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A Reexamination of the Structure of "Honeycomb Cadmium Cyanide"

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The low-temperature crystal structure of $Cd(CN)_2 \cdot 2/3H_2O \cdot t$-BuOH (230 K) is reported, *Pbcm*, $a = 8.694(1)$, $b = 16.908(4)$, $c = 21.157(3)$ Å. Although the cell has approximately twice the volume of the previously reported room temperature cell the 3D cadmium-cyanide framework has essentially the same connectivity. The hydrogen bonded *t*-BuOH/H_2O system is much better defined at low temperature and this new insight together with solid-state NMR data afford an improved model of the room temperature structure, which is now reported in the space group *Cmmm*. © 2001 Academic Press

INTRODUCTION

When cadmium cyanide is recrystallized from water the crystals obtained are anhydrous and consist of two independent but interpenetrating diamond-like networks in which cadmium centers provide the tetrahedral nodes and bridging cyano ligands act as linear connectors (1). It is somewhat surprising therefore that recrystallization from aqueous *t*-butanol generates crystals that now contain water and have the composition $Cd(CN)_2 \cdot 2/3H_2O \cdot t$-BuOH. The structure of this new solvated form of cadmium cyanide was found to contain a novel honeycomb-like infinite 3D $[Cd(CN)_2]_n$ network with linear channels of large hexagonal cross section, as shown in Fig. 1 (2). Only cadmium centers are represented in Fig. 1, the linear cyano bridges that interlink them being omitted, as are two "pendant" *trans* H_2O ligands attached to each of those cadmium centers in the figure that appear to be square planar. This structure represented a new 4-connected net in which square planar nodes and twice as many tetrahedral nodes are combined in an appeallingly simple manner, and as such it is of some fundamental, archetypal significance in the area of extended networks. Since then a variety of cadmium cyanide host networks have been reported (3).

Although the single-crystal data collected at room temperature were of high quality and the topology of the cadmium-cyanide framework described above was beyond any doubt, there was uncertainty regarding the space group and the assignment of C and N atoms. The data were almost equally consistent with five different space groups, all of which yielded similar structural solutions, with few grounds for positive discrimination between them. The space groups *Cmmm*, *Cmm*2, and *C*222 placed the restriction that a twofold axis pass through a point midway between the tetrahedral cadmium atoms, requiring that the C and N atoms be positionally disordered around the twofold axis. The space groups *C*2*mm* and *Cm*2*m* did not require the carbon and nitrogen atoms of the cyanide link between tetrahedral cadmium atoms to be disordered, allowing these atoms to be refined as ordered units. Although the refinement of the structure in all five of the space groups gave very good results and although we stated that "discrimination with absolute certainty is impossible on the basis of the present X-ray data" we tentatively rejected *Cmmm*, C222, and *Cmm*2 on the basis of *R* values while *C*2*mm* was likewise considered less likely on the basis of asymmetric Cd–O distances. We therefore opted with a tentativeness that was appropriate and proper for the space group *Cm*2*m* (reported in its standard setting of *Amm*2) with all cyanide units ordered, as shown in Fig. 2. Despite the uncertainty regarding the space group and the C and N assignments, the novel framework topology seen in Fig. 1 was beyond any doubt.

A subsequent solid state ^{113}Cd NMR study of the structure (4), which impressively demonstrated the power of this technique, afforded unambiguous evidence that the cyano units linking tetrahedral cadmium to tetrahedral cadmium were disordered and that the octahedral cadmium atom was coordinated by four cyano nitrogen donors together with the two *trans* H_2O ligands. It was asserted in Ref. (4) that space groups *C*2*mm* and *Cm*2*m* were invalid on the basis of

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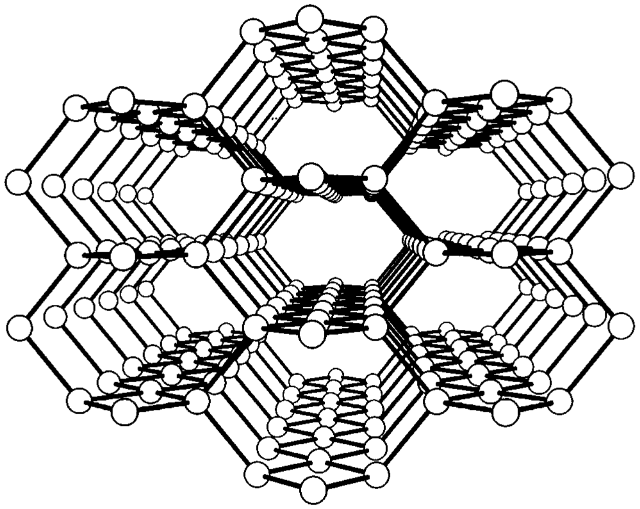

