Two New $[Cd(CN)_2]_n$ Frameworks with Linear Channels of Large, Elongated Hexagonal Cross-section: Structures of Cadmium Cyanide–Guest (Guest = dmf and Me_2SO) Clathrates

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Two new $[Cd(CN)_2]_n$ frameworks with linear channels of large, elongated hexagonal cross-section have been discovered in cadmium cyanide–guest (guest = dmf or Me_2SO) clathrates; the framework in the latter clathrate is the first example of a 3-D net comprising octahedral and tetrahedral cadmium centres in a 2:1 ratio.

Synthesis of new types of inorganic 3-D frameworks having large cavities, windows and channels has drawn much attention recently, since they may be useful as molecular sieves, catalysts, optical materials, *etc.*[1] Recent studies of the inclusion compounds derived from $Cd(CN)_2$ led to the discovery of a variety of 3-D $[Cd(CN)_2]_n$ frameworks which have large channels or cavities for accommodating organic guest molecules.[2–5] Here we report two new $[Cd(CN)_2]_n$ frameworks with linear channels of large, elongated hexagonal cross-section, discovered in cadmium cyanide–guest (guest = dmf or Me_2SO) clathrates.

Layering dmf or Me_2SO over an aqueous solution of $Cd(CN)_2$ yielded colourless crystals of $Cd(CN)_2{\cdot}H_2O{\cdot}$dmf **1** and $Cd(CN)_2{\cdot}\frac{4}{3}Me_2SO$ **2**, respectively.† The structures of **1** and **2** were determined by X-ray crystallography.‡ In the structure of **1** (Fig. 1) two kinds of Cd ion, Cd(1) and Cd(2), are present in a 1:1 ratio; Cd(1) is octahedrally coordinated by four CN ligands and by two *cis* water molecules, Cd(2) by four CN ligands in a tetrahedral geometry. The octahedral Cd centre is linked to four tetrahedral Cd centres and *vice versa*. Two independent dmf molecules are hydrogen-bonded to the water molecules bound to Cd(1) (not shown). The bond parameters are not exceptional. Discrimination between C and N atoms of the cyanides was not possible on the basis of the X-ray data, as in other cases.[2–5]

