

Guest-dependent $[\text{Cd}(\text{CN})_2]_n$ Host Structures of Cadmium Cyanide–Alcohol Clathrates: Two New $[\text{Cd}(\text{CN})_2]_n$ Frameworks formed with Pr^nOH and Pr^iOH Guests

Jaheon Kim, Dongmok Whang, Jong In Lee and Kimoon Kim*

Department of Chemistry and Centre for Biofunctional Molecules, Pohang University of Science and Technology, PO Box 125, Pohang 790-600, South Korea

Crystallization of $\text{Cd}(\text{CN})_2$ from the geometric isomers of propanol, Pr^nOH and Pr^iOH , yielded new cadmium cyanide clathrates whose $[\text{Cd}(\text{CN})_2]_n$ frameworks are topologically and geometrically different not only from those of all the previously known cadmium cyanide clathrates but also from each other: the former has both hexagonal and pentagonal channels whereas the latter has only pentagonal channels.

Building new supramolecular architectures with the desired structures and properties poses a big challenge in chemistry. New types of inorganic 3-D frameworks having large cavities, windows and channels may be useful in areas of *e.g.* molecular sieves and catalysts.¹ Host–guest chemistry and/or self-assembly processes may be employed to build such materials.² Recent studies of the inclusion compounds derived from $\text{Cd}(\text{CN})_2$ led to the discovery of a variety of 3-D $[\text{Cd}(\text{CN})_2]_n$ frameworks which have large channels or cavities for accommodating organic guest molecules.^{3–5} Iwamoto and coworkers reported inclusion compounds $\text{Cd}(\text{CN})_2 \cdot \text{G}$ ($\text{G} = \text{CCl}_4$, MeCCl_3 , cyclohexane, neopentane *etc.*) in which the guest molecules are encaged in the diamond-like $[\text{Cd}(\text{CN})_2]_n$ framework.³ Robson and coworkers reported the cadmium cyanide clathrate $\text{Cd}(\text{CN})_2 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot \text{Bu}^i\text{OH}$ **1** with a honeycomb-like framework.⁴ In exploring new nonlinear optical materials by inclusion of organic chromophore molecules in inorganic hosts we prepared two new cadmium cyanide clathrates formed with the geometric isomers of propanol, Pr^nOH and Pr^iOH . To our surprise, their $[\text{Cd}(\text{CN})_2]_n$ frameworks are topologically and geometrically different not only from those of all the previously known cadmium cyanide clathrates including **1** but also from each other.

Recrystallization of $\text{Cd}(\text{CN})_2$ from 50% aqueous Pr^nOH or Pr^iOH yielded colourless crystals of $\text{Cd}(\text{CN})_2 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot \frac{2}{3}\text{Pr}^n\text{OH}$ **2**[†] and $\text{Cd}(\text{CN})_2 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot \frac{2}{3}\text{Pr}^i\text{OH}$ **3**,[†] respectively, whose struc-

tures were determined by X-ray crystallography.[‡] In the structure of **2** (Fig. 1) two kinds of Cd ion, Cd(1) and Cd(2), are present in a 1 : 4 ratio: Cd(1), which occupies a crystallographic $2/m$ symmetry site, is coordinated by four CN ligands in a square geometry and by two *trans* water molecules; Cd(2), occupying a general position, is coordinated by four CN ligands in a tetrahedral geometry. The octahedral Cd centre is linked to four tetrahedral Cd centres while the tetrahedral Cd centre is connected to three tetrahedral and one octahedral Cd centres. The bond parameters are not exceptional. However, discrimination between C and N of the cyanides was not

[‡] Crystal data for $\text{Cd}(\text{CN})_2 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot \frac{2}{3}\text{Pr}^n\text{OH}$ **2**, $M = 304.71$, monoclinic, $C2/m$, $a = 15.176(5)$, $b = 25.732(3)$, $c = 8.464(2)$ Å, $\beta = 132.722(9)^\circ$, $U = 2428.4(11)$ Å³, $Z = 8$, $D_c = 1.67$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 21.5$ cm⁻¹, $T = 295$ K; 2534 unique reflections measured; 2353 reflections observed [$I > 3\sigma(I)$]; $R = 0.041$, $R_w = 0.052$, GOF = 1.66.

