

suitably modified bridged cubanes, we have no evidence to reject structures which are not based on the assembly of cubanes.

Finally, if P^{OX} is the two-electron oxidized form of P^N , what evidence is there for a cluster state oxidized by one electron relative to P^N ? This state has to be a Kramers system, and we suspect that the $g = 1.94$ EPR signals observed in the early phase of thionin titrations of Av1 represent this state.³⁸ More than 10 years ago we had obtained evidence from Mössbauer spectroscopy that these signals result from the P-clusters. However, since only a small fraction of the clusters were present in the $g = 1.94$ form, the relevant Mössbauer spectrum was masked by the magnetic features of M^N , and for that reason a convincing argument could not be presented for the general reader. However, the availability of isotopic hybrids of the MoFe protein (P-clusters enriched in ⁵⁷Fe; M-centers enriched with the Mössbauer-silent ⁵⁶Fe) will allow

us to study the $g = 1.94$ state with reasonable resolution. It is clear that the new developments in P-cluster research offer a broad spectrum for biophysical, bioinorganic, and biochemical inquiries.

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Note Added in Proof. Based on crystallographic analysis of nitrogenase from *A. vinelandii* at 2.8-Å resolution, Kim and Rees have recently proposed that the P-clusters consist of two cubane Fe_4S_4 clusters bridged by two cysteine residues; Kim, J.; Rees, D. C. *Science*. In press.

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Crystal Structure of $Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH$ Studied by X-ray Diffraction and Solid-State ¹¹³Cd NMR. A New Type of Cristobalite-like Framework Host with a Site Interacting with Cyclohexanol by Hydrogen Bonding[†]

S. Nishikiori,[†] C. I. Ratcliffe,*[§] and J. A. Ripmeester[§]

Contribution from the Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan, and Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9.

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Abstract: The structure of the title clathrate represents the first example of a metal cyanide structural analysis which takes into account explicitly the order/disorder of the metal-linking cyanide units. The structure, which has some unique features, is tetragonal $I4_1/a$, with $a = 20.070$ (2) Å, $c = 12.733$ (3) Å, $V = 5129$ (2) Å³, and $Z = 4$, and was refined to $R = 0.049$ for 2483 independent reflections. ¹¹³Cd NMR was used to determine local order around the metal centers. The two distinct Cd atoms are coordinated by bridging cyanides in tetrahedral positions, one Cd also having a coordinating water molecule. The distorted β -cristobalite framework has two cavities, one containing a cyclohexanol molecule and the other the four coordinating waters. These form a near regular tetrahedron, with four cyclohexanols in neighboring cages coordinating to the four faces of the tetrahedron by hydrogen bonding. ²H NMR indicates that the four water molecules in a cage rapidly interchange positions at ~ 250 K, whereas the cyclohexanol hydroxyl is undergoing an anisotropic motion at this temperature. ¹³C NMR results indicate that the whole cyclohexanol molecule is in motion at room temperature.

Introduction

The structure of $Cd(CN)_2$ consists of two interpenetrating, but nonbonded, cristobalite-like lattices built from Cd atoms linked tetrahedrally by CN bridges. Removal of one of the interpenetrating lattices leaves a structure which has adamantane-shaped cavities, which are large enough to accommodate guest molecules and thus form a clathrate $Cd(CN)_2 \cdot G$. A number of such clathrates are now known with guests $G = CCl_4, CHCl_3, CH_3-CCl_3, (CH_3)_3CCl, C_6H_{12}$, and so on.^{1,2} Recent systematic studies of cadmium cyanide clathrates and related compounds, carried out with a view to developing new materials (having three-dimensional frameworks and large void spaces for accommodating guest molecules), have led to the discovery of a number of different

cadmium cyanide frameworks. Robson et al. reported a new cadmium cyanide clathrate $Cd(CN)_2 \cdot 2/3 H_2O \cdot Bu^4OH$ with a honeycomb-like framework,^{3,4} and Kitazawa et al. have been developing other cadmium cyanide type clathrates of the general formula $[onium][Cd_3(CN)_7] \cdot G$.⁵ Although these new clathrates

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[†] The University of Tokyo.

[§] National Research Council of Canada.

were prepared by methods similar to those used for $Cd(CN)_2 \cdot G$, they have quite different host structures. In most cases their cadmium cyanide complex hosts contain not only tetrahedral cadmium atoms but also octahedral cadmium atoms. Moreover, other ligands as well as cyano groups are often involved in forming the host cadmium complexes. In short, there are many variations in the host structures of cadmium cyanide clathrates and related compounds, to which we now add one with some unusual structural features: $Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH$ clathrate.

