Inorg. Chem. **1995**, *34*, 5698−5700

2D Polymeric Silver(I) Complexes Consisting of Markedly Undulated Sheets of Squares. X-ray Crystal Structures of $[Ag(ppz)_2](BF_4)$ and $[Ag(pyz)_2](PF_6)$ (ppz = Piperazine, pyz = Pyrazine)

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

Dipartimento di Chimica Strutturale e Stereochimica
Inorganica and Centro CNR, Università di Milano,
Via G. Venezian 21, 20133 Milano, Italy

Received March 31, 1995

The architecture of 2D and 3D coordination polymers is attracting ever increasing attention,[1−3] from the standpoint of (i) theoretical implications related to the topologies of novel networks and (ii) potential applications of these materials in many areas, such as electrical conductivity,[4] magnetism,[5] host−guest chemistry,[1,6] and catalysis.[7] Considering the numerous interesting results obtained within the supramolecular chemistry of hydrogen-bonded organic molecules,[8] crystal engineering of coordination polymers still requires much work in order to extend the knowledge of the relevant structural types and to establish proper synthetic strategies leading to species with the desired properties. Nevertheless, many recently reported species, including 3D frameworks with large channels[9,10] and interpenetrating 2D nets[11] and 3D superdiamond[1a,4,11] and α-polonium type frames,[12,13] illustrate the high potential for applications connected with the various coordination abilities of the metallic centers.

We are investigating systems based on the self-assembly of silver(I) cations and bidentate N,N′-donor ligands and recently reported two species containing four interpenetrating diamondoid frameworks, $[Ag(N\text{-}N')_2]X$ (N-N′ = 4,4′-bipyridyl, $X^- = CF_3SO_3^-$; N-N′ = 4-cyanopyridine, $X^- = BF_4^-$), and a polymorph of the latter one, consisting of almost planar 2D sheets of distorted square meshes.[14] We report here two novel polymeric complexes of the same $[Ag(N\text{-}N')_2]X$ type, *namely* $[Ag(ppz)_2](BF_4)$ (ppz = piperazine), **1**, and $[Ag(pyz)_2](PF_6)$ (pyz = pyrazine), **2**, which, in contrast, consist of undulated 2D layers of distorted squares of Ag^+ cations. Flat layers of square grids, with pyrazine[5,15] or 4,4′-bipyridyl[1b,7] rods and octahedral metal ions (using four equatorial sites for networking), have been previously described, but the structural type present in **1** and **2**, based on four-coordinated nonplanar Ag^+ cations, is unprecedented within this class of polymers.

Experimental Section

Materials. All 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.

Isolation of $[Ag(ppz)_2](BF_4)$ (1). In the reactions of $AgBF_4$ with ppz in ethanol (1:1 and 1:2 molar ratios) the immediate formation a powdered product is always observed. This compound is obtained in high yield (*ca.* 90%) and analyzes for $[Ag(ppz)](BF_4)$. Anal. Calcd for $C_4H_{10}AgBF_4N_2$: C, 17.10; H, 3.59; N, 9.98. Found: C, 17.55; H, 3.25; N, 10.08. On careful layering of a solution of ppz (0.167 g, 1.92 mmol) in ethanol (3 mL) upon an ethanolic solution (3 mL) of $AgBF_4$ (0.189 g, 0.97 mmol), a few crystals of $[Ag(ppz)_2](BF_4)$ (**1**) were obtained together with a dominant amount of polycrystalline $[Ag(ppz)](BF_4)$. The products are air stable for days and do not appear to be light sensitive. The nature of **1** has been established by single-crystal X-ray analysis (see below).

Preparation of $[Ag(pyz)_2](PF_6)$ (2). Compound **2** was obtained as fine crystals upon layering a solution of pyz (0.210 g, 2.56 mmol) in ethanol (3 mL) on a water solution (3 mL) of $AgPF_6$ (0.324 g, 1.28 mmol). The crystals were filtered off, washed with ethanol, and dried in air. Yield: *ca.* 20%. Anal. Calcd for $C_8H_8AgF_6N_4P$ (**2**): C, 23.26; H, 1.95; N, 13.57. Found: C, 23.34; H, 1.51; N, 13.40. The product is air stable for days.

