

Ring of 12 Hydrogen-bonded Water Molecules in a Pyrite-like Framework of Heptacyanodicuprato(II)cadmate(II) $[\text{CdCu}_2(\text{CN})_7]^{3-}$

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The single crystal structure of $[\text{H}_{31}\text{O}_{14}][\text{CdCu}_2(\text{CN})_7]$ demonstrates an interpenetrating three-dimensional array of pyrite-like but negatively-charged framework $[\text{Cd}^{2+}\{\text{Cu}_2(\text{CN})_7\}^{5-}]$ and a ring of 12 water molecules connected successively with two other waters, partly protonated, $[\text{H}_x(\text{H}_2\text{O})_2\text{H}_y(\text{H}_2\text{O})_{12}]^{3+}$ ($x + y = 3$), the ring of which encircles the pyrosilicate-like heptacyanate(I) anion about the Cu–(CN)–Cu axis.

We have been developing a number of inorganic inclusion structures mimicking natural minerals such as cristobalite, clays and zeolites using cadmium cyanide and isopolycyanopolycadmate(II).^{1–3} Recently Kitazawa and Takeda⁴ reported a discrete pyrosilicate-like anion $[\text{Cd}_2(\text{CN})_7]^{3-}$ in $[\text{PPh}_4]_3[\text{Cd}_2(\text{CN})_7]$. The tetrahedral coordination behaviour of Cu(I) makes it similar to those of Cd(II) with cyanide groups.⁵ One of our recent attempts is to develop infinite mineralomimetic structures using tetrahedral Cu(I) along with octahedral Cd(II).

Colourless octahedral crystals of the composition $[\text{H}_{31}\text{O}_{14}][\text{CdCu}_2(\text{CN})_7]$ were obtained from aqueous $\text{K}_2[\text{Cd}(\text{CN})_4]$ and CuCN .† The crystal structure was determined by the single crystal X-ray diffraction method.‡ Novel features demonstrated from the crystal structure are: a pyrite-like framework built of Cd^{2+} and $[\text{Cu}_2(\text{CN})_7]^{5-}$ linked to one another by the terminal CN groups of the latter; a ring structure of 12 hydrogen-bonded water molecules encircling the Cu–(CN)–Cu axis of the pyrosilicate-like $[\text{Cu}_2(\text{CN})_7]^{5-}$; a three-dimensional array of the water rings connected with other water molecules; and the interpenetrating frameworks of the cyanometallate and of the hydrogen-bonded water molecules partly protonated.

The cubic crystal of the $Pa\bar{3}$ space group is isostructural to pyrite (FeS_2) with respect to the three-dimensional array, with Cd^{2+} at the position of Fe and $[\text{Cu}_2(\text{CN})_7]^{5-}$ at that of S_2 , as shown in Fig. 1. The octahedral Cd^{2+} is hexacoordinated with the N ends of six $[\text{Cu}_2(\text{CN})_7]^{5-}$, which dimeric anion is also isostructural with the pyrosilicate-like $[\text{Cd}_2(\text{CN})_7]^{3-}$,⁴ including the disorder of the bridging CN group between the pair of the Cu(I) atoms and the staggered orientation of the terminal CN groups. Three of each N ends at both sides of the anion are linked to three of each Cd^{2+} respectively to build up the three-dimensional framework structure. The 14 water mol-

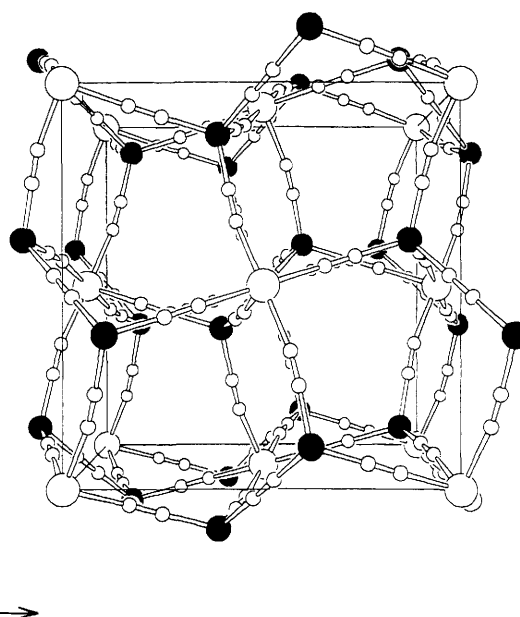


Fig. 1 Perspective view of the $[\text{CdCu}_2(\text{CN})_7]^{3-}$, three-dimensional framework in the unit cell. Cd at 0,0,0 and the equivalent positions; $\text{Cu}_2(\text{CN})_7$ moieties are centred at 0,0,½ and the equivalent positions; the C and N, denoted as X, in the Cu–(CN)–Cu bridge cannot be crystallographically discriminated and the Cu–(CN)–Cu axis is on the 3 axis.