The crystal structure of the new clathrate was elucidated by the combined use of X-ray diffraction and ^{113}Cd NMR spectroscopy. Although X-ray diffraction is, in general, a very powerful tool for determining crystal structures of cadmium cyanide complexes, one often experiences difficulties in assigning the C and N atoms of cyano groups which bridge between two cadmium atoms. Fortunately, additional information about the coordination environment of a cadmium atom can be obtained from ^{113}Cd NMR spectra, which, as we have shown in previous studies, is often enough to resolve the difficulty.^{6,7}

Experimental Section

Preparation. Single crystals of the title compound were prepared by a method similar to that for $Cd(CN)_2 \cdot G$ clathrates.¹ Equivalent volumes of aqueous solutions of 0.07 M $CdCl_2$ and 0.07 M $K_2[Cd(CN)_4]$ were mixed and stirred for 30 min. After the solution was filtered through filter paper, neat cyclohexanol was poured onto the filtrate. On standing at room temperature for a few days colorless crystals with composition $Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH$ grew near the interface of the aqueous and the organic phases. (Anal. Found/Calcd for $Cd_5C_{34}H_{56}N_{10}O_8$: Cd, 43.7/43.4; C, 30.7/31.5; H, 4.12/4.36; N, 11.0/10.8.) Polycrystalline samples for the NMR experiments were precipitated by vigorous mixing of the aqueous and organic phases. D_2O (MSD Isotopes) was used in the preparation of the partially deuterated materials.

NMR Spectra. ^{113}Cd CP/MAS NMR spectra were obtained at 39.92 MHz using a Bruker CXP-180 spectrometer with a 4.24-T cryomagnet and a Doty Scientific magic angle spinning probe. Samples were contained in 7-mm diameter zirconia or silicon nitride rotors with Kel-F or vespel end caps and spun at various speeds. 1H 90° pulse lengths of 5 μs (4.5 μs), a cross-polarization time of 2 ms (6 ms), and a recycle time of 2 s (8 s) were used (values used for the partially deuterated material given in parentheses). Chemical shifts were referenced to $Cd(NO_3)_2 \cdot 4H_2O$. ^{13}C CP/MAS spectra were obtained at 45.26 MHz and are referenced to TMS. ^{13}C dipolar dephased spectra were obtained by interrupting the 1H decoupling for 40 μs immediately after cross-polarization. 2H NMR powder line shapes were obtained at 27.63 MHz at several temperatures, using a variable-temperature N_2 gas-flow probe with a Bruker B-VT-1000 variable-temperature controller. A phase-alternated quadrupole echo pulse sequence⁸ was used with a delay time of 35 μs between X and Y pulses of 2.6–3.0 μs .

X-ray Diffraction Study. The collection of X-ray diffraction intensity data was carried out on a Rigaku AFC-5 automated four-circle diffractometer using graphite monochromated Mo K α radiation at room temperature. The single crystal sample used in the measurement was coated with epoxy resin to prevent it from decomposing via liberation of the guest component. Crystal data and conditions of intensity data collection and structure analysis are summarized in Table I.

In the structure analysis 2483 independent reflections corrected for absorption effects⁹ were used. The space group was determined uniquely to be $I4_1/a$ from systematic absences. The Cd atom positions were determined from a three-dimensional Patterson map. All non-hydrogen atoms were found in electron density maps and were refined with anisotropic thermal parameters by block diagonal least-squares calculations. No hydrogen atoms were included in this refinement. Assignment of the C and N of the cyano groups was carried out based on the analysis of the ^{113}Cd -CP/MAS spectra (see later). In the final stage the extinction correction was applied.¹⁰ The final reliability factors were 0.049 for R and 0.047 for R_w . The largest ratio of shift to estimated standard de-

Table I. Summary of Crystal Data, Data Collection, and Structure Analysis

compd	$Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH$
fw	1294.94
crystal system	tetragonal
space group	$I4_1/a$ (No. 88)
a/ \AA	20.070(2)
c/ \AA	12.733(3)
V/ \AA^3	5129(2)
Z	4
$D_{meas}/g\text{ cm}^{-3}$	1.68
D_{calcd}	1.70
F(000)	2536
crystal size	$0.30 \times 0.30 \times 0.25$ mm
radiation	Mo K α (0.70926 \AA)
monochromator	graphite
μ/cm^{-1}	20.76
scan mode	$2\theta-\omega$
scan range	$4^\circ \leq 2\theta \leq 60^\circ$ $0 \leq h \leq 28$ $0 \leq k \leq 28$ $0 \leq l \leq 17$
no. of reflctns measd	4111
no. of reflctns used	2483 ($\geq 3\sigma(F_o)$)
no. of parameter	130
systematic absences	$hkl: h + k + l = 2n$ $00l: l = 4n$ $hk0: h = 2n \text{ and } k = 2n$
R^a	0.049
R_w^b	0.047
gof ^c	1.139
weighting scheme	$ F_o > 70: w = 4900/ F_o ^2$ $70 \geq F_o \geq 35: w = 1$ $ F_o < 35: w = 0.25$

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^c $gof = [\sum w(|F_o| - |F_c|)^2/(N_{ref} - N_{par})]^{1/2}$.