FIG. 1. The honeycomb-like net of $Cd(CN)_2 \cdot 2/3H_2O \cdot t$-BuOH. Circles represent cadmium centers. Lines represent cyano bridge connections between metal centers.

the NMR data because the symmetry of the space groups did not require C–N disorder. We maintain on the contrary that it is possible and legitimate to model the cyanide link as a disordered unit within these two space groups. Presented here is a low-temperature X-ray study of the structure, a reexamination of the room temperature X-ray data in the light of the low-temperature structure and the published NMR work together with additional variable temperature, solid state ^{113}Cd NMR investigations. Apart from clarifying structural ambiguities we hoped that this more comprehensive study might provide some insight into why the availability of t-BuOH and water to the growing crystal leads to water being incorporated into the crystal and why it has such a profound influence on the structure of the cadmium-cyanide framework.

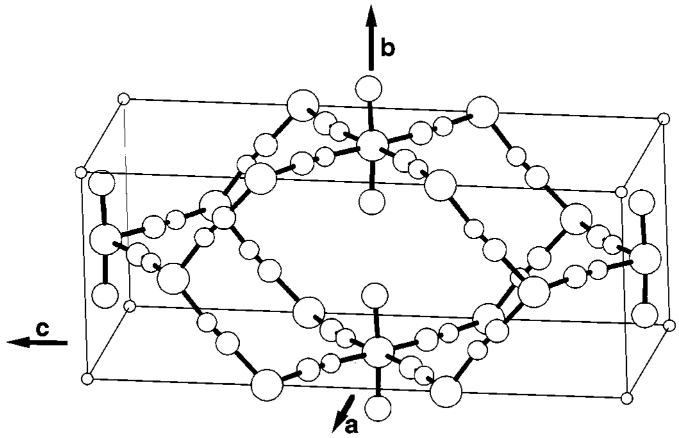

FIG. 2. The originally reported (2) orthorhombic unit cell for the high-temperature phase of $Cd(CN)_2 \cdot 2/3H_2O \cdot t$-BuOH (293 K). The labeling of the axes shown here refers to the originally reported A-centered cell.

EXPERIMENTAL

Crystals of $Cd(CN)_2 2/3H_2O \cdot t$-BuOH were obtained by crystallization of cadmium cyanide from a 50/50 aqueous/t-BuOH solution.

Crystallography

Low-Temperature Diffraction Studies. A single crystal of $Cd(CN)_2 2/3H_2O \cdot t$-BuOH was transferred directly from mother liquor to a protective viscous oil and was then mounted on the end of a glass fibre. The crystal was then cooled in a stream of cold air on an Enraf–Nonius CAD4 diffractometer. Crystal data are as follows: $C_{18}H_{34}Cd_3N_6O_5$ (for $Cd_3(CN)_6.2H_2O.3C_4H_{10}O$), $M = 751.7$, orthorhombic, $a = 8.694(1)$, $b = 16.908(4)$, $c = 21.157(3)$ Å, $U = 3110.0(9)$ Å^3, space group $Pbcm$ (No. 57), $Z = 4$, μ (Mo$K\alpha$) = 2.064 mm^{-1}, 4628 reflections measured, 3663 unique ($R_{\mathrm{int}} = 0.0234$), which were used in all calculations. Final R values are as follows: $wR2 = 0.1435$ (all data), $R1 = 0.0440$ [$I > 2\sigma(I)$]. The structure was solved using heavy atom methods (SHELXS-86 (5)) and refined using a full-matrix least-squares refinement procedure (SHELXL-97 (6)).

Room temperature structure. The data used for the original refinement were again used for this rerefinement. This crystal was sealed in a Lindeman glass tube along with mother liquor to prevent solvent loss from the crystal. Crystal data are as follows: $C_{18}H_{34}Cd_3N_6O_5$ (for $Cd_3(CN)_6.2H_2O.3C_4H_{10}O$), $M = 751.7$, orthorhombic, $a = 8.548(1)$, $b = 21.092(4)$, $c = 8.695(1)$ Å, $U = 1567.6(4)$ Å^3, space group $Cmmm$ (No. 65), $Z = 2$, μ (Mo$K\alpha$) = 2.047 mm^{-1}, 2458 reflections measured, 1049 unique ($R_{\mathrm{int}} = 0.0219$), which were used in all calculations. Final R values are as follows: $wR2 = 0.0839$ (all data), $R1 = 0.0297$ [$I > 2\sigma(I)$]. The structure was refined using a full-matrix least-squares refinement procedure (SHELXL-97 (6)).