Crystallography. Colorless crystals of compounds **1** and **2** were mounted, under a coating of cyanoacrylic glue to prevent decomposition, on an Enraf-Nonius CAD-4 diffractometer. The data collections were performed at 293 K, by the ω-scan method, using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å), within the limits $3 < \theta < 26°$ (**1**) and $3 < \theta < 27°$ (**2**). The pertinent data are summarized in Table 1. Three standard reflections, monitored after every 200, revealed no significant crystal decay. Lorentz−polarization and ψ-scan absorption corrections were applied to the intensities in both cases. The two structures were solved by direct methods (SIR92)[16] and refined by full-matrix least-squares (SHELXL-93).[17] In **1** the cross-linking ppz ligands exhibit disorder of the N atoms, corresponding to the two possible chair conformations of the cycles, with occupancies 0.8 and 0.2 (only the dominant conformer is shown in the figures). Anisotropic thermal factors were assigned to all the non-hydrogen atoms. The hydrogen atoms were located in ideal positions. The molecular drawings were produced with the SCHAKAL[18] program.

---

[1] (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.

[2] Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283.

[3] Moore, J. S.; Lee, S. *Chem. Ind.* **1994**, 556.

[4] (a) Aumuller, A.; Erk, P.; Klebe, G.; Hunig, S.; von Schutz, J. U.; Werner, H.-P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 740. (b) Ermer, O. *Adv. Mater.* **1991**, *3*, 608 and references therein.

[5] See *e.g.*: De Munno, G.; Munoz, M. C.; Julve, M. *Inorg. Chem.* **1991**, *30*, 2701 and references therein.

[6] See *e.g.*: (a) Kitazawa, T.; Nishikiori, S.; Kuroda, R.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 1029 and references therein. (b) Yuge, H.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 1237.

[7] Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

[8] (a) Desiraju, G. R. *Crystal Engineering: Design of Organic Solids*; Elsevier: Amsterdam, 1989. (b) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747. (c) Ermer, O.; Eling, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 925 and references therein. (d) Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *371*, 591.

[9] (a) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Sutherland, E. E. *J. Chem. Soc., Chem. Commun.* **1994**, 1049. (b) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727.

[10] Brimah, A. K.; Siebel, E.; Fischer, R. D.; Davies, N. A.; Apperley, D. C.; Harris, R. K. *J. Organomet. Chem.* **1994**, *475*, 85.

[11] (a) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (b) Soma, T.; Iwamoto, T. *Chem. Lett.* **1994**, 821.

[12] Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665.

[13] (a) Hoskins, B. F.; Robson, R.; Scarlett, N. V. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2025. (b) A reviewer has pointed out that $Rb[Cd(Ag(CN)_2)_3]$ is isomorphous with the previously reported $K[Co(Au(CN)_2)_3]$: Abrahams, S. C.; Bernstein, J. L.; Liminga, R.; Eisenmann, E. T. *J. Chem. Phys.* **1980**, *73*, 4585.

[14] Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755.

[15] (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.

[16] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[17] Sheldrick, G. M. SHELXL-93: program for structure refinement. University of Göttingen, Germany, 1994.

[18] Keller, E. SCHAKAL 92: a computer program for the graphical representation of crystallographic models. University of Freiburg, Germany, 1992.

0020-1669/95/1334-5698$09.00/0

Table 1. Crystallographic Data for [Ag(ppz)$_2$](BF$_4$) (**1**) and [Ag(pyz)$_2$](PF$_6$) (**2**)

	1	**2**
formula	$C_8H_{20}AgBF_4N_4$	$C_8H_8AgF_6N_4P$
fw	366.96	413.02
crystal system	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	6.275(2)	7.286(1)
b, Å	9.900(3)	9.109(2)
c, Å	11.030(3)	10.984(2)
α, deg	89.62(2)	102.00(2)
β, deg	90.55(2)	90.93(1)
γ, deg	97.38(2)	111.20(1)
V, Å^3	679.5(4)	661.5(2)
Z	2	2
d(calc), g cm^{-3}	1.794	2.074
abs coeff, mm^{-1}	1.517	1.710
θ range, deg	3–26	3–27
no. of reflns collcd	2659	2850
obs refln criterion	$>3\sigma(I)$ (2048)	$>3\sigma(I)$ (2526)
R_1,[a] R_2[b]	0.0614, 0.1620	0.0315, 0.0910