Table II. Distances and Angles for $Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH^a$

Distances ($d/\text{\AA}$)			
Cd(1)–O(1)	2.654 (2)	C(5)–C(6)	1.593 (9)
Cd(1)–C(1)	2.180 (2)	C(6)–C(7)	1.46 (1)
Cd(1)–N(2)	2.216 (2)	C(7)–C(8)	1.38 (1)
Cd(1)–C(3)	2.193 (2)	C(8)–C(9)	1.72 (1)
Cd(1)–N(1)* ¹	2.282 (2)	C(9)–C(4)	1.29 (1)
Cd(2)–C(2)	2.189 (2)	O(2)···O(1)	2.836 (3)
C(1)–N(1)	1.135 (3)	O(2)···O(1)* ⁶	2.816 (3)
C(2)–N(2)	1.129 (3)	O(2)···O(1)* ⁷	2.836 (3)
C(3)–C(3)* ²	1.156 (3)	O(1)···O(1)* ⁶	3.864 (2)
O(2)–C(4)	1.396 (5)	O(1)* ⁶ ···O(1)* ⁷	3.897 (2)
C(4)–C(5)	1.369 (8)		
Angles (δ/deg)			
C(1)–Cd(1)–N(2)	119.99 (8)	Cd(2)–C(2)–N(2)	176.6 (2)
N(2)–Cd(1)–C(3)	112.33 (8)	C(2)–N(2)–Cd(1)	172.7 (2)
C(3)–Cd(1)–C(1)	120.01 (8)	Cd(1)–C(3)–C(3)* ²	177.7 (2)
N(1)* ¹ –Cd(1)–C(1)	103.00 (8)	C(2)–Cd(2)–C(2)* ⁴	108.34 (9)
N(1)* ¹ –Cd(1)–N(2)	96.68 (7)	C(2)–Cd(2)–C(2)* ⁵	110.04 (9)
N(1)* ¹ –Cd(1)–C(3)	97.84 (8)	O(2)–C(4)–C(5)	115.5 (4)
O(1)–Cd(1)–C(1)	86.65 (7)	C(4)–C(5)–C(6)	114.7 (6)
O(1)–Cd(1)–N(2)	78.50 (6)	C(5)–C(6)–C(7)	110.0 (5)
O(1)–Cd(1)–C(3)	79.79 (7)	C(6)–C(7)–C(8)	104.4 (7)
O(1)–Cd(1)–N(1)* ¹	173.19 (6)	C(7)–C(8)–C(9)	98.5 (7)
Cd(1)–C(1)–N(1)	177.4 (2)	C(8)–C(9)–C(4)	106.7 (5)
C(1)–N(1)–Cd(1)* ³	174.0 (2)	C(5)–C(4)–C(9)	122.2 (6)

^a Key to symmetry operations: (*1) $1/4 - y, -1/4 + x, -1/4 + z$; (*2) $-x, -y, 1 - z$; (*3) $1/4 + y, 1/4 - x, 1/4 + z$; (*4) $-x, 1/2 - y, z$; (*5) $1/4 - y, 1/4 + x, 1/4 - z$; (*6) $-1/4 + y, 1/4 - x, 5/4 - z$; (*7) $1/4 - y, 1/4 + x, 5/4 - z$; (*8) $-1/4 + y, 1/4 - x, 1/4 - z$; (*9) $x, y, 1 + z$; (*10) $1/2 - x, -y, 1/2 + z$; (*11) $1/4 - y, -1/4 + x, 3/4 + z$; (*12) $-1/4 + y, -1/4 - x, 3/4 + z$; (*13) $x, 1/2 + y, 1 - z$; (*14) $-1/4 - y, 1/4 + x, 1/4 + z$.

viation of the atomic parameters in the final cycle was 0.13 for U_{22} of Cd(1) in the host lattice and was 0.85 for U_{22} of C(7) in the guest molecule. The maximum residual electron density was 0.87 e \AA^{-3} at the position 1.07 \AA from C(7) of the guest molecule. Bond lengths and angles are listed in Table II. (Final coordinates are given in the tables of supplementary data.)

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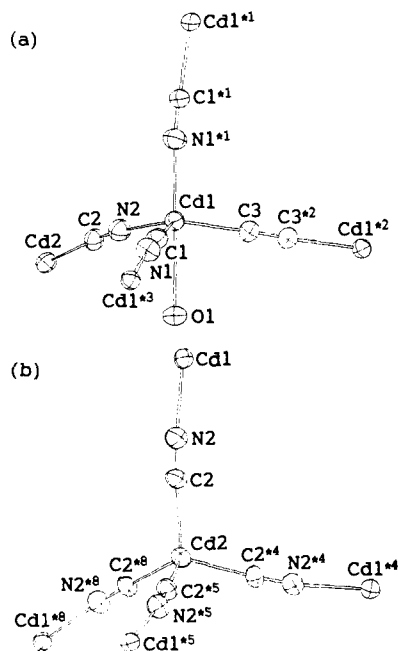


Figure 1. Coordination structures of Cd(1) (a) and Cd(2) (b). Cd(1) has a five-coordinate structure, with four cyano groups coordinating to tetrahedral positions of Cd(1) plus a water oxygen. Cd(2) has an ordinary tetrahedral coordination structure. Atoms labeled C3 are hybrid C/N due to the disorder. For the key to symmetry operations: see the footnote in Table II.

