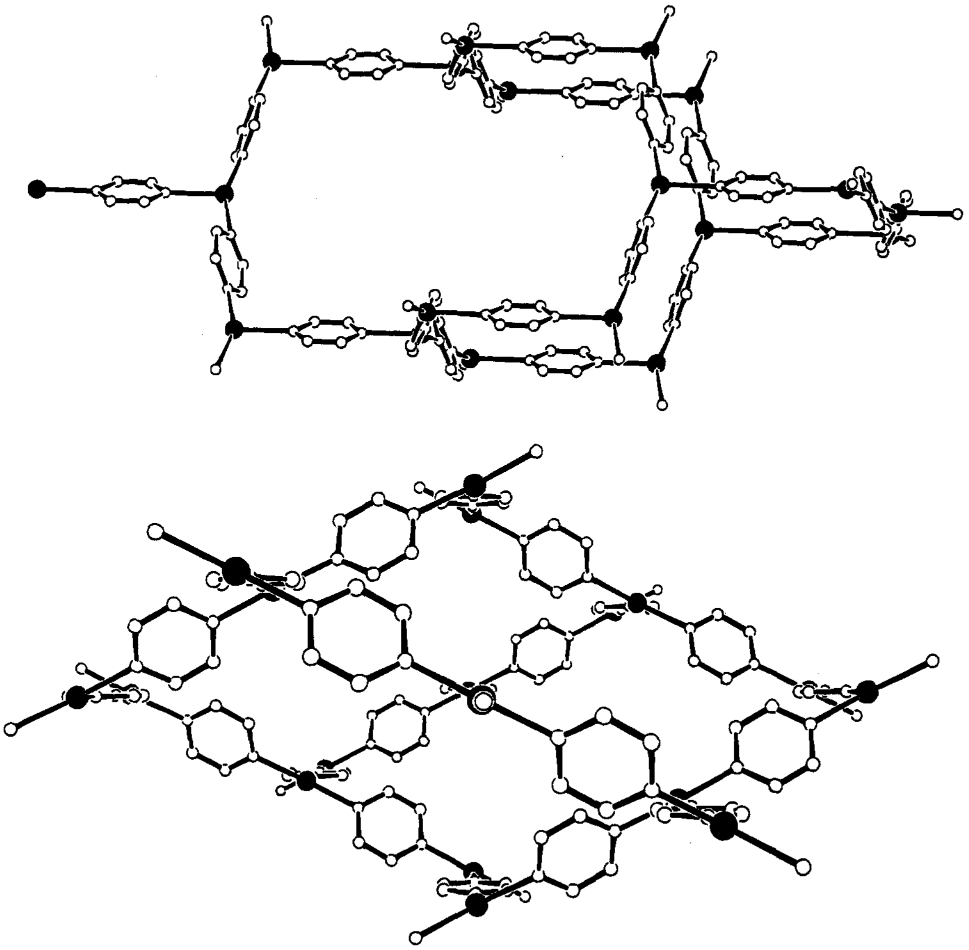

Figure 3. Two orthogonal views of a single polymeric framework in **2b**.

1-D Polymers, Compounds 1 and 3. The polymeric linear chains of **1** develop along the **a** axis, with an Ag••Ag separation [equal to **a**, 7.136(3) Å] which compares well with the corresponding separations in the other known linear silver polymers bridged by 1,4-diazines.[9] All the aromatic rings within each chain are parallel and the chains are disposed in pairs, with a stacking distance of the rings of 3.66 Å. The closest Ag••Ag contact within each pair is 4.283(2) Å, while that involving different pairs is 5.176(2) Å.

Compound **3** contains zigzag chains extending in the direction of the **c** axis. The N—Ag—N angle involving the bridging pyz ligands is 91.8(2)°, and the aromatic rings along the polymer are alternately rotated in opposite directions [dihedral angles between the rings and the N—Ag—N plane of 59.9(5) and 49.6(7)°]. The Ag••Ag separations subtended by these ligands are 7.400(3) and 7.599(3) Å, while a complete step of the polymer corresponds to **c**, 10.768(3) Å. The shortest interchain Ag••Ag contact is 7.002(6) Å.

