

## A Honeycomb Form of Cadmium Cyanide. A New Type of 3D Arrangement of Interconnected Rods generating Infinite Linear Channels of Large Hexagonal Cross-section

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$\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^t\text{OH}$  contains a new type of infinite  $\text{Cd}(\text{CN})_2$  framework consisting of interconnected  $\text{CdCNCd}$  rods which generate linear channels of large hexagonal cross-section; the framework occupies only *ca.* 33% of the volume of the crystal.

Infinite 3D scaffolds constructed from rod-like units interconnected by tetrahedral or octahedral centres may provide a significant new class of solids affording large cavities and access windows.<sup>1</sup> Materials specifically designed for the heterogeneous catalysis of particular reactions could possibly be constructed by functionalising the molecular rods before or after the erection of the scaffolding. The first deliberately designed example of such a scaffolding structure, namely,  $\text{Cu}[\text{4,4}',4'',4'''\text{-tetracyanotetraphenylmethane}]\text{BF}_4 \cdot x\text{PhNO}_2$ , was reported recently.<sup>1</sup> Only approximately one-third of the volume of this unusual material is occupied by the ordered framework which imposes crystallinity, the other two-thirds being occupied by essentially liquid nitrobenzene ( $\geq 7 \cdot 7\text{PhNO}_2$  per Cu) together with disordered anions. Besides constructing frameworks with more elaborate rods, we are also examining some cyanide structures with simple MCNM rods. The isomorphous structures of  $\text{Zn}(\text{CN})_2$ <sup>2</sup> and  $\text{Cd}(\text{CN})_2$ <sup>3</sup> were proposed on the basis of *X*-ray powder diffraction data almost fifty years ago and we have recently re-examined these structures using contemporary single crystal techniques.<sup>4</sup> Not one but two diamond-related frameworks are present, entirely independent of one another and interpenetrating in a highly symmetrical fashion as represented in Figure 1. By contrast,  $[\text{NMe}_4][\text{Cu}^{\text{I}}\text{Zn}^{\text{II}}(\text{CN})_4]$  has only a single diamond-related framework, the cations preventing interpenetration.<sup>4</sup>  $\text{Cd}(\text{CN})_2$  can be obtained as a  $\text{CCl}_4$ -solvate which also consists of a single diamond-like framework with  $\text{CCl}_4$  in the adamantane-like cavities.<sup>5</sup> Reported here is a new type of extended  $\text{Cd}(\text{CN})_2$  framework.

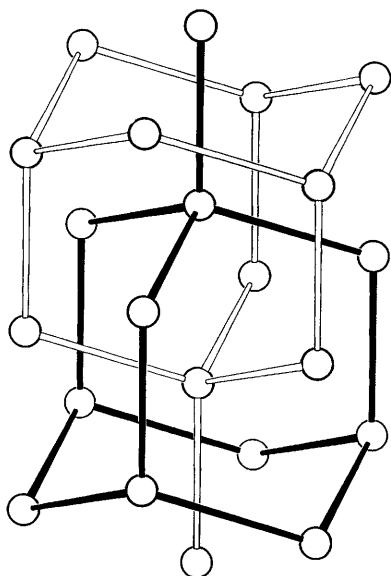
Recrystallisation of  $\text{Cd}(\text{CN})_2$  from 50% aqueous  $\text{Bu}^t\text{OH}$  gave colourless crystals of composition  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^t\text{OH}^\dagger$  whose crystal structure was determined by *X*-ray

<sup>†</sup> The crystals lost  $\text{Bu}^t\text{OH}$  on exposure to the atmosphere. Elemental analysis of a sample dried in air, until a free-running solid was obtained, was consistent with the composition  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot 0.8\text{Bu}^t\text{OH}$ . The composition with one  $\text{Bu}^t\text{OH}$  per Cd was indicated by the structural analysis of the *X*-ray intensity data obtained from a crystal sealed with mother liquor.