The calculations were carried out using a universal crystal structure analysis program system UNICS-III,¹¹ a least-squares calculation program ANYBLK,¹⁰ and a crystal diagram plotting program ORTEP-II¹² on FACOM M-360 of the Educational Computer Center and HITAC M-880 of the Computation Center of the University of Tokyo. Atomic scattering factors used here were taken from ref 13. The averaged values of the atomic scattering factors for C and N atoms were used as the atomic scattering factors for C(3) (see later).

Results and Discussion

X-ray Diffraction Study. The structure contains two kinds of cadmium atoms; Cd(1) and Cd(2) in a ratio of 4:1, whose coordination structures are shown in Figure 1. Cd(1) is five-coordinate with four cyano groups, located close to the vertices of a tetrahedron, and a water molecule. Cd(2) is four-coordinate with four cyano groups arranged tetrahedrally. All the cyano groups bridge between the cadmium atoms, so that the host complex has a cristobalite-like three-dimensional framework structure that is closely related to that of the $\text{Cd}(\text{CN})_2 \cdot \text{G}$ clathrates, but with a distortion due to the five-coordinate structure of Cd(1), see Figure 2.

The two kinds of cadmium atoms and the distortion of the host framework form two kinds of adamantane-like cavities, cavity-A and cavity-B shown in Figures 3 and 4, respectively. Four cavities-A surround one cavity-B, so that there are sixteen A's and four B's in the unit cell. Each cavity-A includes one cyclohexanol molecule, whereas each cavity-B includes four water molecules coordinating to Cd(1). The Cd(1)–O(1) bond is oriented toward the center of cavity-B, so that four O(1) atoms are located at the vertices of a tetrahedron (Figure 4). The C(4)–O(2) bond of the cyclohexanol molecule in cavity-A is oriented toward the center of a triangular face of the tetrahedron formed with the four O(1) atoms (Figures 3 and 5). The distances between O(2) and O(1) atoms are distributed in the range 2.816–2.836 Å (see Figure 3 and Table II). These distances suggest the existence of hydrogen bonds between the OH group and the water molecules. Fur-

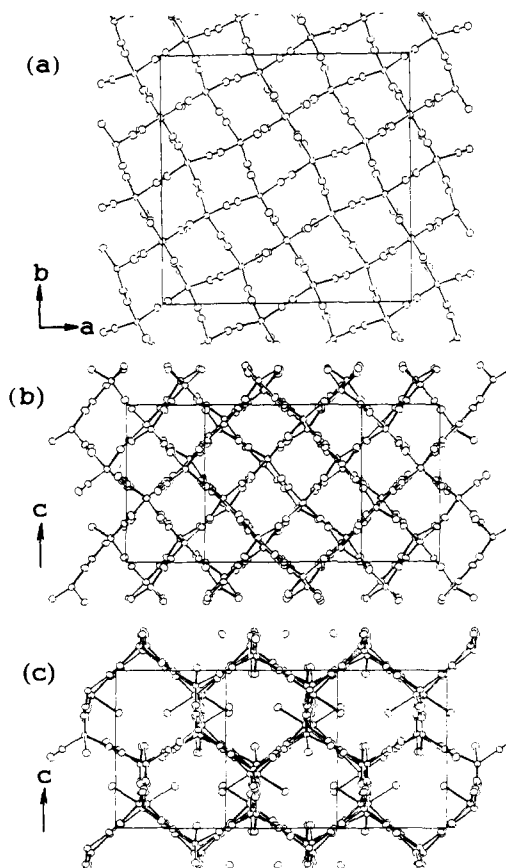


Figure 2. Framework structure of the $\text{Cd}_5(\text{CN})_{10}(\text{H}_2\text{O})_4$ host complex. Hydrogen atoms and cyclohexanol molecules are omitted. (a) Projection down to [00-1], (b) projection down to [130], (c) projection down to [-120]. The whole structure of the framework is a distorted cristobalite-like lattice. In c it is clearly recognized that oxygen atoms of water molecules coordinating to Cd(1) are located in cavity-B.

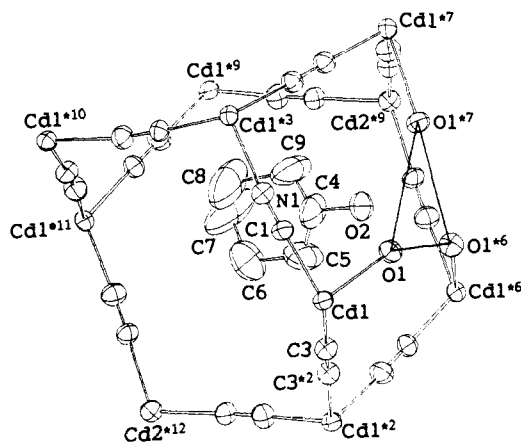


Figure 3. Structure of cavity-A and the guest cyclohexanol molecule. The C(4)–O(2) bond is oriented to the center of a triangle made by O(1), O(1)*₆, and O(1)*₇. Distances between O(2) and three O(1) atoms suggest the existence of hydrogen bonds between them. Atoms labeled C3 are hybrid C/N due to the disorder. For the key to symmetry operations: see the footnote in Table II.

thermore the cyclohexanol molecule is strongly oriented in cavity-A by this hydrogen bonding. On the other hand, the distances between the four O(1) atoms of the water molecules, 3.864–3.897 Å, show no possibility of forming hydrogen bonds. The hydrogen atoms of the water and the OH group could not be found in the final differential electron density map.