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

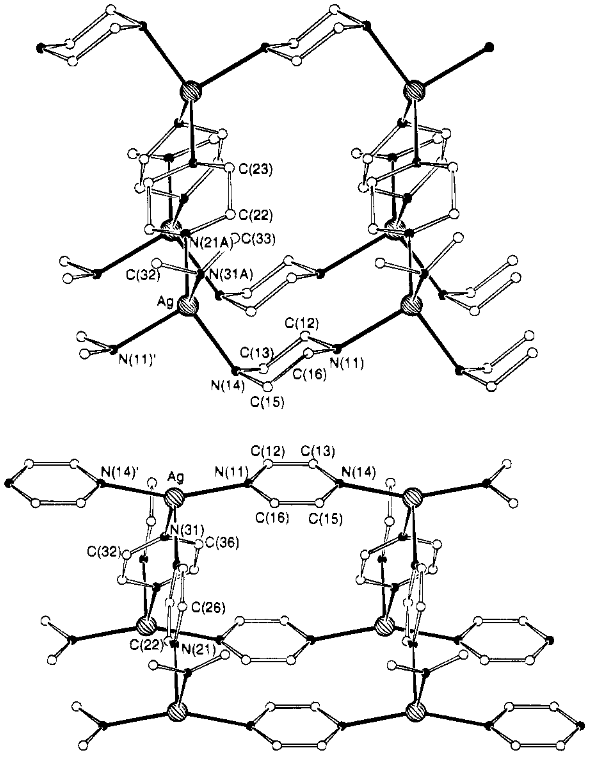

Figure 1. Views of a portion of a single sheet showing the metal ion coordination in **1** (above) and **2** (below).

Results and Discussion

The metal ion coordination in both compounds is illustrated in Figure 1, and the main bond parameters are given in Table 2. In **1**, the Ag$^+$ ions are coordinated to the N atoms of four bridging ppz ligands, displaying distorted tetrahedral geometry. Chains with linear dispositions of the Ag$^+$ ions extend along the *a* axis, cross-linked by the other ppz ligands in the *c* direction. It is noteworthy that, in order to achieve a tetrahedral disposition of the N atoms around each metal ion, two ligands coordinate in an equatorial–equatorial and the other two in an equatorial–axial fashion. This is, to our knowledge, the unique polymeric species assembled with ppz ligands. The intrasheet Ag···Ag separations, *i.e.* the edges of the distorted squares, are 6.275(2) (along the chains), 7.491(3), and 7.520(3) Å.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1** and **2**

Compound 1			
Ag–N11[a]	2.439(6)	Ag–N21A	2.316(8)
Ag–N14	2.350(6)	Ag–N31A	2.438(9)
N11[a]–Ag–N14	94.3(2)	N14–Ag–N21A	126.7(3)
N11[a]–Ag–N21A	112.8(3)	N14–Ag–N31A	114.2(4)
N11[a]–Ag–N31A	111.4(3)	N21A–Ag–N31A	98.0(4)
Compound 2			
Ag–N11	2.292(3)	Ag–N21	2.510(3)
Ag–N14[a]	2.306(3)	Ag–N31	2.389(3)
N11–Ag–N14[a]	155.8(1)	N14[a]–Ag–N21	94.1(1)
N11–Ag–N21	97.6(1)	N14[a]–Ag–N31	98.1(1)
N11–Ag–N31	101.6(1)	N21–Ag–N31	95.7(1)

[a] *x* − 1, *y*, *z*.

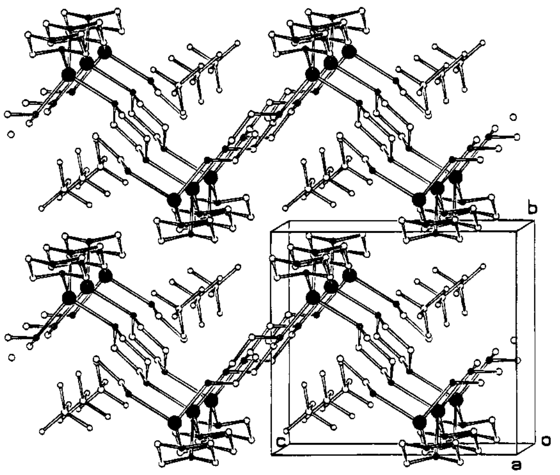

Figure 2. View of the packing of **1** down *a*.