The 2-D Polymeric Compound 2a. The crystal structure of **2a** contains 2-D cationic sheets composed of six-membered rings of pyz-bridged Ag^+ ions. The sheets are markedly undulated and the "waves" propagate along the direction of the **b** axis, with a "wavelength" equal to **b**, 11.785(1) Å. A single sheet is illustrated in Figure 2. These 2-D nets can be described as consisting of parallel zigzag chains [N—Ag—N 152.6(1)°] extending along the [10—1] direction, with an Ag••Ag intrachain separation of 7.226(1) Å. These chains form the corners (*i.e.* crests and valleys) of the folded sheets and are cross-linked by the other pyz molecules, alternately disposed by opposite sides for adjacent Ag^+ ions along each chain [Ag••Ag interchain separation of 7.615(1) Å]. The cross-linking pyz ligands are more weakly bound to the metal ions than the ligands forming the chains [Ag—N 2.419(3) Å *vs* (mean) 2.262 Å] and are more easily removed upon heating, leaving a system of parallel 1-D polymers, which reorganize to give crystalline compound **1** (see above).

The six-membered rings forming the 2-D nets are folded in chair conformation [with dihedral angles in the rings of 127.7(1)°]. Adjacent rings are disposed in a manner similar to that of the rings of *cis*-decaline, and the sheets are reminescent of the structure of As_2O_3 (claudetite-**I** version).[24]

Some examples of six-membered layer structures, based on Cu^+ centers and 1,4-diazines, have been reported in recent times,[7,8,15-17] and they exhibit different extents of deviation from planarity. Two structures exhibit closer resemblance with **2a**, *namely* $[Cu_2(2,3\text{-}Me_2pyz)_3](ClO_4)_2$[16] and $[Cu_2(2,5\text{-}Me_2pyz)_3](PF_6)_2$,[7] both containing significantly pleated layers. Their crystals are both monoclinic, and the "waves" propagate, in both cases, in the direction of the unique axis **b**, as in **2a**, with "wavelengths" of 14.737(2) and 15.862(1) Å, respectively. These values, together with the fact that the ligand-bridged Cu••Cu separations are 0.4—0.6 Å shorter than the Ag••Ag separations, make evident a progressive flattening of the sheets on passing from **2a** to $[Cu_2(2,3\text{-}Me_2pyz)_3](ClO_4)_2$ and to $[Cu_2(2,5\text{-}Me_2pyz)_3](PF_6)_2$, which seems to be related to the presence of the substituents on the pyz rings and of the slightly bulkier anions. The marked folding of the sheets of **2a** and the deep mutual joints of the complementary crests and valleys of adjacent sheets [shortest internet Ag••Ag separation of 5.910(1) Å] represent quite peculiar structural features of this 2-D polymer.

---

[24] Frueh, A. J. *Am. Mineral.* **1951**, *36*, 316.

The 3-D Polymeric Compound 2b. Compound **2b** displays a complex crystal structure containing three identical interpenetrating 3-D 3-C cationic frameworks. Each frame is topologically equivalent to the extended network formed by the silicon atoms in α-ThSi$_2$,[25] which is the most famous example of one of the three simplest 3-D nets built up with 3-C centers only.[26a] Wells indicates this frame as a uniform (10,3) net, meaning that the shortest complete circuits including any pair of links from any point are 10-gons.[26] A 3-D net of this type in its most symmetrical configuration is tetragonal ($I4_1/amd$); the other two simplest 3-D 3-C nets are cubic and hexagonal, examples (in less symmetrical arrangements) being found in SrSi$_2$[27] and B$_2$O$_3$,[28] respectively.