In the case of cadmium cyanide cyclohexane clathrate $\text{Cd}(\text{C}-\text{N})_2 \cdot \text{C}_6\text{H}_{12}$, the structure of the cyclohexane molecule could not be determined by X-ray diffraction.¹ ²H NMR studies have

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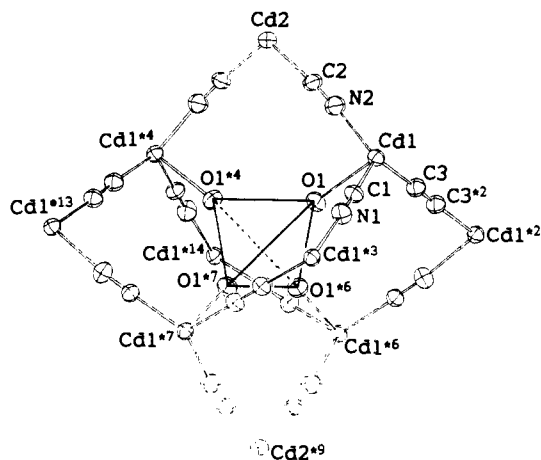


Figure 4. Structure of cavity-B with the four water molecules. The water oxygen atoms, O(1), O(1)^{*4}, O(1)^{*6}, and O(1)^{*7} are located at the vertices of a tetrahedron. Atoms labeled C3 are hybrid C/N due to the disorder. For the key to symmetry operations: see the footnote in Table II.

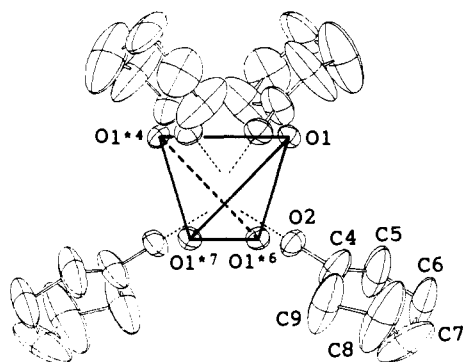


Figure 5. The tetrahedron of four H_2O oxygen atoms showing the four cyclohexanols hydrogen bonding over each face of the tetrahedron.

indicated rapid pseudoisotropic reorientation of the cyclohexane molecule at temperatures above 140 K.⁶ These results being considered, the cyclohexanol molecule might be expected to have a high degree of freedom in cavity-A whose structure is similar to that of $Cd(CN)_2 \cdot C_6H_{12}$. In fact, because the OH group is fixed by the hydrogen bonds, partially restricted rather than isotropic motion of the cyclohexanol molecule is observed: The results of the X-ray structure analysis show that the fixed oxygen atom O(2) has reasonable temperature factors for an atom of a trapped guest molecule but the carbon atoms have very large temperature factors. The derived structure of the cyclohexyl group is consequently very distorted, and its position is only roughly determined. In particular the anisotropy of the thermal ellipsoid along the direction perpendicular to the plane of the cyclohexyl ring is very large. These findings suggest a large thermal motion of the cyclohexyl group, presumably inversion or similar motion. Motion of the cyclohexyl group is supported by the ^{13}C -CP/MAS results (see below).

There are three crystallographically independent cyano groups, CN1, CN2, and CN3. As mentioned in the Experimental Section, assignment of C and N of the cyano groups was carried out based on the evidence of ^{13}C -CP/MAS spectra. The center of the CN3 link is an inversion center, so that, based on the X-ray results alone, this group must be in the 1:1 disordered state. The ^{13}Cd NMR results also require this link to be disordered. Averaged values of the atomic scattering factors of C and N were applied for these hybrid atoms, labeled C(3), in our structure refinement. From an apparent difference between bond lengths $Cd(1)-C(1)$ and $Cd(1)-N(1)$ and the ^{13}Cd NMR results (see below), cyano group CN1 is found to be very nearly but not completely ordered. Discreet C or N atoms were therefore used in the final refinement for CN1. The X-ray results were ambiguous with respect to CN2, but ^{13}Cd NMR clearly showed CN2 to have an imbalanced

