Interpenetrating Diamondoid Frameworks of Silver(I) Cations Linked by N,N'-Bidentate Molecular Rods

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Three novel coordination polymers, [Ag(N–N)$_2$]X (N–N = 4,4'-bipyridyl, X = CF$_3$SO$_3^-$ 1; N–N = 4-cyanopyridine, X = BF$_4^-$, in two polymorphs, 2 and 3)], are prepared and investigated by single crystal X-ray analysis; 1 and 2 contain three-dimensional cationic frameworks, both consisting of four equivalent interpenetrating diamondoid lattices, while 3 is formed by two-dimensional layers of distorted squares.

A great deal of interest has recently been devoted to the development of rational synthetic routes to novel 2D and 3D crystal frameworks for their potential applications in many areas. Organic supramolecular chemistry has afforded many interesting results,[1] including various 3D hydrogen-bonded frames of super-diamond[2] and super-wurtzite[2b] structures. In the field of inorganic and coordination polymers, Hoskins and Robson[3a,b] have proposed a strategy in the design of new 3D phases, indicated as 'scaffolding-like materials', which are assembled by using suitable metal centres and molecular rods of different nature and length, and have potential utility in host–guest chemistry, ion exchange and catalysis. This rationale has been fruitfully applied in some recent studies, leading to new frameworks, eventually exhibiting interwoven nets.[3–6] A significant part of this research has concerned 2D and 3D systems assembled by using Cu$^+$ salts and N,N'-donor bidentate linear ligands, with different rod lengths, such as pyrazine, quinoxaline, phenazine, 4-cyanopyridine, 4,4'-bipyridyl, 1,4-dicyanobenzene and related species. We report here the results of our studies on systems based on Ag$^+$ centres, with poorly coordinating counter-ions, and the bases 4,4'=bipyridyl (4,4'-bipy) and 4-cyanopyridine (4-cnpy). Few polymeric 1D silver complexes with the above mentioned N,N'-ligands have been reported.[7] The products described herein represent the first examples of 3D and 2D polymeric silver complexes of this class. They are stable compounds, synthesized in air.

Crystals of [Ag(4,4'-bipy)$_2$](CF$_3$SO$_3$) 1† were obtained by slow diffusion, on layering a solution of Ag(CF$_3$SO$_3$) in Pr^{i}OH over a solution of the base in acetone (molar ratio 1:2). 1 Contains four interpenetrating diamondoid frameworks, based on adamantanoid cages, illustrated in Fig. 1 (Ag···Ag intraframe separations of ca. 11.6 Å). The shortest vector relating the four independent networks is close to 1/2c (Ag···Ag internet contact of ca. 6.69 Å). The Ag$^+$ cations

display a distorted tetrahedral geometry [N–Ag–N in the range 98.8(2)–128.2(2)°], with Ag–N contacts different for the two independent 4,4'-bipy ligands (mean 2.270 vs. 2.380 Å). The unique previous example of a 3D coordination polymer containing 4,4'-bipy‡ is [Cu(4,4'-bipy)$_2$](PF$_6$),[6] containing a similar fourfold diamondoid frame, in spite of the shorter Cu···Cu intraframe separation of 11.16 Å.

Slow diffusion of an ethanolic solution of AgBF$_4$ placed over 4-cyanopyridine dissolved in THF (molar ratio 1:2) afforded multifaced cuboidal crystals of [Ag(4-cnpy)$_2$](BF$_4$) 2,† and in a smaller amount another crystalline species 3 with an elongated prismatic shape, a polymorph of 2.† Compound 2 is topologically equivalent to 1; the four independent interwoven diamondoid networks have now an Ag···Ag intraframe separation of 9.93 Å, and the shortest vector relating adjacent nets is now exactly c (Ag···Ag interframe contact 4.822 Å). Fig. 2 shows the four interpenetrating nets (4-fold diamondoid) in 2. The Ag$^+$ cations, lying on mm special positions, exhibit markedly flattened tetrahedral geometry, with N(py)–Ag–N(py), N(cn)–Ag–N(cn) and N(py)–Ag–N(cn) angles of 127.7(5), 126.5(5) and 101.45(12)°, respectively. These local distortions result into a global compression of the adamantanoid cages along c, not observed in 1, the ratio between the longest parallel and orthogonal (to c) Ag···Ag intracage distances being 0.79 in 2 vs. 1.01 in 1. The Ag–N bond lengths have values of 2.270(6) Å [Ag–N(py)] and 2.350(10) Å [Ag–N(cn)]. The presence of iso-orientated anisobidentate (with donor ends differing both in steric need and in basic character) ligands gives rise for 2, at variance from 1, to a polar axis (c). Fig. 2 shows the stacking of the aromatic rings, a general feature for such ligands, and these π–π interactions can play an important role in orienting the self-assembly of the unit frames. The BF$_4^-$ anions (disordered about fourfold axes) occupy channels of square section, along the c axis. This is the unique diamondoid framework assembled with 4-cnpy ligands only.§
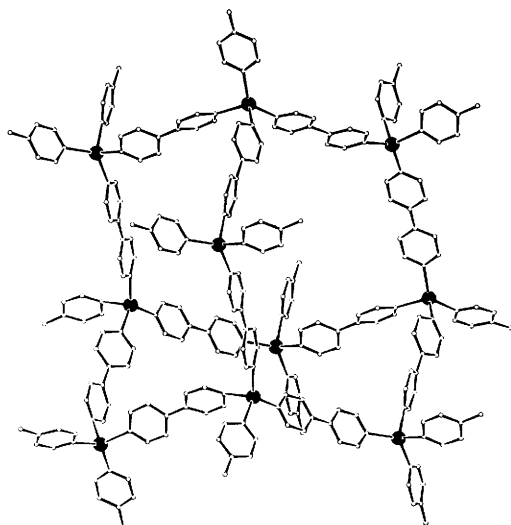