A single cationic net of **2b** is shown in Figure 3. The Ag$^+$ ions lie on 2-fold crystallographic axes and, as in **2a**, are bridged by two different types of pyz ligands, both lying about special positions. The ligands of the first type, more strongly bound to the silver ions, are located about inversion centers and form 1-D zigzag chains [Ag−N 2.239(3) Å, N−Ag−N 155.2(2)°], while those of the second type, placed about sites of 222 symmetry, cross-link the chains [Ag−N 2.375(8) Å]. The subtended Ag$\cdots$Ag separations are 7.238(2) and 7.514(2) Å, respectively, similar to the corresponding values in **2a**. Parallel zigzag chains are disposed on layers (normal to the **a** axis) and their direction changes on passing from one layer to the adjacent layer, with a rotation of 55.4° around **a**, turning from [011] to [0−11] and *vice versa*, in a sequence *ABAB*. Note that in α-ThSi$_2$ the chains on adjacent layers are mutually perpendicular (rotation of 90° about the tetragonal axis), while a rotation of 60° about the unique axis on passing to each sequent layer is required in the hexagonal 3-D 3-C net mentioned above (sequence *ABCABC*).[26a]

Interpenetration of nets in **2b** arises from the necessity to fill the very large empty cavities of a single framework, which should have an anomalously low density of only 0.72 g cm^{-3}. The three identical interwoven nets are schematically illustrated in Figure 4. Repeated application of a proper translation vector allows the generation of the other frames from a single one. Out of the six simplest translations of the space group, three [(0,1/2,1/2), (0,1,0), (0,0,1)] always lead inside the same frame, while the other three [(1/2,1/2,0), (1/2,0,1/2), (1,0,0)] generate a different frame. Application of any of the latter three vectors to the atoms of frame I generates frame II when applied singly, frame III on two applications, and frame I again after three applications of the same vector. The shortest vector relating equivalent atoms of the independent nets is (1/2,1/2,0), 8.81 Å. Much shorter internet Ag$\cdots$Ag contacts, however, are observed, down to 4.065(1) Å (contact indicated in Figure 4).

In order to obtain a complete repeat unit of *each* single net, three unit cells in the **a** direction must be considered. This triple cell contains 48 Ag$^+$ ions, 16 for each net (see Figure 5 left). Note that the Ag$^+$ ions present in the crystallographic cell (16) are unevenly distributed among the three nets (6/6/4), while this is not true in the supercell (16/16/16).

It seemed to us an interesting point to assign the space group, within a (3 × 1 × 1) orthorhombic supercell, to (a) an ideal single net of equal atoms spanning the geometry observed in **2b** and (b) a system of three interwoven nets of different scatterers (three "colored" frames) of the above type. Fourier transforms of such arrays (using arbitrary scattering centers) have shown that the single frame belongs to space group *Fddd* (see Figure 5 center), with one independent atom on a 2-fold axis, while the "colored" array can be assigned to space group *F2dd* (No. 43), with two independent atoms for each frame, lying on 2-fold axes (see Figure 5 right). Atomic coordinates for both cases are given in the Supplementary Material.