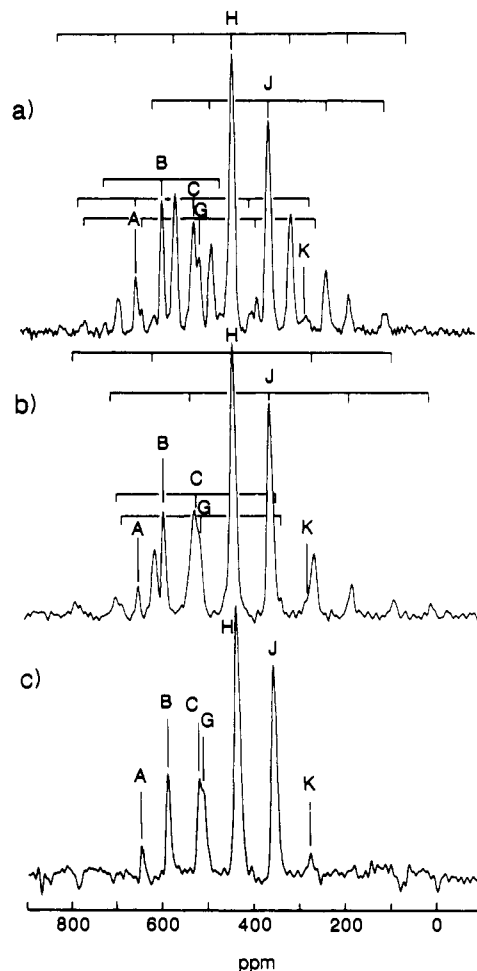


Figure 6. ^{13}Cd -CP/MAS NMR spectra of (a) $Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH$ spinning at 5 kHz, (b) $Cd_5(CN)_{10}(D_2O)_4 \cdot 4C_6H_{11}OH$ spinning at 7 kHz, (c) as in b but with suppression of the first-order spinning sidebands to confirm the presence of line K (second-order sidebands appear inverted). A = $Cd(2)C_4$, B = $Cd(2)C_3N$, C = $Cd(2)C_2N_2$, G = $Cd(1)OC_2N_2$, H = $Cd(1)OC_2N_2$, J = $Cd(1)OCN_3$, K = $Cd(1)ON_4$. The spinning sideband manifolds are indicated above the spectra in a and b.

Table III. ^{13}Cd Chemical Shifts,^a Intensities, and Assignments

assignt	spinning 5 kHz (H) ^b	spinning 7 kHz (D)	spinning 10 kHz (H)	approx rel inten ^c
$Cd(2)C_4$	643	643	633	0.08
$Cd(2)C_3N$	584	585	576	0.44
$Cd(2)C_2N_2$	515	517	{ 505 }	0.46
$Cd(1)OC_3N$	502	507	{ overlap }	0.42
$Cd(1)OC_2N_2$	428	432	425	2.22
$Cd(1)OCN_3$	349	352	344	1.38
$Cd(1)ON_4$	265–275	272	265–275	0.06

^aIn ppm. ^bH or D in parentheses indicates fully protonated or partially deuterated sample. ^cSince there are 4 times as many Cd1 atoms as Cd2 the relative intensities have been scaled so that the total intensity of all the lines is 5.

disorder, with a preference for C on the Cd(2). Considering the relatively large imbalance and the difference between bond length $Cd(2)-C(2)$ and $Cd(1)-N(2)$, the atomic scattering factors of C and N atoms were applied for C(2) and N(2), respectively, in the final refinement.

NMR Results. A ^{13}Cd -CP/MAS NMR spectrum obtained at a spinning speed of about 5 kHz is shown in Figure 6. From this and spectra obtained at other spinning speeds, isotropic shift lines can be clearly identified at 643, 584, 515, 502, 428, and 349 ppm. Most of the lines have several spinning sidebands, identified in Figure 6. Isotropic chemical shifts and approximate intensities taking into account the spinning sidebands are given in Table III.

Table IV. Possible Models of Cd/CN Configurations

model	ordered links	disordered links	possible coordinations of		no. of distinct Cd sites
			Cd(2)	Cd(1)	
1	CN1, CN2	CN3	(C ₄) ^a or (N ₄)	(OCNN)C (OCNN)N or (OCNC)C (OCNC)N	3
2		CN1, CN2, CN3	C ₄ C ₃ N C ₂ N ₂ CN ₃ N ₄	(O)C ₄ (O)C ₃ N (O)C ₂ N ₂ (O)CN ₃ (O)N ₄	10
3	CN2	CN1, CN3	(C ₄) or (N ₄)	(ON)C ₃ (ON)C ₂ N (ON)CN ₂ (ON)N ₃ or (OC)C ₃ (OC)C ₂ N (OC)CN ₂ (OC)N ₃	5
4	CN1	CN2, CN3	C ₄ C ₃ N C ₂ N ₂ CN ₃ N ₄	(OCN)C ₂ (OCN)CN (OCN)N ₂	8

^a Coordinating atoms which are ordered are shown inside parentheses.

Before going into a more detailed analysis of the observed ¹¹³Cd spectrum it is useful to anticipate what possibilities might occur, based on the initial X-ray structural information. Any model must obey the apparent symmetries when spatial averaging is taken into account. The structural requirements are as follows:

(1) Cd(2) has four equivalent CN2 links to Cd(1). CN may be disordered.

