

Synthesis and Structure of $[\text{NMe}_4][\text{CuPt}(\text{CN})_4]$: An Infinite Three-dimensional Framework Related to PtS which generates Intersecting Hexagonal Channels of Large Cross Section

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$[\text{NMe}_4][\text{CuPt}(\text{CN})_4]$ contains an infinite 3D $[\text{Cu}^{\text{I}}\text{Pt}^{\text{II}}(\text{CN})_4]_n^{n-}$ framework related to the PtS structure, which generates two mutually perpendicular and equivalent sets of hexagonal channels of large cross-section (largest Pt...Pt diagonal, 13.50 Å) together with large empty square channels perpendicular to the hexagonal channels.

The deliberate construction of a wide range of new and potentially useful scaffolding structures related to diamond may be possible by replacing each of the carbon centres of the prototype by an appropriate tetrahedral unit and each C-C bond by a rod-like unit. Some initial work along these lines has been reported.^{1,2} As a part of our programme of exploratory crystal engineering we are devising and studying simple cyano-metal frameworks involving M-C≡N-M rods, in order to acquire some feeling for the sorts of infinite frameworks that might ultimately be accessible using longer, more

complex rods. Several diamond-related cyano-frameworks are now known.¹⁻³ Cadmium cyanide, whose normal structure consists of two independent but interpenetrating diamond-related frameworks,² adopts a new infinite framework structure when recrystallised from aqueous Bu¹OH, the crystals having the composition $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^1\text{OH}$.⁴ The infinite 3D framework in this case provides parallel channels of large cross-section and consists of tetrahedral and octahedral Cd centres in 2:1 proportions (the octahedral cadmiums having two *trans* water ligands) linked together by CN rods. Infinite 3D frameworks constructed from tetrahedral centres and square-planar centres in 1:1 proportions

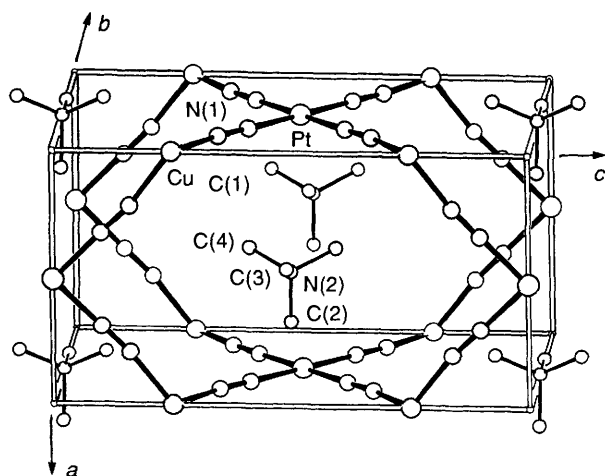


Figure 1. The tetragonal unit cell of $[\text{NMe}_4][\text{CuPt}(\text{CN})_4]$. Selected bond distances (Å) and angles (°): Pt-C(1) 1.96(2), Cu-N(1) 2.006(14), C(1)-N(1) 1.13(2); Cu-N(1)-C(1) 172(2), Pt-C(1)-N(1) 179(2), N(1)-Cu-N(1') 106.4(5), N(1)-Cu-N(1'') 111.0(4), C(1)-Pt-C(1'') 91.2(8), C(1)-Pt-C(1''') 88.8(8). Only one orientation of the disordered NMe_4^+ cation is shown.

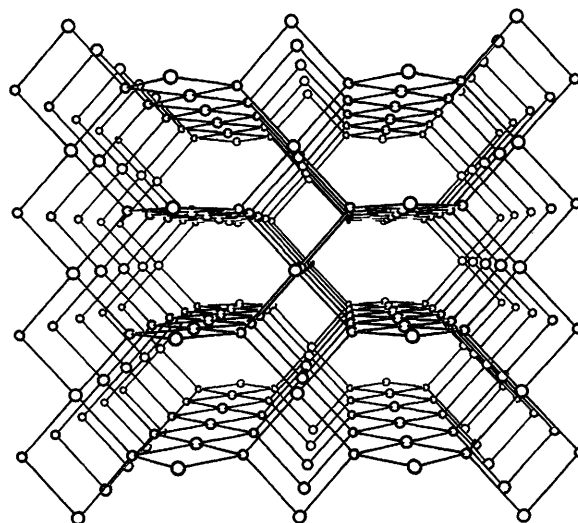


Figure 2. Perspective view of $[\text{CuPt}(\text{CN})_4]_n^{n-}$ extended framework. Only metal centres are shown, the larger being Pt.

linked together by rods would constitute a new structural class for which PtS⁵ can be regarded as the prototype. We report here a new PtS-related framework in which each sulphur of the prototype has been replaced by a tetrahedral Cu^I centre and each Pt–S bond by a Pt–C≡N–Cu rod.