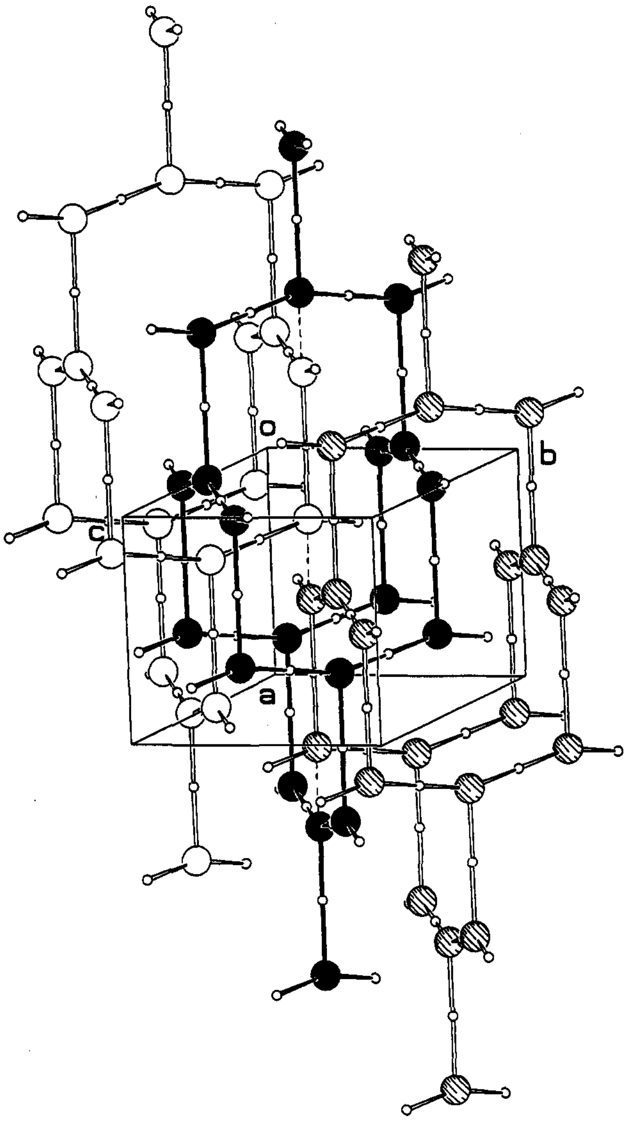

Figure 4. A schematic view of the three interpenetrating nets of **2b** (represented as open, solid, and cross-hatched balls for clarity). Dashed lines represent the shortest internet Ag−Ag contacts of 4.065(1) Å.

The fascinating structure of **2b** is unique for different aspects. It is the first 3-D coordination polymer based on 3-C metal centers[29] [few known 2-D 3-C nets of Cu(I) have been quoted previously, in discussing the structure of **2a**]. Polymeric frames of this type are expected to be quite less common than those based on 4-C tetrahedral centers, in covalent solids as well as in coordination compounds. Another relevant feature is the interpenetration of three nets. Interwoven 2-D and 3-D frameworks are rather rare. Various examples of interpenetrating super-tetrahedral frames are known in the supramolecular chemistry of hydrogen-bonded molecules,[30] and some interpenetrating diamondoid polymeric complexes,[6,8,31] up to 7-fold,[32] have been described. We have recently found two cases of 4-fold diamondoid frames in the species [Ag(4,4′-bipyridyl)$_2$](CF$_3$-

---

[25] Brauer, G.; Mitius, A. *Z. Anorg. Chem.* **1942**, *249*, 325.

[26] (a) Wells, A. F. *Acta Crystallogr.* **1972**, *B28*, 711. (b) Wells, A. F. *Acta Crystallogr.* **1954**, *7*, 535.

[27] (a) Janzon, K. H.; Schafer, H.; Weiss, A. *Angew. Chem.* **1965**, *77*, 258. (b) Pringle, G. E. *Acta Crystallogr.* **1972**, *B28*, 2326.

[28] Strong, S. L.; Kaplow, R.; *Acta Crystallogr.* **1968**, *B24*, 1032.

[29] A complex species containing Ag$^+$ ions bridged by large aromatic tridentate trinitrile ligands has been recently shown to display a triple 3-D frame of the α-ThSi$_2$ type, with mixed metallic and organic 3-C centres; Lee, S., personal communication.

