Synthesis and Structure of $Rb[Cd\{Ag(CN)_2\}_3]$ Containing Three Independent, Interpenetrating α-Polonium-related Nets

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Enantiomorphic crystals of $Rb[Cd\{Ag(CN)_2\}_3]$ contain three identical, independent and interpenetrating 3D nets, each related to the net observed in the Prussian blue family, with an approximately linear $NCAgCN^-$ connector in place of the CN^- of the parent.

The current interest in cyano-bridged polymers manifested in numerous recent reports which collectively reveal a remarkable diversity of structural types[1] has been heightened by the recently reported ferrimagnetism of some simple chromium-containing examples.[2] We report here a cyano-bridged 3D structure based on the 6-connected net related to α-polonium which, in its geometrically most symmetrical form, consists of octahedral centres linked together in a simple cubic network of squares, *i.e.* 3D space tessellated by cubes. Well-known examples of this topology are provided by ReO_3 and the Prussian blue family of solids, to which the above-mentioned ferrimagnetic chromium derivatives belong. The structure we describe now can be regarded as an expanded variant on the Prussian blue prototype, in which each linear CN^- connector has been replaced by a linear $Ag(CN)_2^-$ unit. The much larger intraframework spaces resulting from this expansion are occupied by two other identical but independent networks, which interpenetrate the first and each other (together with Rb^+ counter-cations). Interpenetrating networks are of interest not only at the fundamental structural level as special geometrical–topological types but also because they may show unusual properties (chemical, electronic *etc.*) stemming from the intimate entanglement, *e.g.* the 'organic metal' $Cu(Me_2DCNQI)_2$ (where Me_2DCNQI = 2,5-dimethyl-*N,N′*-dicyanoquinodiimine) consists of seven independent and interpenetrating 4-connected diamond-related nets.[3] Although examples of interpenetrating diamond-related nets are becoming more common,[4] interpenetrating 3D nets of other types remain rare. The mineral neptunite has long been known to contain two independent, interpenetrating 3D 3-connected nets[5] and recently examples of interpenetrating rutile-related nets[6] and interpenetrating PtS-related nets[7] were reported by us. To the best of our knowledge the only crystallographically characterised examples of interpenetrating 6-connected nets of the α-polonium type, other than the one we report here, contain Zr/transition metal clusters each of which is chloro-bridged to six neighbouring clusters; two such independent nets then interpenetrate with every 6-connecting cluster located at the centre of a cubic cavity formed by the other net.[8]

Crystals of $Rb[Cd\{Ag(CN)_2\}_3]$ were grown from aqueous mixtures containing RbCl, $AgNO_3$, $Cd(NO_3)_2$ and NaCN and their structure was determined by single-crystal X-ray diffraction.† The unit cell is shown in Fig. 1 and the extended structure viewed from an angle slightly displaced from the 3-fold, *c*-axis is shown in Fig. 2. There is only one type of atom for each of the elements present, *i.e.* all cadmiums are equivalent, all silvers equivalent *etc.* Each silver is bonded to two cyanide carbon atoms in an almost linear fashion [C–Ag–C, 177.0(4)°, Ag–C–N, 178.8(5)°] and each cadmium is octahedrally coordinated by six cyanide nitrogen donors [Cd–N, 2.324(3) Å]. There is a bend at the nitrogen centres in each essentially rod-like Cd–N–C–Ag–C–N–Cd system [Cd–N–C, 160.8(4)°].

Cube-like components characteristic of the α-polonium net can be discerned in Fig. 2 in which they are viewed from an angle slightly displaced from one of the cube solid diagonals which coincides with the crystallographic *c*-axis, *e.g.* the two cadmium centres nearest to and furthest from the reader in the bank of four cadmiums at the very centre of Fig. 2 represent the near and far corners of a particular cuboid viewed almost along a solid diagonal. As can be seen, the corners of two other independent cubes lie on the line between these two cadmium centres. An alternative view of the cuboid structures, indicating more clearly the way they interpenetrate, is shown in Fig. 3. The cuboids are somewhat elongated along the solid diagonal coincident with the crystallographic 3-fold *c*

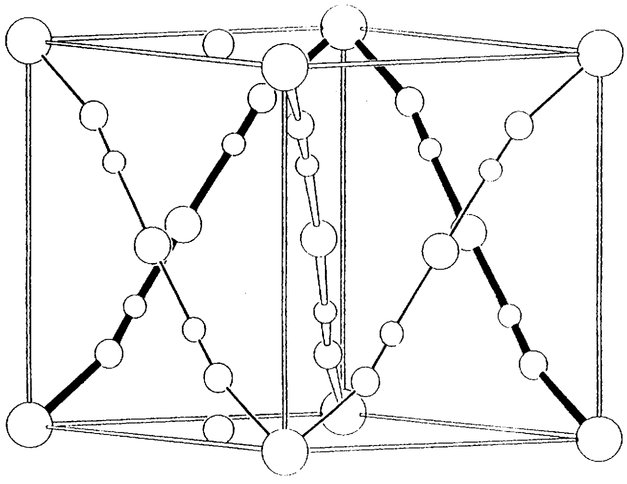

Fig. 1 The unit cell of $Rb[Cd\{Ag(CN)_2\}_3]$. Components of the three independent networks are indicated by 'heavy' bonds, 'thin' bonds and 'open' bonds. Circles in order of decreasing size represent Cd, Ag, Rb, N and C respectively.