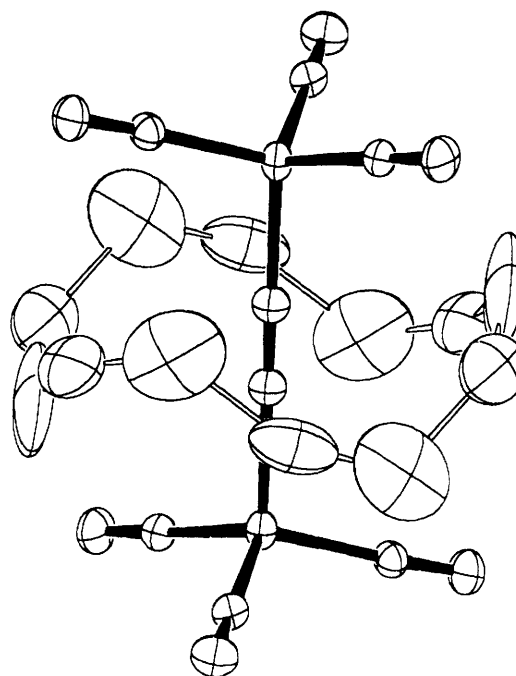


Fig. 2 Ring of the 12 hydrogen-bonded water molecules encircling the $\text{Cu}_2(\text{CN})_7$ moiety about the 3 axis. Each of O(1)–O(2) and equivalent pairs is ca. 3 Å apart from O(3) and equivalents respectively.

† *Preparation*: into 100 cm³ of water, $\text{K}_2\text{Cd}(\text{CN})_4$ (0.007 mol) was dissolved, then CuCN (1 equiv.) was dissolved during 30 min with vigorous stirring. After the solution was filtered and stood at 278 K for a few days, the title compound was obtained as colourless octahedral crystals (ca. 0.1–1.0 mm diameter) (Satisfactory elemental analysis). In the air the product rapidly became white and opaque because some of the water was lost from the crystal. However, rehydration of the sample was observed, too. The powdered sample warmed up to 383 K in the air showed weak IR peaks for water and showed a powder X-ray diffraction pattern different from that of the fresh sample. After leaving the dehydrated sample in the air for one day, the IR peaks and the X-ray powder pattern were almost recovered. However, the dehydrated sample left in a silica gel desiccator did not show the recovery of the IR peaks and the X-ray powder pattern.

‡ *Crystal data*: $[\text{H}_{31}\text{O}_{14}][\text{CdCu}_2(\text{CN})_7]$, $M = 676.86$, cubic, space group $Pa\bar{3}$ (No. 205), $a = 12.9401(9)$ Å, $U = 2166.8(5)$ Å³, $Z = 4$, $D_m = 1.98$, $D_x = 2.07$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 30.7$ cm⁻¹, $F(000) = 1360$, absorption-corrected 1883 reflections ($4^\circ \leq 2\theta \leq 60^\circ$), measured for a crystal (0.3 mm diameter) coated with epoxy resin on a Rigaku AFC-5 at room temp., anisotropically refined for all non-hydrogen atoms to $R = 0.043$, $R_w = 0.048$ and $\text{GOF} = 1.311$ for independent 702 reflections. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

ecules in the formula unit should be protonated by three H^+ to neutralize the negative charge of the cyanometallate framework. As shown in Fig. 2, 12 water molecules, designated with two crystallographically independent O(1) and O(2) and their equivalents, make a puckered ring encircling the Cu-(CN)-Cu $\bar{3}$ axis of the pyrosilicate-like $[Cu_2(CN)_7]^{5-}$ with an approximated radius of *ca.* 3.2–3.4 Å to give a rotaxane structure. Due to the extremely large thermal parameters of the O atoms, 13.0(6) for O(1) and 21(1) for O(2) in $B_{eq}/\text{Å}^2$, the observed O–O distances 2.03(2) Å for O(1)–O(2) and 1.76(3) Å for O(1)–O(2)* are apparently too short for a normal hydrogen bond. Another crystallographically independent O atom, O(3), is within the distance of normal hydrogen-bonding from O(1), 2.96(2) and O(2), 2.99(2) Å, so that the rings connected with O(3) and equivalents extend a three-dimensional linkage of hydrogen-bonded water molecules. Each ring is surrounded by six O(3) and equivalents, each O(3) being surrounded by three rings. Finally, the whole crystal structure is built of two three-dimensional extensions, one of the heptacyanodicuprato(1)cadmate(II) and the other of the hydrogen-bonded water molecules, interpenetrating each

other. At the present stage of the structure refinement no significant positions can be located for protons experimentally.

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References

- 1 T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *Chem. Lett.*, 1988, **459**, 1729; T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1992, 413.
- 2 T. Iwamoto, *Chemistry of Microporous Crystals*, ed. T. Inui, S. Namba and T. Tatsumi, Kodansha-Elsevier, Tokyo, 1991, p. 3; T. Kitazawa, S. Nishikiori and T. Iwamoto, *Mater. Sci. Forum*, 1992, **91–93**, 257.
- 3 T. Iwamoto, *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, Oxford, 1991, vol. 5, p. 177.
- 4 T. Kitazawa and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 1993, 309.
- 5 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.