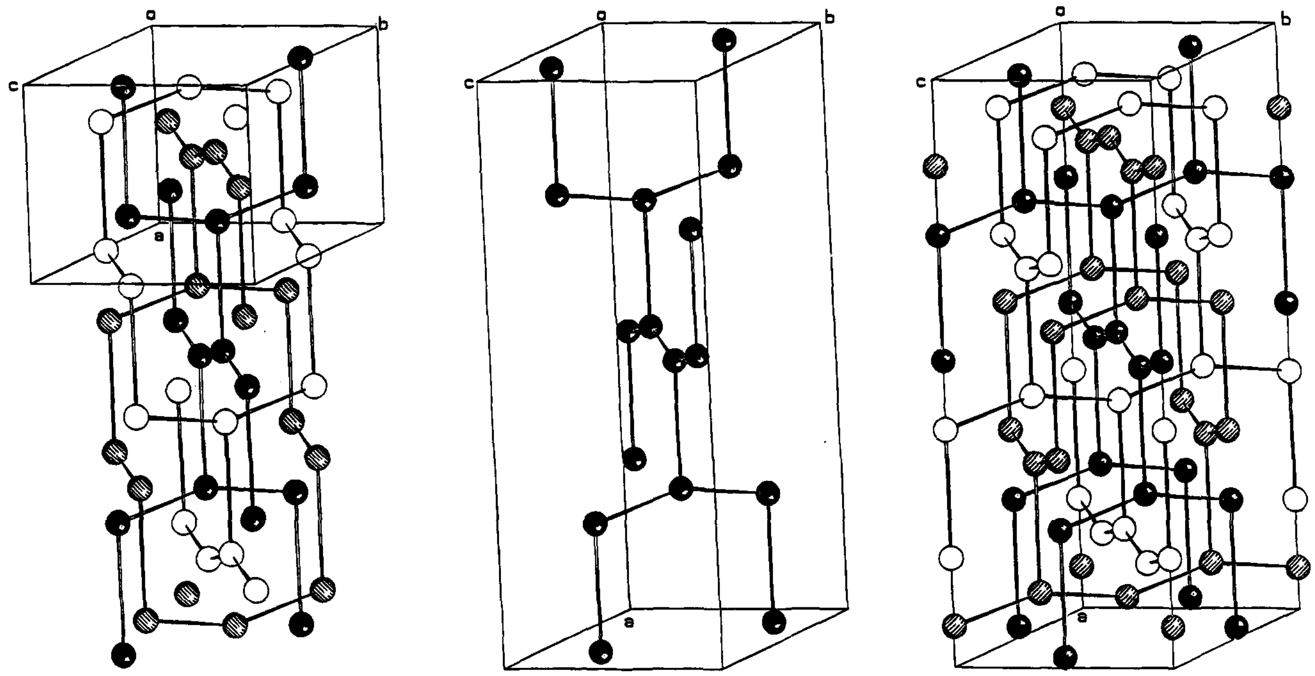

Figure 5. Comparative views of the Ag frames in the real structure of **2b** (left), in the ideal 3-D structure of a single net (centre), and in the ideal 3-D structure formed by three interpenetrating independent "colored" nets (right) (see text).

SO_3) and $[Ag(4\text{-CN-pyridine})_2[(BF_4)$.[33] A limited number of interpenetrating frames based on octahedral centers (α-polonium type structures) is also known.[34] On the other hand, there is, to our knowledge, only one other example of interpenetration involving 3-D 3-C nets, *namely* the silicate neptunite.[35] In this species the SiO_4 tetrahedra form two identical interwoven nets of the α-$ThSi_2$ type, with $^1/_3$ of the edges elongated by the presence of two biconnected SiO_4 units.

Finally, a comparison of the calculated densities (2.151 g cm^{-3} in **2b** *vs* 2.209 g cm^{-3} in **2a**) indicates that the 3-D polymer has a slightly lower packing efficiency than its 2-D polymorph, and this probably can account for its relative instability.

Conclusions

The polymeric species described here show the versatility of silver (in the presence of a noncoordinating counterion) to give, with proper molecular rods, interesting self-assembling frames. A variety of novel coordination polymers, with unprecendented topologies and potential useful properties, can be expected on varying the reaction conditions. Crystal engineering of these coordination polymers, for which some useful basic ideas have been proposed recently, especially in relation to nanoporosity and host-guest chemistry,[6,36] is a stimulating challenge. However, much experimental work is still required in order (i) to increase the, at present limited, number of structurally characterized 2-D and 3-D networks, (ii) to establish the appropriate synthetic strategies to approach the specific problems, and (iii) to disclose the structure/property correlations that are the ultimate aim of these researches. We are currently investigating along these lines.

Experimental Section

General Comments. All the reagents and solvents employed were commercially-available high-grade-purity materials (Merck and Aldrich Chemicals), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of this University.

Physical Measurements. Infrared spectra were recorded on an ATI-Mattson Genesis FT/IR spectrophotometer (range 4000–500 cm^{-1}) in Nujol mull. Thermal analyses were carried out on Perkin Elmer DSC7 and TGA7 instruments. The purgue gas was nitrogen and the scan rate was 10 °C/min for both techniques. X-ray powder patterns were collected on a Rigaku D-III/MAX horizontal scan diffractometer, equipped with parallel (Soller) slits and a graphite monochromator in the diffracted beam (Cu Ka radiation).