When Cu(MeCN)₄BF₄ in acetonitrile is added to an aqueous solution of K₂Pt(CN)₄ and NMe₄BF₄ a precipitate of [NMe₄][CuPt(CN)₄][†] forms. X-Ray crystallographic analysis of this material[‡] reveals an infinite [CuPt(CN)₄]_nⁿ⁻ anionic framework related to PtS. The tetragonal unit cell is shown in Figure 1. Pt^{II} centres are found in an essentially square-planar 4C environment and Cu^I centres in an approximately tet-

rahedral 4N environment. The PtCNCu rods of length 5.087(1) Å are close to linear. Figure 2 presents one view of the extended 3D framework structure, looking down the *a*-axis (or the equivalent *b*-axis). Hexagonal channels of large dimensions similar in structure to those present in Cd(CN)₂·2/3H₂O·Bu^tOH⁴ are evident. The longest Pt...Pt separation across the hexagonal channel is 13.50 Å, somewhat smaller than the corresponding Cd...Cd diagonal of 14.08 Å in Cd(CN)₂·2/3H₂O·Bu^tOH.⁴ This difference arises from the distinctly shorter metal–cyanide bonds in the present case. The channel system described here differs from that in Cd(CN)₂·2/3H₂O·Bu^tOH in that two perpendicular and equivalent sets of parallel hexagonal channels are present which, in addition, intersect. Another difference is that the hexagonal channels in the Cu, Pt framework are interspersed by parallel channels of approximately square cross-section as is evident in Figure 2. Orthogonal to the two sets of hexagonal channels are square channels of a second type of larger cross-section (edge 7.61 Å) than the first which can be seen in Figure 1 running in the direction of the *c*-axis. The cations are located in the hexagonal channels and are disordered over four equivalent orientations only one of which is shown in Figure 1. The larger square channels are essentially empty, except for those parts of the NMe₄⁺ cations that protrude into them.

We regard this framework as important because of the general potential which it reveals for the construction of related frameworks with longer connecting rods and/or larger square-planar building blocks than those used here. New structures of this PtS-type may offer great scope for deliberately designing new catalysts related in some ways to the much used and studied zeolites.

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[†] Satisfactory elemental analysis.

[‡] Crystals of [NMe₄][CuPt(CN)₄] suitable for diffraction studies were grown by heating in a steambath the lower 10 cm of an 80 cm long tube (1 cm diameter) filled with an aqueous solution containing K₂Pt(CN)₄ (0.060 g) and NMe₄BF₄ (0.172 g) and containing suspended solid CuCN (0.023 g); the upper regions of the tube were in contact with the room atmosphere and the crystals grew here over a period of two weeks.

The space groups *P4₂mc*, *P $\bar{4}$ 2c*, and *P4₂/mmc* are all consistent with the diffraction data recorded for [NMe₄][CuPt(CN)₄]. Refinements were carried out in all three space groups which yielded essentially identical results; the details reported here refer to those obtained for the centrosymmetric space group.

Crystal data for [NMe₄][CuPt(CN)₄]: C₈H₁₂CuN₅Pt, *M* = 436.9, tetragonal, space group *P4₂/mmc* (No. 131), *a* = 7.613(2), *c* = 13.501(2) Å, *U* = 782.5 Å³, *F*(000) = 404, *Z* = 2, *D_c* = 1.852 g cm⁻³, *D_m* = 1.85(1) g cm⁻³, μ(Mo-Kα) = 103.4 cm⁻¹. Intensity data were collected on an Enraf-Nonius CAD-4F single-crystal automatic diffractometer employing the ω–2θ scan method; absorption corrections were applied. The structure was refined using a full-matrix least-squares refinement procedure (SHELX-76), with anisotropic thermal parameters assigned to the Pt, Cu, and the C and N atoms of the cyanide units, and isotropic thermal parameters for the C and N atoms of the disordered NMe₄⁺ cation; at convergence *R* = 0.078 and *R_w* = 0.102 for the 360 observed reflections [*I* ≥ 3σ(*I*)]. The assignment of the C and N atoms of the cyanide group, made on the basis of the X-ray data, was consistent with the expected Pt–C and Cu–N bonds, but only a neutron diffraction study would remove all uncertainty on this point. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.