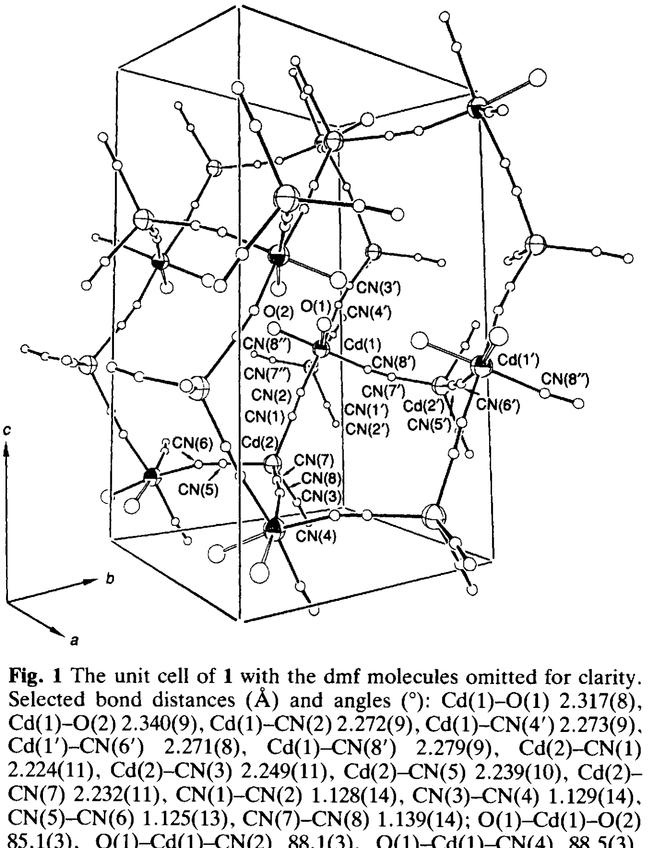

Fig. 1 The unit cell of **1** with the dmf molecules omitted for clarity. Selected bond distances (Å) and angles (°): Cd(1)–O(1) 2.317(8), Cd(1)–O(2) 2.340(9), Cd(1)–CN(2) 2.272(9), Cd(1)–CN(4′) 2.273(9), Cd(1′)–CN(6′) 2.271(8), Cd(1)–CN(8′) 2.279(9), Cd(2)–CN(1) 2.224(11), Cd(2)–CN(3) 2.249(11), Cd(2)–CN(5) 2.239(10), Cd(2)–CN(7) 2.232(11), CN(1)–CN(2) 1.128(14), CN(3)–CN(4) 1.129(14), CN(5)–CN(6) 1.125(13), CN(7)–CN(8) 1.139(14); O(1)–Cd(1)–O(2) 85.1(3), O(1)–Cd(1)–CN(2) 88.1(3), O(1)–Cd(1)–CN(4) 88.5(3), O(1′)–Cd(1′)–CN(6′) 170.6(3), O(1)–Cd(1)–CN(8′) 89.4(3), CN(2)–Cd(1)–CN(4′) 172.8(3), CN(6′)–Cd(1′)–CN(8″) 98.5(3), CN(2)–Cd(1)–CN(8′) 89.1(3), CN(1)–Cd(2)–CN(3) 110.9(4), CN(1)–Cd(2)–CN(5) 107.3(4), CN(1)–Cd(2)–CN(7) 114.6(4), CN(3)–Cd(2)–CN(5) 108.2(4), CN(3)–Cd(2)–CN(7) 105.1(4), CN(5)–Cd(2)–CN(7) 110.6(4), Cd(1)–CN(2)–CN(1) 173.4(9), CN(1)–CN(2)–Cd(2) 176.6(9), Cd(1)–CN(8′)–CN(7′) 167.0(8), CN(7′)–CN(8′)–Cd(2′) 173.1(9). CN represents C or N atom of the disordered cyanides.

The framework built of Cd–CN–Cd linkages in **1**, viewed along the *a* axis (Fig. 2) consists of two types of linear channels, large elongated-hexagonal and small rectangular. The cross-sectional dimension of the hexagonal channel is *ca.* 16.5 × 6.7 Å. Such large channels in the cadmium cyanide framework have not been observed before. The hexagonal channels in **1** contain dmf molecules, which form hydrogen bonds with the water molecules coordinated to Cd atoms (not shown).

The crystal structure of **2** (Fig. 3) also contains two types of Cd centre, octahedral Cd(1) and tetrahedral Cd(2), now in a 2:1 ratio. To the best of our knowledge, this is the first example of a 3-D net structure comprising octahedral and tetrahedral centres in a 2:1 proportion. Here the octahedral Cd(1) is coordinated by four CN ligands and by two Me_2SO molecules in a *trans* geometry. Each octahedral Cd centre is linked to two tetrahedral and two other octahedral Cd centres while each tetrahedral Cd centre is connected to four