NMR

$Cd(CN)_2.2/3H_2O.t$-BuOH was packed into a 5-mm magic angle spinning (MAS) rotor as a slurry in 50/50 aqueous/t-BuOH solution, which was required to prevent loss of solvent from the crystals and consequent degeneration. ^{113}Cd CP (cross polarization (7)) MAS NMR spectra were recorded at 66.555 MHz on a 300 Varian Inova spectrometer (Palo Alto, CA, USA) equipped with a Doty probe (Columbia, SC, USA). The ^{113}Cd chemical shift was referenced against Cd (II) perchlorate hexahydrate. ^{113}Cd spectra were obtained at room and low temperature using a CP contact time of 4 ms, delay time 7 s, proton $\pi/2$ pulse of 3.3 μs, and spinning rate ~6000 Hz. Low-temperature

CP MAS experiments were performed by cooling the bearing and drive input nitrogen gas using liquid nitrogen and ethanol in dry ice, respectively. The low-temperature measurements were calibrated (8) using the ^{207}Pb chemical shift resonance of solid $Pb(NO_3)_2$.

RESULTS AND DISCUSSION

Crystallographic Phase Changes

At room temperature the compound $Cd(CN)_2 \cdot 2/3\ H_2O \cdot t$-BuOH has a *C*-centered orthorhombic cell with cell dimensions of $a = 8.548(1)$, $b = 21.092(4)$, $c = 8.695(1)$ Å. The cell was originally reported as an *A*-centered cell, shown in Fig. 2, in keeping with the standard setting of the chosen space group ($a = 8.695(1)$, $b = 8.548(1)$, $c = 21.092(4)$ Å). This cell is retained as the crystal is cooled to 260 K. Between 240 and 260 K a phase change occurs whereby the cell becomes primitive orthorhombic with a cell volume almost doubled. In order to ensure that the unit cell found at 240 K is not present at temperatures above 260 K, a series of reflections found at 240 K were remeasured at a temperature of 260 K. Reflections that were common to both the large (240 K) and small (260 K) unit cells were easily located, whereas the reflections consistent only with the larger cell were absent at 260 K. This result indicates the doubling of the $\sim$8.5-Å axis as the temperature is decreased to 240 K.

This phase observed at 240 K persists as the crystal is cooled to approximately 200 K. Below this temperature and down to the 130-K limit of our equipment, the cell cannot be indexed, but the crystal's diffraction suggests the presence of an ill-defined supercell. It is interesting to note that the same crystal could be repeatedly cooled and warmed so as to pass through these phase changes without any effect on the quality of the crystal as gauged by the intensities and widths of diffraction peaks.

The Crystal Structure at 230 K

The unit cell determined on the basis of data collected at 230 K, shown in Fig. 3, is primitive orthorhombic with dimensions $a = 8.694(1)$, $b = 16.908(4)$, and $c = 21.157(3)$ Å, very similar to the room temperature *C*-centered orthorhombic cell except that the *b* dimension has been almost exactly doubled. The gross framework topology is the same as that observed at room temperature shown in Fig. 1.

We observed no significant change in the ^{113}Cd solid state NMR spectrum of $Cd(CN)_2 \cdot 2/3H_2O \cdot t$-BuOH as the temperature was lowered below the phase change. Chemical shifts for the different cadmium environments at various temperatures are presented in Table 1. Thus the published interpretation of the room temperature spectrum (4) in terms of an octahedral cadmium center coordinated by four cyano nitrogen donors together with two *trans* water ligands and disordered cyanide units linking tetrahedral cadmium centers applies equally well at low temperature, and in the X-ray structural solution carbon and nitrogen atoms were assigned accordingly. A decrease in proton T_1 relaxation time by more than a factor of 2 at low temperature most likely results from a change in mobility of the solvent molecules.