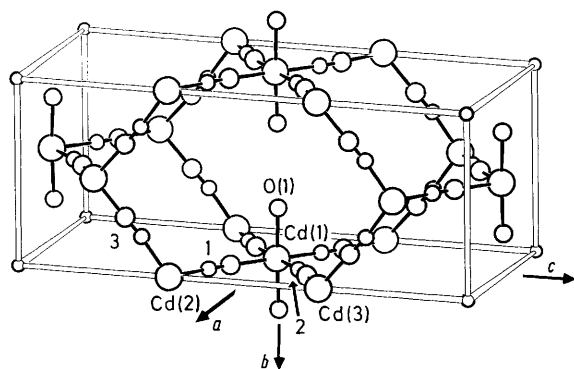
crystallography.<sup>‡§</sup> The orthorhombic unit cell is represented in Figure 2. The infinite  $\text{Cd}(\text{CN})_2$  framework consists of  $\text{CdCNCd}$  rods, 5.55–5.60 Å in length, which are distinctly bent, interconnected *via* Cd centres. Two-thirds of the cadmium atoms are tetrahedrally co-ordinated by four cyanides. The remaining metal centres are octahedral with two *trans* water ligands and an approximately square arrangement of cyanides. *X*-Ray crystallographic studies of cyanides have generally failed to discriminate between C and N, but in our recent re-investigation of the  $\text{Zn}(\text{CN})_2$  structure,<sup>4</sup> we were able to assign the shorter metal–cyanide linkage to a Zn–C bond. Although discrimination with absolute certainty is impossible on the basis of the present *X*-ray data, we

<sup>‡</sup> The space groups *Ammm*, *A222*, *A2mm*, *Am2m*, and *Amm2* are all consistent with the *X*-ray diffraction data recorded for  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^t\text{OH}$  and a refinement was carried out in each space group. The essential features of the framework were common to all solutions. For *Ammm*, *A222*, and *A2mm*, the *R* and *R<sub>w</sub>* values were significantly greater than those obtained for either *Am2m* or *Amm2*. Although the values of *R* and *R<sub>w</sub>* resulting from the refinements in *Am2m* and *Amm2* were not significantly different, *Am2m* was rejected because it yielded a solution with unreasonably asymmetric metal–oxygen distances about the octahedral Cd atom.

<sup>§</sup> *Crystal data:*  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^t\text{OH}$ , *M* = 250.6, orthorhombic, space group *Amm2* (No. 38), *a* = 8.695(1), *b* = 8.548(1), *c* = 21.092(4) Å, *U* = 1568 Å<sup>3</sup>, *Z* = 6, *D<sub>c</sub>* = 1.59 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 20.2 cm<sup>-1</sup>, *F*(000) = 736.0. Intensity data were measured at 295(1) K with Mo-*K*<sub>α</sub> radiation (graphite crystal monochromator) using an Enraf-Nonius CAD-4F diffractometer and employing the  $\omega/2\theta$  scan method; absorption corrections were applied. A full-matrix least-squares refinement method (SHELX-76) was employed with common isotropic thermal parameters applied to the C and O atoms of each of the disordered  $\text{Bu}^t\text{OH}$  molecules and anisotropic thermal parameters assigned to the remaining atoms; at convergence *R* = 0.033 and *R<sub>w</sub>* = 0.044 for the 761 observed reflections [*I* ≥ 3σ(*I*)]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



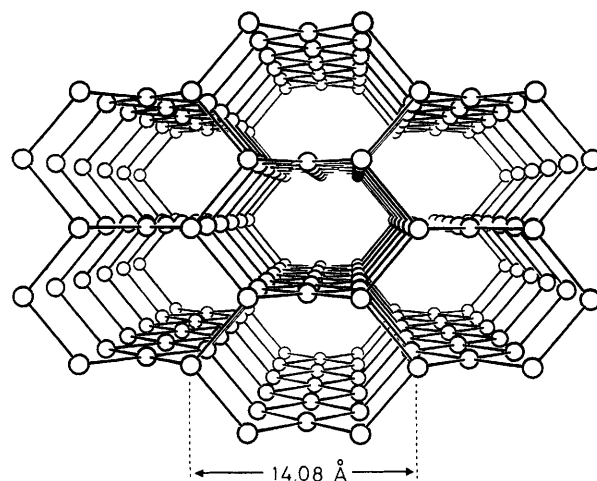
**Figure 1.** View of  $\text{Zn}(\text{CN})_2$  and  $\text{Cd}(\text{CN})_2$  structures revealing interpenetrating adamantane units of the two independent infinite frameworks. Metal centres only are shown, MCNM ( $M = \text{metal}$ ) rods being linear.



