A three-dimensional ‘racemate’. Interpenetration of two enantiomeric networks of the $SrSi_2$ topological type in the polymeric complex $[Ag_2(2,3\text{-}Me_2pyz)_3][SbF_6]_2$ (2,3-Me_2pyz = 2,3-dimethylpyrazine)

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The polymeric species $[Ag_2(2,3\text{-}Me_2pyz)_3][SbF_6]_2$ contains two three-dimensional three-connected cationic networks, belonging to the $SrSi_2$ topological type, which are enantiomeric and interpenetrating, to give an unique case of a three-dimensional ‘racemate’.

Crystal engineering of two- and three-dimensional polymers[1] has recently shown that novel types of molecular based frameworks can be assembled using proper metallic centres and suitable polydentate ligands.[2] Nowadays many examples of three-dimensional super-diamond nets are known,[3] exhibiting up to nine-fold interpenetration.[4] More rare are the known examples of three-connected three-dimensional frames; they present, in the highest symmetry, two main topological types, indicated by Wells[5] as 10^3-a (cubic) and 10^3-b (tetragonal), which are represented by the prototypal structures of $SrSi_2$ and α-$ThSi_2$, respectively. Three recently reported examples of the latter type are known, all containing interpenetrating networks.[6–8] The 10^3-a net, the three-connected analogue of the (four-connected) diamond net, is even more elusive; we have recently found an example of such a topological type in $[Ag(hmt)]PF_6{\cdot}H_2O$ (hmt = hexamethylenetetramine),[9] which was precedented, in coordination polymer chemistry, only by the iron(II)–oxalate anionic frame in $[Fe^{II}(2,2'\text{-}bipy)_3][Fe^{II}_2(ox)_3]$.[10]

Wells[6c] has suggested the possibility that a chiral frame of the 10^3-a type (aristotypic space group $I4_132$ cubic) could be interpenetrated by a second frame of the same type, but with opposite chirality, thus resulting in a three-dimensional solid-state ‘racemate’ (aristotypic space group $Ia\bar{3}d$ cubic, see Fig. 1). We report here on the synthesis and X-ray single-crystal characterization of the polymeric complex $[Ag_2(2,3\text{-}Me_2pyz)_3][SbF_6]_2$ (2,3-Me_2pyz = 2,3-dimethylpyrazine), **1**, which contains two enantiomeric interpenetrating networks of the above described topology.

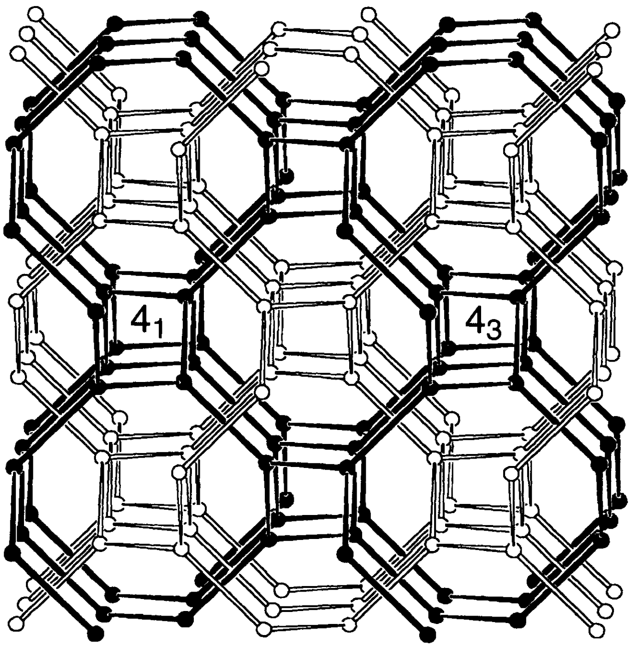

Fig. 1

Compound **1** was prepared on layering over a solution of 2,3-dimethylpyrazine (0.038 ml, 0.35 mmol) in CH_2Cl_2 (3 ml) a layer of ethanol (1 ml) and, over this, a solution of $AgSbF_6$ (0.061 g, 0.18 mml) in ethanol (3 ml). After a few days large fine colourless crystals of **1** were isolated in high yield (> 85%); they are air and light stable and their nature has been established by single-crystal X-ray analysis.† The analogous PF_6^- derivative, prepared in a similar manner, is isomorphous with **1**.‡