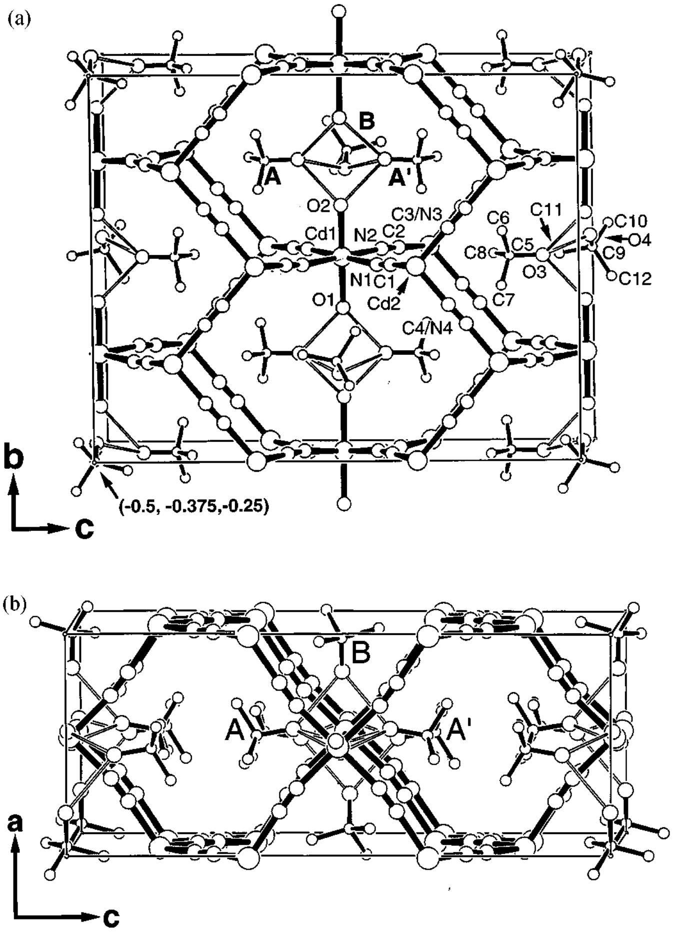

FIG. 3. The primitive orthorhombic unit cell of the low-temperature phase of $Cd(CN)_2.2/3H_2O.t$-BuOH (230 K). (a) Viewed along the *a* axis. (b) Viewed down the *b* axis. Only one orientation for each of the *t*-butanol molecules is shown.

The crystallographically unique cyanide units that link the octahedral Cd1 and the tetrahedral Cd2 (see Fig. 3) are ordered with four nitrogen atoms bound to the octahedral centre. The cyanide links (C3–N3 and C4–N4) between tetrahedral cadmium centers (Cd2) are disordered across sites of crystallographic symmetry with the result that these carbon and nitrogen sites are superimposed.

A number of important differences between the structures at 230 K and at room temperature are apparent. First and foremost, solvent molecules are much better resolved at the lower temperature and, in addition, the O–Cd–O vectors, in contrast to those in the previously reported room

TABLE 1
Variable Temperature ^{113}Cd Chemical Shifts[a] (ppm)

Cadmium center	Room temp.[b]	Room temp.	− 23°C	− 38°C	− 100°C	− 120°C
CdN_4O_2	149	149	149	154	163	167
CdC_2N_2	523	526	526	530	530	540
CdC_3N	589	591	590	597	609	612
CdC_4	645	646	646	652	665	668

[a] To allow comparison with the earlier study, chemical shifts are reported relative to $Cd(NO_3)_2 \cdot 4H_2O$.

[b] Previous study (4).

temperature structure, are significantly tilted relative to the *b* axis. This can be clearly seen in Fig. 4, which shows two adjacent channels running parallel with *a* seen "side-on" from a direction close to *c*; the two channels in the 230 K structure are shown in Fig. 4a and those in the the previously reported room temperature structure in Fig. 4b. As can be seen in Fig. 4a the direction of this tilting of the O–Cd–O vectors around *c* and away from *b* at low temperature alternates along *b* and this feature can also be discerned in Fig. 3a. This tilting is intimately involved in the orientations of the *t*-BuOH molecules located in the extensive intraframework spaces as described in more detail below.