**Figure 2.** The orthorhombic unit cell of  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^i\text{OH}$  with the  $\text{Bu}^i\text{OH}$  molecules omitted for clarity. The largest circles denote the Cd atoms and the smallest carbon atoms; the crystallographically unique cyanide groups are designated as 1, 2, and 3. Selected bond distances (Å) and angles (°):  $\text{Cd}(2') \cdots \text{Cd}(3'')$  14.083(3),  $\text{Cd}(1) \cdots \text{Cd}(1')$  8.548(1),  $\text{Cd}(1)-\text{N}(1)$  2.281(7),  $\text{Cd}(1)-\text{C}(2)$  2.170(9),  $\text{Cd}(1)-\text{O}(1)$  2.330(5),  $\text{Cd}(2)-\text{C}(1)$  2.161(7),  $\text{Cd}(2)-\text{C}(3)$  2.170(8),  $\text{Cd}(3)-\text{N}(3')$  2.244(7),  $\text{Cd}(3)-\text{N}(2)$  2.326(8);  $\text{N}(1)-\text{Cd}(1)-\text{C}(2)$  89.9(3),  $\text{O}(1)-\text{Cd}(1)-\text{N}(1)$  91.4(3),  $\text{O}(1)-\text{Cd}(1)-\text{C}(2)$  88.6(6),  $\text{C}(2)-\text{Cd}(1)-\text{Cd}(2')$  87.7(3),  $\text{N}(1)-\text{Cd}(1)-\text{N}(1')$  92.5(3),  $\text{O}(1)-\text{Cd}(1)-\text{O}(1')$  176.1(5),  $\text{N}(1)-\text{Cd}(1)-\text{C}(2')$  177.6(3),  $\text{C}(3)-\text{Cd}(2)-\text{C}(1)$  109.1(2),  $\text{C}(3)-\text{Cd}(2)-\text{C}(3')$  108.5(4),  $\text{C}(1)-\text{Cd}(2)-\text{C}(1')$  111.8(3),  $\text{N}(3')-\text{Cd}(3)-\text{N}(2)$  110.9(2),  $\text{N}(3')-\text{Cd}(3)-\text{N}(3'')$  96.7(3),  $\text{N}(2)-\text{Cd}(3)-\text{N}(2')$  114.9(3).

tentatively assign the shorter linkages to Cd–C bonds which leads to the tetrahedral Cd centres having either  $\text{C}_4$  [for  $\text{Cd}(2)$ ] or  $\text{N}_4$  [for  $\text{Cd}(3)$ ] co-ordination as in the parent  $\text{Cd}(\text{CN})_2$ ; selected distances and angles are listed in the caption to Figure 2.

The extended framework of Cd atoms (Figure 3) presents a honeycomb-like appearance with infinite linear channels of large hexagonal cross-section; the greatest  $\text{Cd} \cdots \text{Cd}$  distance across a channel is 14.083(3) Å. The *trans* water molecules co-ordinated to the octahedral Cd(3) centres protrude into the



**Figure 3.** Honeycomb-like extended framework of Cd atoms in  $\text{Cd}(\text{CN})_2 \cdot 2/3\text{H}_2\text{O} \cdot \text{Bu}^i\text{OH}$ . The lengths of the Cd to Cd linkages are in the range 5.55–5.60 Å.

channels which are filled by  $\text{Bu}^i\text{OH}$  molecules disordered over a number of crystallographic sites. Because of the complexity of this disorder and because we regard the framework structure as the aspect of major interest, the  $\text{Bu}^i\text{OH}$  has been omitted from Figures 2 and 3.

Estimation of the fraction of the unit cell occupied by the  $\text{Bu}^i\text{OH}$  and water, based on the average volumes occupied by these molecules in solid  $\text{Bu}^i\text{OH}$  and liquid water, indicate that only *ca.* 33% of the total structure is occupied by the framework. Figure 3 provides some appreciation of the unusual spaciousness of the framework. This material, in contrast to zeolites, provides channels separated by structural components only one atom thick (if the water molecules are regarded as inessential to the 3D framework).

It remains to be seen whether or not the framework survives removal of the  $\text{Bu}^i\text{OH}$ . If it does, this cheap, readily available material may show considerable promise in its own right as a heterogeneous catalyst, providing Cd centres as potential acidic reaction sites with readily displaceable water ligands, the channels affording access of reactants and egress of products.

The structure represents a new type of framework consisting of rod-like units linked by tetrahedral centres and half as many essentially square planar centres. This arrangement could be used as a model for the construction, using square and tetrahedral building blocks, of more elaborate frameworks with longer rods, more spacious hexagonal channels and greater resistance to chemical degradation.

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