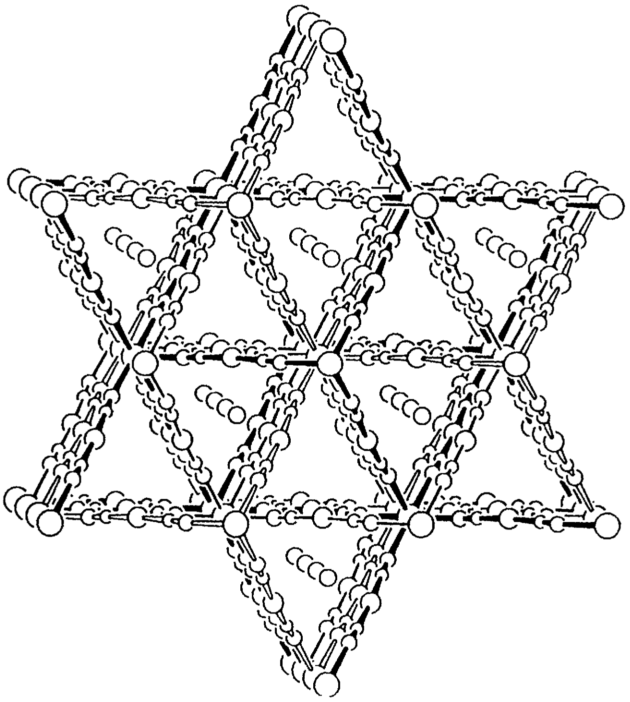

Fig. 2 Extended structure of $Rb[Cd\{Ag(CN)_2\}_3]$ viewed from an angle slightly displaced from the *c* axis. Circles and the different bond representations have the same meaning as in Fig. 1.

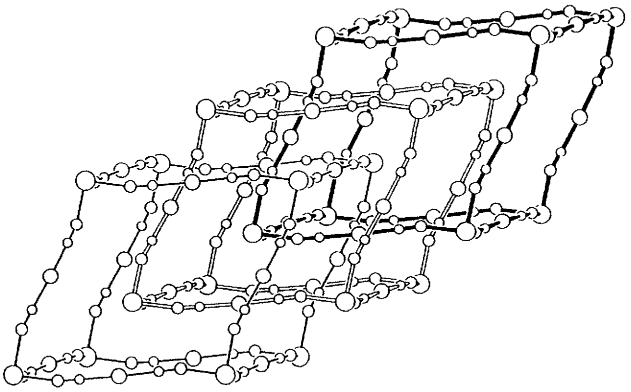

Fig. 3 View of the interpenetrating cuboid components of the three separate frameworks. Circles and the different bond representations have the same significance as in Fig. 1.

axis as a result of the kinks at the nitrogen centres in the cuboid edge connectors [Cd···Cd, 24.528(1) Å]; the other three solid diagonals of the cuboid are contracted [Cd···Cd, 16.478(1) Å] and remain equivalent to each other. Passing through every cuboid 'face', all of which are equivalent, are two Cd–N–C–Ag–C–N–Cd 'rods', one from each of the other two independent frameworks; examples of this structural feature can be seen in the right and top 'faces' of the lower left cuboid in Fig. 3.

Clearly apparent in Fig. 2 are channels of trigonal cross-section bounded by Cd–N–C–Ag–C–N–Cd rods arranged in a helical fashion that imparts handedness to a particular channel. The $[Cd\{Ag(CN)_2\}_3]^-$ anionic network contains equal numbers of right-handed and left-handed helices but the rubidium cations are all located in channels of the one type (left handed in the particular crystal studied†) making the crystal as a whole enantiomorphic.

The rubidium cations are in a roughly octahedral environment of six cyanides [Rb–N, 3.052(5) Å; Rb···C, 3.370(5) Å; C–N–Rb, 96.3(4)°].

The basic structural type reported here would appear to lend itself to wide compositional variation; *e.g.* many octahedral metal centres other than Cd^{2+} could conceivably be incorporated. The number of independent nets could possibly be a controllable variable; *e.g.* cations other than rubidium may promote the formation of interpenetrating structures with different numbers of independent nets; we are presently investigating possibilities of this type.

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Footnote

† *Crystal data*: $Rb[Cd\{Ag(CN)_2\}_3]$, $M = 677.6$, trigonal, space group $P312$ (No. 149), $a = 7.151(2)$, $c = 8.1758(8)$ Å, $U = 362.1(1)$ Å^3, $Z = 1$, $D_c = 3.108$ g cm^{-3}, μ(Mo-Kα) = 8.77 mm^{-1}, $F(000) = 304$. Intensity data were measured at 295(1) K with Mo-Kα radiation (graphite crystal monochromator) using an Enraf-Nonius CAD-4MachS diffractometer and employing the ω–2θ scan method; absorption corrections were applied. A full-matrix least-squares refinement method based on F^2 (SHELXL-93[9]) was employed and anisotropic thermal parameters assigned to all atoms; at convergence $R1 = 0.0305$ and $wR2 = 0.0765$ for the 946 observed reflections $[I > 2\sigma(I)]$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$. An identical refinement using the inverse set of coordinates converged with $R1$ and $wR2$ of 0.0349 and 0.0901 respectively indicating that the original assignment of absolute configuration was correct.

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