In the earlier reported room temperature structure the intraframework *t*-BuOH molecules were ill defined and badly disordered. Although some of the disorder persists at low temperature, the 230-K data do permit accurate modeling of the remnant disorder. In Fig. 3a the two coordinated water molecules projecting into the upper hexagonal channel are both tilted toward the viewer in the manner discussed in the previous paragraph while those in the channel below are tilted in the opposite direction. The two water molecules in the upper hexagonal channel in Fig. 3a are hydrogen bonded to two symmetry-related *t*-BuOH molecules, labeled A and A′ in the figure, located somewhat more remote from the viewer than the water molecules; this feature is also apparent in Fig. 3b. A and A′ in turn are hydrogen bonded to a second type of *t*-BuOH, labeled B, with its C–O bond approximately parallel to *a* located even more remote from the viewer in Fig. 3a and with its oxygen atom pointing toward the viewer; this feature can also be seen in Fig. 3b. In this way all the type B *t*-BuOH molecules in one channel have their oxygen atoms pointing in the same direction, as can be seen in Fig. 4a. Because of the coupling between the orientation of the type B *t*-BuOH molecules and the inclinations of the O–Cd–O units and because the latter inclinations alternate from one channel to the next, the type B *t*-BuOH molecules in adjacent channels point in opposite directions as can be seen in Fig. 4a. As indicated above, the C–O bond of the type B *t*-BuOH is approximately parallel with *a*, and although the central carbon atom (C9) is well ordered, the oxygen atom is disordered over two sites so that the C–O bond is inclined slighty up or down relative to *a*. By virtue of the hydrogen bonding interactions the hydroxy groups of the *t*-BuOH molecules of both types are reasonably well ordered but the methyl groups are disordered.

4.3. Reexamination of Room Temperature Data

We have now reinterpreted our original room temperature X-ray data bearing in mind the insights provided by both the more recent solid state NMR data (4) and the low-temperature X-ray study. Accordingly the octahedral cadmium atom has now been modeled with an ordered CdN_4O_2 environment in contrast to the $CdC_2N_2O_2$ environment used in the earlier study (2). The high quality of the data allowed the refinement of different positions for the C and N atoms of the disordered cyanide unit linking tetrahedral centers, despite the fact that the carbon and nitrogen sites were almost superimposed. In the new room temperature structural model (the unit cell of which, it should be recalled, has only approximately half the volume of the 230-K cell considered above) the two different orientations for the B-type *t*-BuOH molecules have been superimposed with 50% disorder and the two different orientations of the A-type molecules have also been superimposed with 50% disorder. In the original refinement of the room temperature structure the oxygen atoms of the coordinated water molecules were refined as ordered atoms; in the new refinement a superior model was obtained with this water molecule disordered over two positions with 50% site occupancy. Although the *t*-butanol and water molecules exhibit a greater degree of disorder at room temperature it seems likely, given the close relationships between the low- and room temperature structures, that the hydrogen bonding leading to the aggregation of water and *t*-butanol molecules still persists but that the long range ordering of these individual systems is absent at room temperature.

The model described above was examined in each of the five space groups (*Cmmm*, C222, *C*2*mm*, *Cm*2*m*, and *Cmm*2), and as we found in our earlier study, a satisfactory refinement could be obtained in all cases with *R* 1 values less than 0.030. Although the refinements in the noncentrosymmetric space group *Cm*2*m* led to a marginally superior *R*1 value of 0.0271, we have nevertheless opted for the centrosymmetric space group *Cmmm*. Our choice of space group is not unambiguous but it does represent a chemically sensible result obtained in the highest symmetry possible given the diffraction data. The choice of *Cmmm* is supported by convincing arguments put forward by Marsh (9) regarding the preference for centrosymmetric models if the refinement in such space groups is satisfactory.

The above results provide important clues as to why this structure is radically different from the parent