(2) Cd(1) has four different CN links; (a) One CN2 link to Cd(2). CN may be disordered. (b) One CN3 link to a Cd(1). The inversion center in this link requires a 1:1 disorder of the CN. (c) Two CN1 links to Cd(1). On the basis of distances from the centers of electron density to the Cd(1) atom it appears that these CN may be ordered such that the C of one and the N of the other attach to the Cd(1). However, it is possible that they are also disordered but with a strong preference for either C or N at one end. The crystal symmetry allows this as the CN1 are on general positions. Assuming that the CN are static, there are four possible models of disorder; refer to Figure 1 and Table IV. Each of these would give rise to a different number of ¹¹³Cd NMR lines. Models 1 and 3 give fewer lines than are observed and can therefore be discarded. Models 2 and 4 are related in that model 4 is an extreme case of model 2, where the weighting of the disorder in the CN1 links has moved completely to one end. Both models suggest that there should be five lines for the Cd(2). Indeed three of the observed lines (at 643, 584, and 515 ppm) can be assigned to the carbon rich end of the distribution, i.e., to Cd(2)C₄, Cd(2)C₃N, and Cd(2)C₂N₂ (where the formulas give the atoms directly attached to the Cd), by comparison with results for Cd(CN)₂, Cd(CN)₂·C₆H₁₂,⁶ and Cd(CN)₂·2/3H₂O·Bu'OH,⁷ see Table V. The Cd(2)C₄ line does not have any spinning sidebands as expected for a nearly perfect tetrahedral site, whereas the Cd(2)C₃N and Cd(2)C₂N₂ both have spinning sidebands indicating substantial chemical shift anisotropies. Based on the shift differences observed for Cd(CN)₂ and Cd(CN)₂·C₆H₁₂,⁶ the Cd(2)CN₃ line would be expected at about 442 ± 2 ppm and if present would be under the wing of the very strong line at 428 ppm. This leaves three other obvious resonances at 502, 428, and 349 ppm. The latter two resonances are the strongest in the spectrum.

If the disordered links were to have a purely statistical (1:1) probability of having either C or N at any one site, then the

intensities of the peaks for Cd(2) in models 2 and 4 and for Cd(1) in model 2 would follow the symmetrical pattern 1:4:6:4:1, and the three peaks for Cd(1) in model 4 would have a 1:2:1 intensity pattern. The observed intensities for Cd(2) show a strong weighting toward the carbon rich end. For detailed balance this requires that the Cd(1) be weighted toward the N rich end. In either case (model 2 or 4) the assignment of the three peaks at 502, 428, and 349 ppm must be Cd(1)OC₃N, Cd(1)OC₂N₂, and Cd(1)OCN₃, respectively, since, although model 2 has all its CN molecules disordered, the weights of the C and N in the two CN1 links must still be close to the ordered case of model 4. However, model 2 does allow for OC₄ and ON₄. Since we need an overall weighting to N on the Cd(1) the OC₄ peak would likely be negligibly small, but the ON₄ peak might have some intensity. There is in fact a small amount of intensity in the region 265–275 ppm which is not attributable to sidebands of any of the other peaks, see Figure 6a. It is also too low in shift to be Cd(2)N₄, which would appear in the 355–365 ppm region.⁶ It was difficult to find a spinning speed which gave a window where this peak would not be overlapped by spinning sidebands of stronger lines, so its presence was initially only detected as a weak shoulder or extra intensity on the sidebands. However, by using a first-order spinning side band suppression pulse sequence¹⁴ at 7 kHz, one can definitely see this weak and broad feature, see Figure 6c. Model 2 therefore is the most consistent.

If the disorders were purely statistical it would be a simple matter to simulate the observed intensities for different weightings of C:N in the various links. Previous studies, however, have shown that usually there are sizeable departures from the statistical model, apparently because some configurations are more energetically favorable than others. This makes it impossible to predict the intensities since the distribution can be shifted around considerably while still maintaining the detailed balances of 1:4 for Cd(2):Cd(1) and 1:1 for overall C:N. The approximate relative intensities observed are given in Table III. Upon consideration of the errors involved (which may be as high as 20% for some of the weaker lines and those which are only partly resolved), the possibility that some weak lines may be hidden under stronger ones, and that there is a possibility that Cd(1) and Cd(2) may cross-polarize slightly differently, the sums of intensities are remarkably close to the requirements of detailed balance. This lends weight to the basic correctness of the assignments made, since any different assignments create large mismatches in the numbers of C and N.

There are two other points of interest concerning the ¹¹³Cd NMR spectra: (1) The half-widths of the lines increase as the number of N atoms on the Cd increases, in line with previous observations of Cd(CN)₂ and Cd(CN)₂·G.⁶ This broadening arises mainly from J-coupling to ¹⁴N, and there may be some incomplete averaging of dipolar coupling because of the ¹⁴N quadrupole. (2) Chemical shifts of lines which were resolved from overlapping lines or spinning sidebands at a spinning speed of 10 kHz are also given in Table III. There appears to be some sensitivity to the spinning rate. This most probably is a pressure induced effect, since the forces inside the spinning tube are quite considerable.