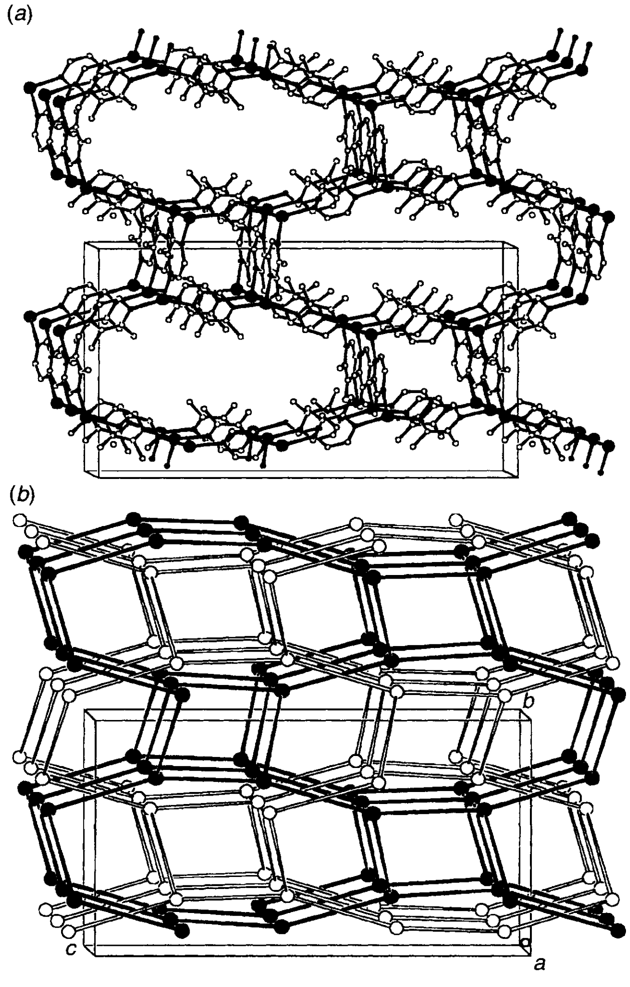

Fig. 2 SCHAKAL views down the *a* axis of (*a*) a single network of **1** and (*b*) a schematic view of the two interpenetrating networks of **1**

A single cationic network of **1** is shown in Fig. 2(*a*). Zigzag chains of ligand-bridged silver ions, displaying Ag···Ag contacts of 7.161(4) and 7.231(4) Å, extend in the direction of the crystallographic *c* axis, with alternate N–Ag–N angles of 148.0(8) and 143.8(7) °. These chains are cross-linked by other bridging ligands [Ag···Ag interchain contacts of 7.580(4) Å, N–Ag–N 104.1(7)–111.8(6) °] to give a three-dimensional enantiomorphic network of the 10^3-a topological type, heavily stretched in the *c* direction (as clearly evidenced by the anisotropy of the cell edges). The metal ions exhibit a planar coordination geometry, intermediate between trigonal and T-shaped, with two shorter (intrachain) Ag–N bonds (mean 2.25 Å) and a longer one, involving the cross-linking ligands (mean 2.44 Å). Similar (2 + 1) coordination modes of Ag^I ions are often observed in framework structures bridged by linear bidentate ligands, as, for instance, in the two α-$ThSi_2$ species $[Ag_2(pyz)_3][BF_4]_2$,[6] and $[Ag(4,4'\text{-bipy})]NO_3$.[8] This perturbed form of the usual twofold linear silver coordination, presenting two stronger *transoid* bonds, a third weaker interaction and, more importantly, N–Ag–N angles substantially different from the ideal trigonal value, is at the origin of the drastic distortion of the frame in **1** with respect to the ideal cubic geometry. Thermal analyses of **1** confirm that one of the ligand molecules is more weakly bound and more easily removed on heating.§