Crystal data for $\text{Cd}(\text{CN})_2 \cdot \frac{2}{3}\text{H}_2\text{O} \cdot \frac{2}{3}\text{Pr}^i\text{OH}$ **3**: $M = 324.78$, monoclinic, $C2/c$, $a = 14.251(3)$, $b = 17.797(2)$, $c = 13.043(2)$ Å, $\beta = 111.247(8)^\circ$, $U = 3083.2(8)$ Å³, $Z = 8$, $D_c = 1.40$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 20.2$ cm⁻¹, $T = 295$ K; 3767 unique reflections measured; 2274 reflections observed [$I > 3\sigma(I)$]; $R = 0.045$, $R_w = 0.065$, GOF = 1.94.

The crystals were sealed in capillaries with mother liquor before the intensity data were collected with an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K α radiation [$\lambda(\text{Mo-K}\alpha) = 0.71073$ Å]. The structures were solved by Patterson and difference Fourier methods and refined by full-matrix least-squares method. Non-hydrogen atoms were refined anisotropically. Discrimination between C and N of the cyanides was not possible in either structure; therefore, each atom was assigned as half-carbon and half-nitrogen.

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.

[†] We could not obtain satisfactory elemental analyses for the crystals of **2** or **3** as they lost guest molecules quickly upon exposure to air. The compositions given in the text were determined by X-ray structural analysis.

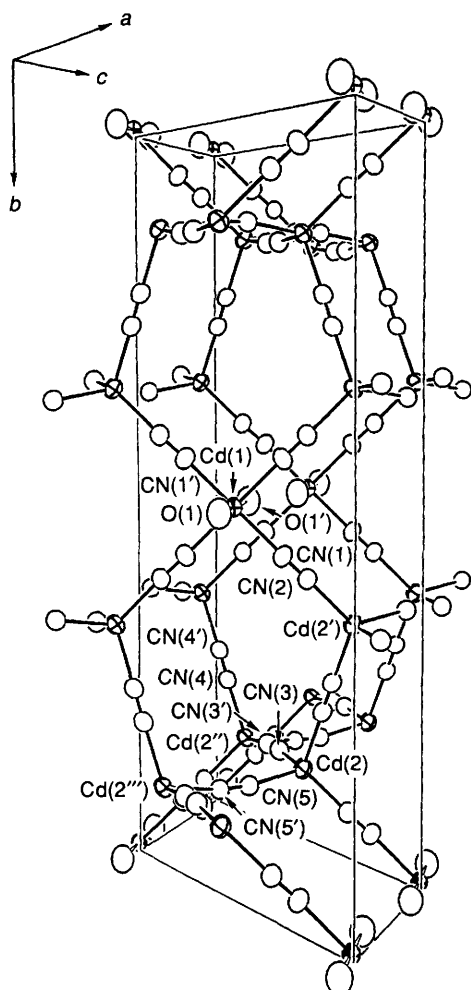


Fig. 1 The unit cell of **2** with the Pr^{OH} molecules omitted for clarity. Selected bond distances (\AA) and angles ($^{\circ}$): $\text{Cd}(1)\text{--O}(1)$ 2.345(9), $\text{Cd}(1)\text{--CN}(1)$ 2.276(5), $\text{Cd}(2)\text{--CN}(2)$ 2.205(6), $\text{Cd}(2)\text{--CN}(3)$ 2.227(8), $\text{Cd}(2)\text{--CN}(4)$ 2.202(6), $\text{Cd}(2)\text{--CN}(5)$ 2.196(5), $\text{CN}(1)\text{--CN}(2)$ 1.110(7), $\text{CN}(3)\text{--CN}(3')$ 1.143(12), $\text{CN}(4)\text{--CN}(4')$ 1.128(8), $\text{CN}(5)\text{--CN}(5')$ 1.129(7); $\text{O}(1)\text{--Cd}(1)\text{--O}(1')$ 180.0, $\text{O}(1)\text{--Cd}(1)\text{--CN}(1)$ 94.2(2), $\text{O}(1)\text{--Cd}(1)\text{--CN}(1')$ 85.8(2), $\text{CN}(1)\text{--Cd}(1)\text{--CN}(1)$ 180.0, $\text{CN}(1)\text{--Cd}(2)\text{--CN}(1')$ 91.4(2), $\text{CN}(2)\text{--Cd}(2)\text{--CN}(3)$ 107.3(3), $\text{CN}(2)\text{--Cd}(2)\text{--CN}(4)$ 115.9(2), $\text{CN}(2)\text{--Cd}(2)\text{--CN}(5)$ 120.4(3), $\text{CN}(3)\text{--Cd}(2)\text{--CN}(4)$ 105.4(3), $\text{CN}(3)\text{--Cd}(2)\text{--CN}(5)$ 101.3(3), $\text{CN}(4)\text{--Cd}(2)\text{--CN}(5)$ 104.9(2). CN represents C or N of the disordered cyanides.

possible on the basis of the present X-ray data. Selected bond parameters are given in the caption to Fig. 1.