Fig. 1 A view of a single adamantanoid cage of 1. Note, one of the two independent 4,4'-bipy ligands is not planar and gives one bent interaction with the Ag$^+$ ions.
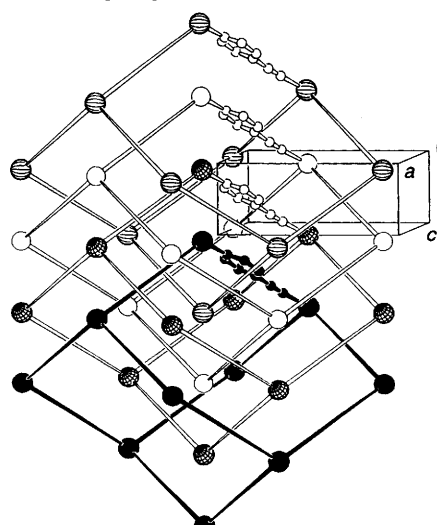

Fig. 2 A schematic view of the four equivalent interpenetrating diamondoid frames in 2. Only one set of stacked ligands (interplanar distance of 4.0 Å) is shown for clarity.
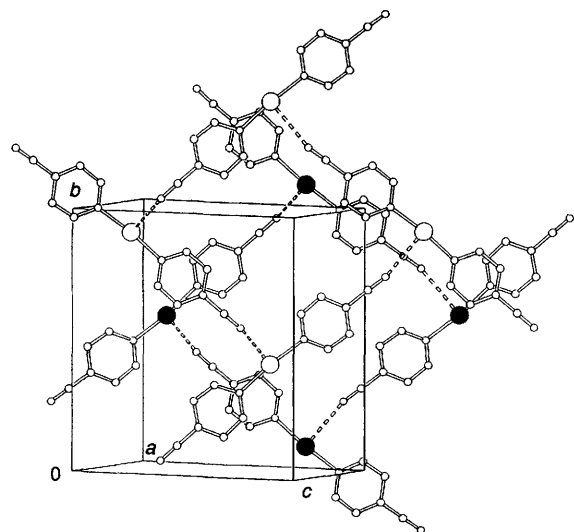
Fig. 3 A view of two sheets of **3** [white (*a*) and black (*b*) balls for the silver ions], down the (−2,1,0) direction

Compounds **1** and **2** are novel members of the limited family of super-diamond networks in coordination polymer chemistry. Interpenetration, which arises by the necessity to fill the empty spaces inside the large cages, is the rule rather than the exception in these species.[10] The structural variability is large, including the presence of: *i*, different interpenetrating frames;[11] *ii*, different types of tetrahedral centres;[3a,12] *iii*, anisobidentate ligand, as in **2**; *iv*, mixed rods;[9] *v*, chiral metallic centres;[9] and *vi*, polymetal centres.[13]

Compound **3** contains Ag$^+$ ions which are linearly coordinated to two N(py) atoms [mean Ag–N(py) 2.175 Å, N(py)–Ag–N(py) 173.4(3)°] and weakly intereacting also with two N(cn) atoms [Ag–N(cn) 2.71(1), 3.06(1) Å] of two other ligands, affording a distorted square planar coordination. The structure of the cationic frame can be described as consisting of almost planar sheets of distorted square meshes (see Fig. 3). These sheets are superimposed, in the crystal, at a distance of 3.56 Å and alternately shifted of *ca.* 6.2 Å, in a sequence *abab* (Ag···Ag shortest intersheet contact of 6.03 Å). Interestingly, the two polymorphs **2** and **3** can be structurally correlated in a simple way, since also **2** contains a sequence of superimposed planar layers of squares of Ag$^+$ ions and, grossly speaking, the main difference in the two structures arises from the different disposition of the bridging ligands, laying within the layers in **3** but joining adjacent layers in **2**. The ideal breaking of all the Ag–N(cn) bonds in **2** followed by the synchronous falling or rising (depending upon the versus of the polar *c* axis) of all the 4-cnpy ligands on the planes of their residually connected [to the N(py) end] Ag$^+$ ions afford layers as those in **3**. Note that **3** can also be considered a frozen intermediate state of the interconversion of the two polar structures of **2**. The above process implies large distortions of the square meshes in the layers and variations of the interlayer distances and offsets. Such distortions, however compensate, since the two species have almost the same density.