Synthesis of $[Ag(pyz)](BF_4)$ (1). $AgBF_4$ (0.188 g, 0.97 mmol) was dissolved in 8 cm^3 of ethanol and then pyz was added under stirring in an equimolar ratio (0.077 g, 0.97 mmol). Microcrystals formed, which were filtered off, washed with ethanol, and dried in air. Yield 0.232 g (88%). The product is soluble in MeCN and insoluble in ethanol and in common polar and nonpolar solvents. Anal. Found: C, 17.20; H, 1.44; N, 10.10. Calcd for $C_4H_4AgBF_4N_2$: C 17.48; H, 1.47; N, 10.20. The principal IR bands (cm^{-1}) are as follows: 1432 (vs), 1377 (m), 1290 (mw), 1151 (s), 1136 (vs), 1082 (vs), 1051 (vs), 808 (s), 522 (m).

Synthesis of $[Ag_2(pyz)_3](BF_4)_2$ (2). Compound **1** (0.112 g, 0.41 mmol) was suspended in 10 cm^3 of ethanol and an ethanolic solution of pyz (0.034 g, 0.42 mmol) was added. The mixture was left to stand for 4–7 days in the dark. The crystalline material formed was filtered off, washed with ethanol, and dried in air. Yield 0.093 g (72%). The product is soluble in MeCN and insoluble in ethanol and in common organic solvents. Anal. Found: C, 22.92; H, 1.81; N, 13.23. Calcd for $C_{12}H_{12}Ag_2B_2F_8N_4$: C, 22.89; H, 1.92; N, 13.35. Main IR bands (cm^{-1}): 1423 (s), 1417 (vs), 1377 (s), 1290 (m), 1151 (s), 1087 (vs), 1050 (vs), 1036 (vs), 807 (s), 792 (s), 522 (s).

---

(30) See, *e.g.*: (a) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747. (b) Ermer, O.; Eling, A. *J. Chem. Soc., Perkin Trans.* **1994**, 925 and references therein.

(31) (a) Cromer, D. T.; Larson, A. C. *Acta Crystallogr.* **1972**, *B28*, 1052. (b) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878. (c) Michaelides, A.; Kiritsis, V.; Skoulika, S.; Aubry, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1495.

(32) Ermer, O. *Adv. Mater.* **1991**, *3*, 608 and references therein.

(33) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755.

(34) (a) Schafer, H.; von Schnering, H. G.; Niehues, K. J.; Nieder-Vahrenholz, H. G. *J. Less-Common Met.* **1965**, *9*, 95. (b) Pauling, L.; Pauling, P. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *60*, 362. (c) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665. (d) Hoskins, B. F.; Robson, R.; Scarlett, N. V. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2025.

(35) Cannillo, E.; Mazzi, F.; Rossi, G. *Acta Crystallogr.* **1966**, *21*, 200.

(36) (a) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283. (b) Moore, J. S.; Lee, S. *Chem. Ind.* **1994**, 556.