A network of the 10^3-a type exhibits large channels of octagonal section (see Fig. 1), whose dimensions are related to the length of the rods connecting the centres; these large holes are usually filled by the counter ions. So, in the archetypal $SrSi_2$ (rod length 2.39 Å) the channels contain the Sr^{2+} cations, in $[Ag(hmt)]PF_6{\cdot}H_2O$ (rod length 3.85 Å) an interpenetrated hydrogen-bonded network involving the PF_6^- anions and the water molecules, and in $[Fe^{II}(2,2'\text{-bipy})_3]$ $[Fe^{II}_2(ox)_3]$ (rod length 5.48 Å) the cationic complexes $[Fe^{II}(2,2'\text{-bipy})_3]^{2+}$.¶ In the present case the SbF_6^- anions associated with a single frame (rod length 7.16–7.58 Å) are not sufficient to fill the whole free space and a second network of the same type, but of opposite chirality, interpenetrates the former one. The two enantiomeric frames are centrosymmetrically related, giving a three-dimensional enmeshed 'racemate', whose potential existence and definition was anticipated by Wells many years ago.[5c] A schematic view of this double network is shown in Fig. 2(*b*). While examples of interpenetrating three-dimensional networks of the same handedness are known, such as the sixfold enmeshed quartz-like species $[MAu_2(CN)_4]$ (M = Co,[11] Zn[12]), and balanced (or unbalanced) packings of infinite helices are rather common, the structural features of **1** are unique, making it a fascinating solid-state rarity. The only comparable example is the above-mentioned $[Ag(hmt)]PF_6{\cdot}H_2O$, containing a 10^3-a type frame of alternating Ag^I ions and hexamethylenetetramine ligands interpenetrated by a disordered hydrogen-bonded net, of alternating PF_6^- and water molecules, of the same topology but opposite chirality.

The open 10^3-a net seems a good candidate as structural model for scaffolding-like materials,[1] alternative to the diamondoid net; however, interpenetration should be avoided, and the structure of **1** shows that it represents a problem, as in diamondoid polymers, when the rods become relatively long.

Footnotes

† *Crystal data:* $C_{18}H_{24}Ag_2F_{12}N_6Sb_2$, M_w = 1011.67, orthorhombic, space group *Pcab* (no. 61), *a* = 13.648(2), *b* = 15.437(5), *c* = 27.366(6) Å, *U* = 5766(2) $Å^3$, *Z* = 8, D_c = 2.331 Mg m^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) 3.291 mm^{-1}. The data collection was performed at 293 K on an Enraf-Nonius CAD4 diffractometer, by the ω-scan method, within the limits 3 < θ < 26°; an empirical absorption correction was applied. The structure was solved by direct methods (SIR92) and refined on F_o^2 by full-matrix least squares (SHELX-93). One of three independent (2,3-Me_2pyz) ligands exhibits a statistical disorder of the two methyl groups on the four carbon atoms. Anisotropic thermal parameters were assigned only to the Ag, Sb and F atoms. The final agreement indices *R* and wR^2 for all the 2203 independent observed $[F_o > 4\sigma(F_o)]$ data were 0.0818 and 0.1381, respectively. All the diagrams were obtained using the SCHAKAL program.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/68.

‡ *Crystal data* for $[Ag_2(2,3\text{-}Me_2pyz)_3][PF_6]_2$: orthorhombic, space group *Pcab* (no. 61), *a* = 13.232(2), *b* = 15.064(1), *c* = 27.420(2) Å, *U* = 5465(1) $Å^3$.

§ DSC and TG analyses of **1** show that the compound is thermally stable up to *ca.* 180 °C, then it shows a mass loss of about 11% at *ca.* 215 °C, corresponding to one molecule of ligand per formula unit [ΔH *ca.* 11 kcal mol^{-1} (cal = 4.184 J)], followed by a complex decomposition process starting at *ca.* 250 °C, involving in sequence the other ligands and the anions.

¶ Detailed investigation in the Cambridge Database has revealed only one other case of a 10^3-a net, not alluded to by the authors, consisting of Zn^{2+} centres bridged by bis(2-pyrrolidonato)mercury(II), in which the same large ligands occupy the distorted octagonal channels: D. M. L. Goodgame, D. J. Williams and R. E.P. Winpenny, *Polyhedron*, 1989, **8**, 1913.

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