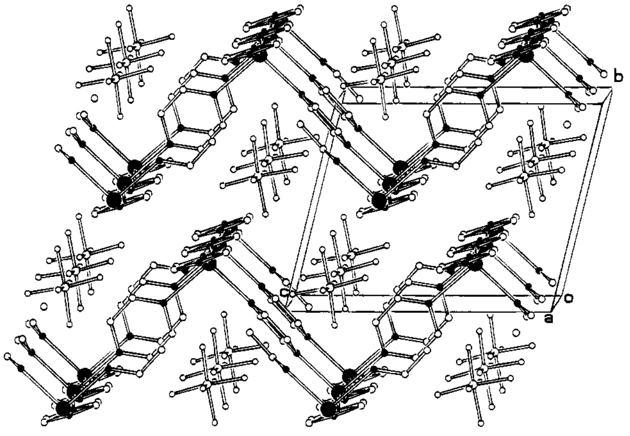

Figure 3. View of the packing of **2** down *a*.

While the nonrigidity and versatility of ppz in its coordination modes can readily account for the polymeric structure of **1**, more surprising and unpredictable is the finding of the same type of 2D sheets in **2**, self-assembled with the rigid linear pyz ligands. In fact, the metal ions assume an unusual strained coordination (see Figure 1), similar to the disphenoidal (or seesaw) geometry observed for the AB$_4$E systems as SF$_4$. Almost linear polymeric chains develop along *a*, cross-linked by the other pyz ligands in the *c* direction. The Ag···Ag separations within the sheets are 7.286(2) (along the chains), 7.555(2), and 7.781(2) Å.

In both **1** and **2**, the layers are markedly pleated, as illustrated in Figures 2 and 3, respectively, which show also the channels occupied by the anions. The superimposing 2D nets form "waves", in-phase in **1** and somewhat out-of-phase in **2**, propagating in the direction of the *c* axis (in both compounds), with "wavelengths" of 11.030(3) and 10.984(2) Å, respectively. The piling of the sheets occurs with a small relative shift in **1**, while in **2** they exhibit a displacement of half the period along *a* on passing to each successive layer. The mutual joints of the complementary corners (*i.e.* crests and valleys) of the folded sheets determine values of the shortest intersheet Ag···Ag contacts which are comparable to or shorter than the intrasheet ones [7.369(3) Å in **1** and 5.955(1) Å in **2**].

It is worth mentioning that the structures of **1** and **2** have some resemblance to those of the 2D species so far reported, [Cu(glutaronitrile)$_2$](NO$_3$)[19a] and [Ag(adiponitrile)$_2$](ClO$_4$),[20] which contain planar layers of squares of tetrahedral metal centers. However, with such long-chain flexible bridges, there are no steric problems encountered in the metals attaining their preferred geometries; for analogous reasons, polyselenide chains can generate diamondoid frameworks in K_2PdSe_{10} based on square-planar Pd centers instead of tetrahedral ones.[21]

We recently discussed the possible interconversion between two polymorphs of [Ag(4-cyanopyridine)$_2$](BF$_4$), one consisting of four interpenetrating diamondoid frames and the second of planar sheets of square meshes.[14] Also the structures here described can be related and represent a possible structural alternative (in the self-assembly) to diamondoid networks, the main difference consisting in the fact that the ligands cross-linking the chains in **1** and **2** bond adjacent chains always by the same side instead of alternately (along the chains) up and down. Note that the complex [Cu(2,5-dimethylpyrazine)$_2$](PF$_6$),[22] strictly related to **2**, contains a single diamondoid frame; comparable packing efficiencies are achieved in both cases, as indicated by the very close values of the average volume *per* non-hydrogen atom. Moreover, a similar relationship holds for the above mentioned 2D polymer [Ag(adiponitrile)$_2$](ClO$_4$) and for [Cu(adiponitrile)$_2$](NO$_3$), which contains a 6-fold diamondoid network.[19b] Subtle factors, together with small differences in steric requirements of the components, can drive the self-assembly in either one or the other direction.

Supporting Information Available: Tables listing complete crystal data and refinement details, atomic positional parameters, thermal parameters, hydrogen atom parameters, and complete distances and angles (15 pages). Ordering information is given on any current masthead page.

IC950393G

---

(19) (a) Kinoshita, Y.; Matsubara, I.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1216. (b) Kinoshita, Y.; Matsubara, I.; Hibuchi, T.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1221.

(20) Barnhart, D. M.; Caughlan, C. N.; Ul-Haque, M. *Inorg. Chem.* **1969**, *8*, 2768.

(21) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 4878.

(22) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Inorg. Chem.* **1993**, *32*, 1607.