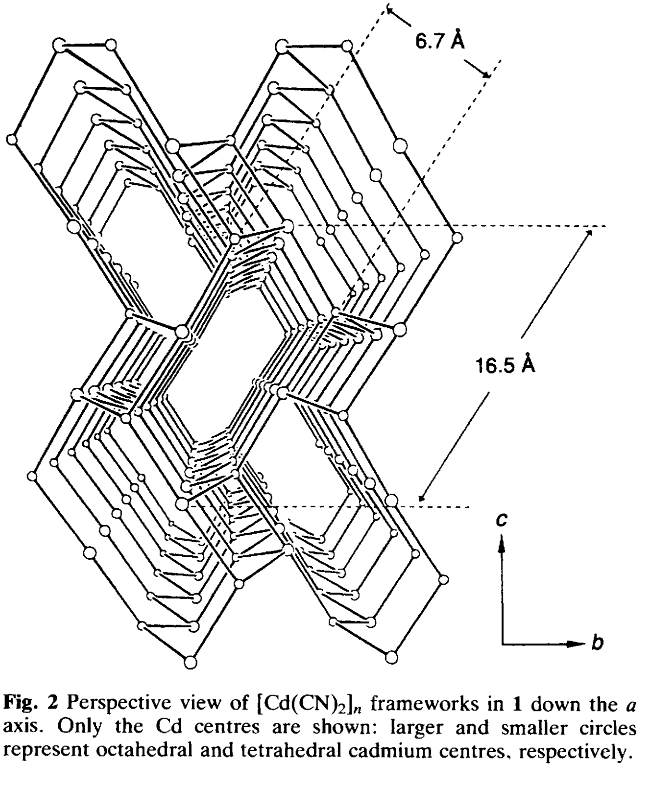

Fig. 2 Perspective view of $[Cd(CN)_2]_n$ frameworks in **1** down the *a* axis. Only the Cd centres are shown: larger and smaller circles represent octahedral and tetrahedral cadmium centres, respectively.

octahedral Cd centres. This mode of connectivity is also unprecedented.

The cadmium cyanide framework in **2** has repeating units consisting of two successive arrays of octahedral Cd atoms and an array of tetrahedral Cd atoms stacked along the *c* axis direction (Figs 3 and 4). This framework may be viewed as being generated by the introduction of an extra octahedral centre next to the octahedral centre of the Hofmann-Td type structure[6] having octahedral and tetrahedral Cd centres in a 1:1 ratio, as represented by Cd(NH$_3$)$_2$Cd(CN)$_4$·2C$_6$H$_6$. More interestingly, the cadmium cyanide framework in **2**, viewed down the [$\bar{1}$10] direction, shows large elongated-hexagonal and small square channels (Fig. 4). The introduction of two successive octahedral centres between two tetrahedral centres results in the elongation of the hexagonal channels in the *c* axis direction. The cross-sectional dimension of the hexagonal channel is *ca.* 18.9 × 7.3 Å, the largest among all the known cadmium cyanide frameworks. The *trans* Me$_2$SO molecules bound to the octahedral Cd(1) centres protrude into the channels (not shown).