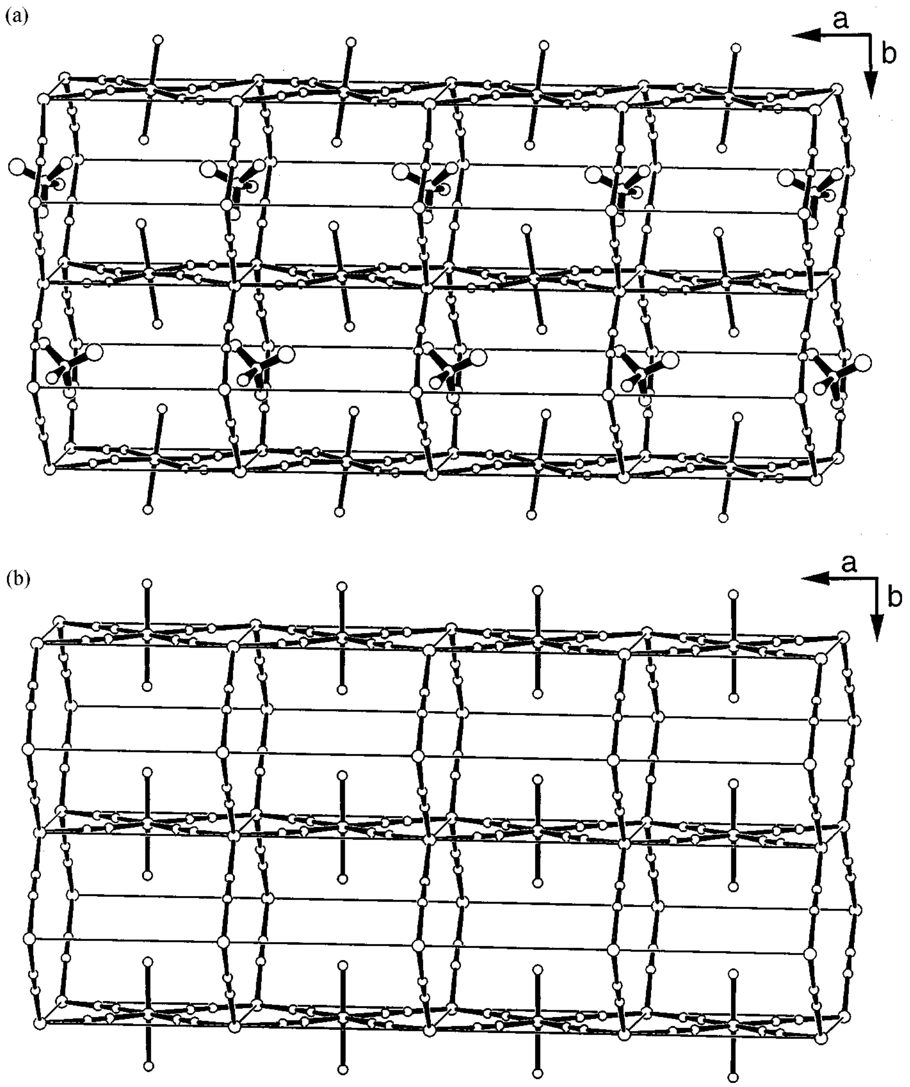

FIG. 4. "Side" view of two adjacent channels that run parallel to *a* as seen from a direction close to *c*. (a) The channels in the 230-K structure showing the orientations of the B-type *t*-BuOH molecules, those of type A having been been omitted for clarity. (b) The channels analogous to those shown in (a) in the previously reported room temperature structure. The labeling of the axes in (b) refers to the originally reported *A*-centered cell.

cadmium-cyanide structure, which is solvent-free and based upon two interpenetrating diamond nets formed by linking tetrahedral metal centers with linear cyanide ions. It is apparent from both the low- and room temperature structures that the hydrogen bonding between two coordinated water ligands and three *t*-butanol molecules, two of type A and one of type B, is an important structural feature. The dimensions of this hydrogen-bonded cluster are nicely compatible with the separation between neighboring octahedral cadmium atoms required by the coordinative network. At the same time the *t*-butyl groups extend into hydrophobic voids, allowing efficient packing within the structure that undoubtedly contributes to the stability of the crystal. It is interesting to note that the incorporation of solvent molecules of a similar size to *t*-BuOH but with no opportunity for hydrogen bonding, such as carbon tetrachloride (10), do not give rise to the honeycomb structure but rather a single diamond-like net with the occluded solvent filling adamantane cavities.

If the presence of the hydrogen-bonded aggregates is essential to the stability of the network by maintaining the required separation between octahedral cadmium atoms and satisfactorily filling the intraframework spaces, then it may be expected that upon loss of the occluded solvent molecules the stability of this network would be reduced. This is consistent with our earlier report that the honeycomb cadmium cyanide reverts to the parent cadmium cyanide upon solvent loss (11).

There are now numerous examples in the literature of cadmium-cyanide structures adopting other topologies with the occlusion of guest molecules of various sizes, shapes and polarities (12). As has been indicated before, this considerable variation possibly reflects an inherent instability in the structure of the parent $Cd(CN)_2$ due to its inability to fill space efficiently (1b). It is therefore not surprising that secondary bonding interactions can have such a dramatic effect on the topology adopted by the cadmium-cyanide framework.

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