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Footnotes

† *Crystal data* for **1**: [Ag(4,4′-bipy)$_2$](CF$_3$SO$_3$), *M* = 569.31, orthorhombic *Pbca* (No. 61), *a* = 16.119(2), *b* = 20.898(3), *c* = 13.325(2) Å, *U* = 4488.6 Å^3, *Z* = 8, *D*$_c$ = 1.685 mg m^{-3}, Mo-Kα radiation (λ =

0.71069 Å). The data collection was performed on an Enraf-Nonius CAD4 diffractometer, by the ω-scan method, within the limits 3 < θ < 26°. The structure was solved by direct methods (SIR92) and the refinements (SHELX-93), by full-matrix least-squares analysis, gave a final agreement index *R* of 0.0373 for 1799 significant [$F_o > 4\sigma(F_o)$] absorption corrected data, out of the 4008 unique collected reflections.

Crystal data for **2**: [Ag(4-cnpy)$_2$](BF$_4$), *M* = 402.90, tetragonal, *P4bm* (No. 100), *a* = 12.269(1), *c* = 4.822(1) Å, *U* = 725.9 Å^3, *Z* = 2, *D*$_c$ = 1.843 mg m^{-3}. Data collection, in the range 3 < θ < 28°, afforded 520 unique reflections. The anions are disordered on fourfold axes. The refinements lead to a final *R* of 0.0295 for 370 significant [$F_o > 4\sigma(F_o)$] absorption corrected data.

Crystal data for **3**: [Ag(4-cnpy)$_2$](BF$_4$), *M* = 402.90, monoclinic, *P2$_1$/a* (No. 14), *a* = 7.994(5), *b* = 13.544(6), *c* = 13.450(10) Å, β = 95.00(6)°, *U* = 1451 Å^3, *Z* = 4, *D*$_c$ = 1.845 mg m^{-3}. The measured independent intensities in the range 3 < θ < 25° were 2528. The anions were found to be disordered. The final *R* value for 1175 absorption corrected significant [$F_o > 4\sigma(F_o)$] data was 0.0549.

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.

‡ We have very recently characterized the structure of [Cu(4,4′-bipy)$_2$](CF$_3$SO$_3$) [tetragonal, *P4/n*, *a* = 13.367(2), *c* = 6.090(1) Å], containing another example of a fourfold diamondoid network. A 3D frame (fourfold diamondoid), based on the assembly of [Mn$_4$(CO)$_{12}$(OH)$_4$] units *via* hydrogen bonds with 4,4′-bipy, has also been reported.[8]

§ The interesting species [Cu(4-cnpy)$_2$](ClO$_4$), cited as an example of a twofold diamondoid network in Ref. 3(*c*), has never been published. The super-diamond nature of the 3D framework in the related, so far reported, [Cu(CN)(4-cnpy)] (3-fold diamondoid) was then ignored.[9]

References

1 G. R. Desiraju, *Crystal Engineering: Design of Organic Solids*, Elsevier, Ambsterdam, 1989.
2 See *e.g.* (*a*) O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747; (*b*) O. Ermer and A. Eling, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 925, and refs. therein.
3 (*a*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; (*b*) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecture*, 1992, ch. 19; (*c*) R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1677; (*d*) B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and E. E. Sutherland, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1049; (*e*) B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727.
4 S. Kitagawa, M. Munakata and T. Tanimura, *Inorg. Chem.*, 1992, **31**, 1714.
5 T. Otieno, S. J. Rettig, R. C. Thompson and J. Trotter, *Inorg. Chem.*, 1993, **32**, 1607.
6 L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1325.
7 R. G. Vranka and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1020; T. Tsuda, S. Ohba, M. Takahashi and M. Ito, *Acta Cryst.*, *Sect. C*, *Cryst. Struct. Commun.*, 1989, **45**, 887; M. Munakata, S. Kitagawa, N. Ujimaru, M. Nakamura, M. Maekawa and H. Matsuda, *Inorg. Chem.*, 1993, **32**, 826.
8 S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1078.
9 D. T. Cromer and A. C. Larson, *Acta Cryst.*, *Sect. B*, 1972, B, **28**, 1052.
10 O. Ermer, *Adv. Mater.*, 1991, **3**, 608, and refs. therein.
11 K.-W. Kim and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1992, **114**, 4878.
12 T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1029.
13 A. Michaelides, V. Kiritsis, S. Skoulika and A. Aubry, *Angew. Chem. int. Ed. Engl.*, 1993, **32**, 1495.