The crystal structure of **3** (Fig. 2) also contains two types of Cd centre, octahedral Cd(1) and tetrahedral Cd(2), but in a 1:2 ratio in this case. Here also Cd(1) is coordinated by four CN ligands and by two water molecules; however, the water molecules are now in a *cis*-geometry whereas they were *trans* in **1** and **2**. Each octahedral Cd centre is linked to four tetrahedral Cd centres while each tetrahedral Cd centre is connected to two tetrahedral and two octahedral Cd centres.

The different coordination geometry around the octahedral Cd centre and the different connectivity between the octahedral and tetrahedral Cd centres make the $[\text{Cd}(\text{CN})_2]_n$ frameworks in **2** and **3** topologically and geometrically different from each other. Fig. 3 compares the frameworks built of Cd–CN–Cd linkages in **2** and **3**. The framework in **2**, viewed along the *c* axis, has two types of linear channels, hexagonal and pentagonal, while that in **3**, viewed along the *a* axis, has only pentagonal channels. These frameworks are also topol-

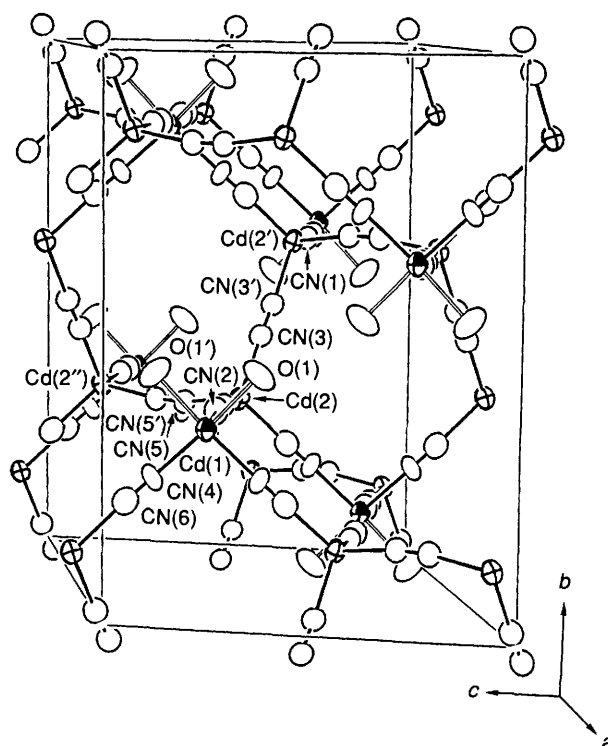


Fig. 2 The unit cell of **3** with the Pr^{OH} molecules omitted for clarity. Selected bond distances (\AA) and angles ($^{\circ}$): $\text{Cd}(1)\text{--O}(1)$ 2.375(7), $\text{Cd}(1)\text{--CN}(2)$ 2.266(6), $\text{Cd}(1)\text{--CN}(4)$ 2.270(7), $\text{Cd}(2)\text{--CN}(1)$ 2.276(8), $\text{Cd}(2)\text{--CN}(3)$ 2.221(6), $\text{Cd}(2)\text{--CN}(6)$ 2.245(8), $\text{CN}(1)\text{--CN}(2)$ 1.072(10), $\text{CN}(3)\text{--CN}(3')$ 1.131(9), $\text{CN}(4)\text{--CN}(6)$ 1.103(11), $\text{CN}(5)\text{--CN}(5')$ 1.149(11); $\text{O}(1)\text{--Cd}(1)\text{--O}(1')$ 87.2(3), $\text{O}(1)\text{--Cd}(1)\text{--CN}(2)$ 87.0(3), $\text{O}(1)\text{--Cd}(1)\text{--CN}(4)$ 89.1(3), $\text{CN}(2)\text{--Cd}(1)\text{--CN}(4)$ 93.4(3), $\text{CN}(1)\text{--Cd}(2)\text{--CN}(3)$ 110.3(3), $\text{CN}(1)\text{--Cd}(2)\text{--CN}(5)$ 109.8(3), $\text{CN}(1)\text{--Cd}(2)\text{--CN}(6)$ 111.4(3), $\text{CN}(3)\text{--Cd}(2)\text{--CN}(5)$ 101.8(3), $\text{CN}(3)\text{--Cd}(2)\text{--CN}(6)$ 109.0(3), $\text{CN}(5)\text{--Cd}(2)\text{--CN}(6)$ 114.2(3). CN represents C or N of the disordered cyanides.