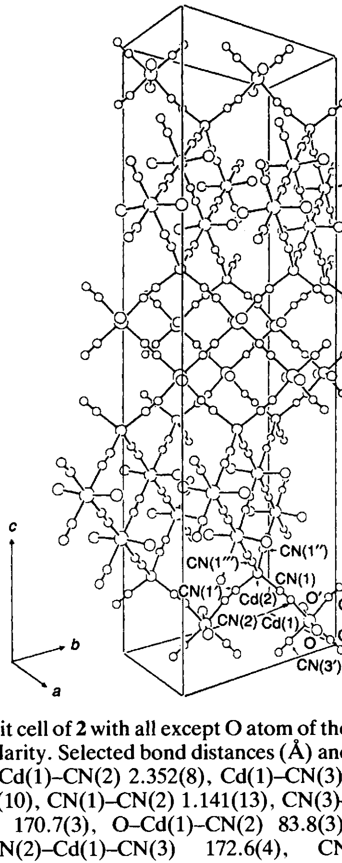

Fig. 3 The unit cell of **2** with all except O atom of the Me$_2$SO molecules omitted for clarity. Selected bond distances (Å) and angles (°): Cd(1)–O 2.358(8), Cd(1)–CN(2) 2.352(8), Cd(1)–CN(3) 2.244(10), Cd(2)–CN(1) 2.216(10), CN(1)–CN(2) 1.141(13), CN(3)–CN(3'') 1.189(15); O–Cd(1)–O' 170.7(3), O–Cd(1)–CN(2) 83.8(3), O–Cd(1)–CN(3) 94.6(4), CN(2)–Cd(1)–CN(3) 172.6(4), CN(2)–Cd(1)–CN(3') 90.0(3), CN(2)–Cd(1)–CN(2') 84.1(3), CN(3)–Cd(1)–CN(3') 96.1(4), CN(1)–Cd(2)–CN(1') 105.6(4), CN(1)–Cd(2)–CN(1'') 121.5(3), CN(1)–Cd(2)–CN(1''') 102.1(4), CN(1')–Cd(2)–CN(1'') 102.1(4), CN(1')–Cd(2)–CN(1''') 121.5(3), CN(1'')–Cd(2)–CN(1') 105.6(4), Cd(1)–CN(2)–CN(1) 171.9(8), CN(3'')–CN(3)–Cd(1) 177.5(9), CN(2)–CN(1)–Cd(2) 170.7(9). CN represents C or N atom of the disordered cyanides.

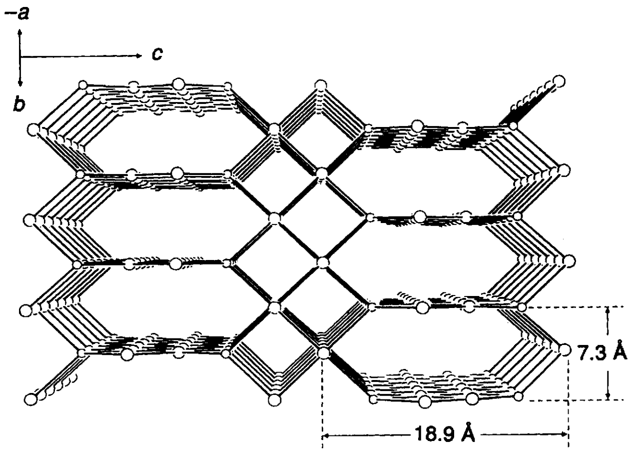

Fig. 4 Perspective view of [Cd(CN)$_2$]$_n$ frameworks in **2** down the [$\bar{1}$10] direction. Only the Cd centres are shown: larger and smaller circles represent octahedral and tetrahedral cadmium centres, respectively.

This work demonstrates once again the remarkable flexibility of [Cd(CN)$_2$]$_n$ framework and guest dependence of the host structure. A number of possible combinations of the octahedral and tetrahedral Cd centres and the *cis* or *trans* geometry of water or guest molecules bound to the octahedral Cd centre lead to a variety of [Cd(CN)$_2$]$_n$ frameworks topologically and/or geometrically different from one another.

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Footnotes

[†] Satisfactory elemental analyses were obtained for the crystals of **1** and **2**.

[‡] *Crystal data* for **1**: $M = 511.11$, monoclinic, $P2_1/c$, $a = 9.003(7)$, $b = 12.046(3)$, $c = 18.870(15)$ Å, $\beta = 96.23(4)$°, $U = 2034(2)$ Å^3, $Z = 4$, $D_c = 1.669$ g cm^{-3}, μ(Mo-Kα) = 21.04 cm^{-1}, $T = 295$ K; 3371 unique reflections measured; 2374 reflections observed [$I > 3\sigma(I)$]; $R = 0.045$, $R_w = 0.048$, goodness of fit (gof) = 0.599. **2**: $M = 805.85$, orthorhombic, $Fddd$, $a = 8.504(2)$, $b = 14.441(1)$, $c = 45.883(6)$ Å, $U = 5635(2)$ Å^3, $Z = 8$, $D_c = 1.900$ g cm^{-3}, μ(Mo-Kα) = 25.0 cm^{-1}, $T = 295$ K; 1405 unique reflections measured; 967 reflections observed [$I > 3\sigma(I)$]; $R = 0.054$, $R_w = 0.067$, gof = 2.338.

The crystals were sealed in capillaries before the intensity data were collected with an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation [λ(Mo-Kα) = 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 atoms 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 Information for Authors, Issue No. 1.

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