Table 2. Crystal Data and Structure Refinement Parameters for **1−3**

formula	$C_4H_4AgBF_4N_2$ (**1**)	$C_6H_6AgBF_4N_3$ (**2a**)	$C_6H_6AgBF_4N_3$ (**2b**)	$C_{12}H_{12}AgBF_4N_6$ (**3**)
molar weight	274.77	314.82	314.82	434.96
crystal system	orthorhombic	monoclinic	orthorhombic	triclinic
space group	*Pmcb*(55)	$P2_1/n$(14)	*Fddd*(70)	$P\bar{1}$(2)
a, Å	7.136(3)	8.385(1)	11.579(2)	7.994(5)
b, Å	7.217(1)	11.785(1)	13.272(3)	10.253(3)
c, Å	14.855(4)	9.797(1)	25.304(5)	10.768(3)
α, deg				90.04(2)
β, deg		102.15(1)		102.63(5)
γ, deg				111.47(5)
V, Å^3	765.0(4)	946.4(2)	3888.6(13)	798.3(6)
Z	4	4	16	2
d(calc), cm^{-3}	2.386	2.209	2.151	1.810
μ, mm^{-1}	2.646	2.157	2.100	1.312
crystal size, mm	0.25 × 0.02 × 0.02	0.30 × 0.22 × 0.20	0.20 × 0.12 × 0.32	0.14 × 0.09 × 0.08
scan method	ω	ω	ω	ω
θ range, deg	3−26	3−26	3−25	3−25
no. of reflcns collected	1493	1845	1653	2791
no. of independent reflcns	814 [R(int) = 0.0323]	1845	860 [R(int) = 0.0330]	2791
obs reflcn criterion	$>1\sigma(I)$	$>1\sigma(I)$	$>1\sigma(I)$	$>1\sigma(I)$
a, b^a	0.0285, 0.2404	0.0368, 0.9000	0.0355, 0.0	0.0361, 1.1126
data/restrain/parameters	658/0/69	1643/0/187	605/59/91	1982/0/244
GOF^b on F_o^2 (all data)	1.112	1.096	1.107	1.105
final R indices^c [$F_o > 4\sigma(F_o)$]	R1 0.0266, wR2 0.0577	R1 0.0255, wR2 0.0649	R1 0.0267, wR2 0.0577	R1 0.0417, wR2 0.0864
R indices^c (all data)	R1 0.0421, wR2 0.0645	R1 0.0319, wR2 0.0748	R1 0.0685, wR2 0.0692	R1 0.0953, wR2 0.1129

[a] Weights during refinement were the following: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters. [c] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. wR2 = $[\sum(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Crystallography. Colorless crystals of compounds **1−3** were mounted under a coating of cyanoacrylate glue on an Enraf-Nonius CAD-4 diffractometer, and 25 intense reflections having a θ value in the range 9.0−12.0° were centered using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 2.

Crystal data and details associated with data collections and structure refinements are also given in Table 2. Intensities were checked by monitoring three standard reflections every 3 h; no significant crystal decay was observed in all cases.

The diffracted intensities were corrected for Lorentz, polarization, and background effects. An empirical absorption correction was applied based on ψ-scans of three suitable reflections having χ values close to 90° (ψ 0−360°, every 10°). The structures were solved by a combination of direct methods (SIR92)[37] and difference Fourier methods and refined by full-matrix least-squares, minimizing the function $\sum w\Delta F^2$, using all reflections having $I > \sigma(I)$. The BF_4^- anions were found disordered in all cases and were refined using a model involving two tetrahedra of equal weight, centered on the unique B atom.

Anisotropic thermal displacement parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps and refined for **1** and **2a**; calculated positions in the cases of **2b** and **3** were assumed and introduced in the final stages of refinement as fixed atom contributions riding on their parent atoms with d_{C-H} = 0.93 Å. The final difference maps were flat, showing some peaks not exceeding *ca.* 0.57 e$^-$/Å^3. All calculations were performed using SHELXL-93.[38] Final atomic coordinates for **1−3** are given in the supplementary material. Molecular drawings were produced with SCHAKAL[39] and ORTEP[40] programs.

Acknowledgment. We thank Dr. P. Cairati for the collection of X-ray powder data and Mr. G. Mezza for technical support.

Supplementary Material Available: Tables of atomic positional parameters for the ideal single net and triple "colored" net related to **2b** (see text, Table S1), positional and thermal parameters for compounds **1−3**, and a complete list of bond distances and angles for **1−3** (Tables S2-S21) (8 pages); tables of experimental and structure refinement details and structure factors (Tables S22-S25) (13 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.

JA943793W

---

(37) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(38) Sheldrick, G. M. SHELXL-93: program for structure refinement: University of Goettingen: Germany, 1994.

(39) Keller, E. SCHAKAL 92: a computer program for the graphical representation of crystallographic models; University of Freiburg: Germany, 1992.

(40) Johnson, C. K. ORTEP: a FORTRAN thermal-ellipsoid-plot program for crystal structure illustrations; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.