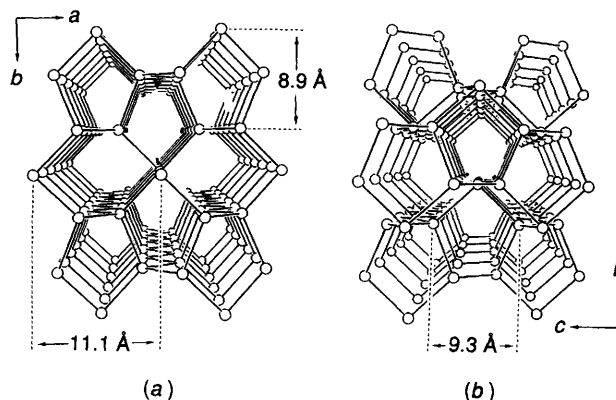


Fig. 3 Perspective view of $[\text{Cd}(\text{CN})_2]_n$ frameworks: (a) in **2** down the *c* axis; (b) in **3** down the *a* axis. Only the Cd centres are shown.

ogically and geometrically different from that in **1** which has only linear hexagonal channels along the *a* axis (see Fig. 7 of ref. 4b) or hexagonal and square channels along the *b* axis (see Fig. 9 of ref. 4b). In **2** the cross-sectional dimensions of the hexagonal channel are *ca.* $11.1 \times 7.8 \text{ \AA}$ and that of the pentagonal channel is *ca.* $8.9 \times 7.6 \text{ \AA}$. The cross-sectional dimension of the pentagonal channel in **3** (*ca.* $9.3 \times 9.7 \text{ \AA}$) is somewhat larger than that of the pentagonal channel in **2**. Both the channels in **2** are filled with disordered Pr^{OH} molecules forming hydrogen bonds with the water molecules

coordinated to Cd atoms (not shown). Similarly, the pentagonal channels in **3** contain disordered Pr³⁺OH molecules engaged in hydrogen bonds with the coordinated water molecules (not shown).

It is remarkable that such a subtle structural difference in the guests leads to totally different host structures of the clathrates formed by a self-assembly process. This work also demonstrates the flexibility of the [Cd(CN)₂]_n framework which can adopt different 3-D structures depending on the guest molecules. A systematic study is necessary to establish the relationship between the structures of guest molecules and the resulting host structures of the cadmium cyanide-guest clathrates, and to understand what plays an important role in determining the host structures. It also remains to be seen whether the crystals of **1**, **2** and **3** can be converted to one another by a guest exchange process. A 'guest exchange' process and concomitant structural rearrangement have recently been observed with crystals of **1** upon exposure to chloroform vapour.⁶

This research was kindly supported by Korea Science and Engineering Foundation. We also thank Pohang University of

Science and Technology (POSTECH) for partial support of the X-ray analysis.

Received, 28th May 1993; Com. 3/03069E

References

- 1 For an example see R. C. Haushalter and L. A. Mundi, *Chem. Mater.*, 1992, **4**, 31.
 - 2 H. Reuter, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1185.
 - 3 (a) T. Kitazawa, S. Nishikori, R. Kuroda and T. Iwamoto, *Chem. Lett.*, 1988, 1729; (b) T. Kitazawa, S. Nishikori, A. Yamagishi, R. Kuroda and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1992, 413.
 - 4 (a) B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 60; (b) B. F. Abrahams, B. F. Hoskins, J. Liu and R. Robson, *J. Am. Chem. Soc.*, 1991, **113**, 3045.
 - 5 S. Nishikori, C. I. Ratcliffe and J. A. Ripmeester, *J. Am. Chem. Soc.*, 1992, **114**, 8590.
 - 6 B. F. Abrahams, M. J. Hardie, B. F. Hoskins, R. Robson and G. A. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 10641.
-