The ¹³C CP/MAS spectra shown in Figure 7 show resonances of cyclohexanol at 72.2, 36.3, and 25.1 ppm with the intensity ratios 1:2:3 corresponding to C1, attached to OH, 2 × C2, attached to C1, and overlapping lines for 2 × C3 and C4 respectively. The shifts compare favorably with values for the liquid¹⁵ of 69.5 (C1), 35.5 (C2), 24.4 (C3), and 25.9 (C4) ppm. The interesting result is that all three lines also appear in the dipolar dephased¹⁶ spectrum with intensities of about 0.4 to 0.5 of that of the normal spectrum. Since all the carbons have directly attached H atoms they should not appear in the dephased spectrum unless the C–H bonds involved are undergoing rapid reorientation (which reduces the dipolar coupling to H). This confirms that a large thermal motion

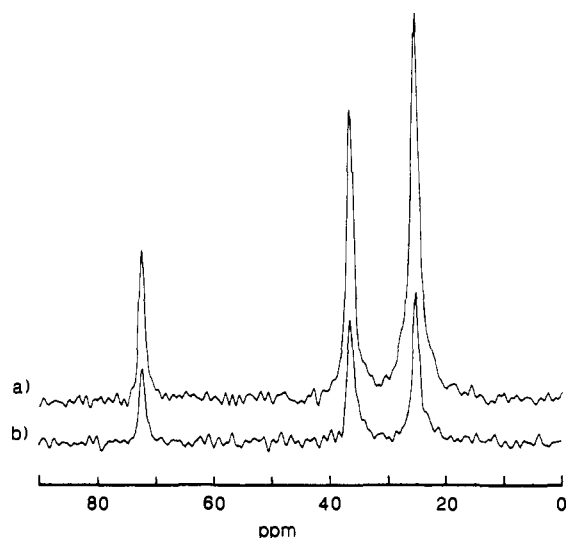
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Table V. Comparison of ^{113}Cd NMR Chemical Shifts^a of Cd Coordinated by Four CN Groups on Pseudotetrahedral Sites

compd	C ₄	C ₃ N	C ₂ N ₂	CN ₃	N ₄	ref
Cd(CN) ₂	636	578	510	439	~366	6
Cd(CN) ₂ /C ₆ H ₁₂	621.6	562	492.7	417.8	~336	6
Cd(CN) ₂ /Bu'OH	645.3	589.4	523.2			7
Cd(CN) ₂ /H ₂ O/C ₆ H ₁₁ OH	643	584	515	(442) ^b		this work

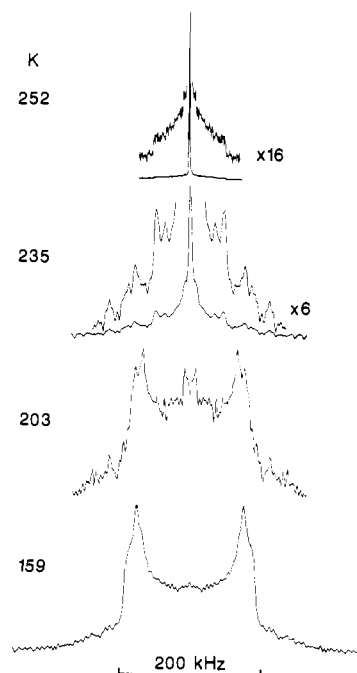
^aIn ppm. ^bProjected value.**Figure 7.** ^{13}C -CP/MAS NMR spectra of $Cd_5(CN)_{10}(D_2O)_4 \cdot 4C_6H_{11}OH$ spinning at 4.2 kHz. The CN region is not shown. (a) Normal spectrum, (b) dipolar dephased spectrum.

of the ring is occurring, as suggested by the X-ray results.

The 2H NMR line shapes (Figure 8) show that the D_2O and alcohol OD are essentially static at 160 K. The line shape can be characterized with a single quadrupole coupling constant (QCC) of 226.5 kHz and asymmetry parameter (η) of 0.104, though it is likely that the apparent single line shape is produced by overlap of two unresolved but slightly different line shapes corresponding to the D_2O and OD. Motion of both types of molecule sets in at around 200 K. The motion of the D_2O appears to become pseudoisotropic by about 250 K, whereas the cyclohexanol OD at first has an anisotropic motion, giving rise to a nonaxial line shape at 250 K (QCC = 79.6 kHz and $\eta = 0.717$), and at higher temperatures becomes pseudoisotropic. This separation of behavior is based on the relative intensities of the two components at 250 K, which should be in a 2:1 ratio ($4D_2O:4C_6H_{11}OD$). Currently there is not enough information here to characterize these motions in detail, but one can suggest a likely picture. Since there are 4 D_2O in cavity-B arranged at the corners of a tetrahedron, their interchange would be sufficient to average the effective quadrupole coupling constant of the 2H to zero, and thus give an isotropic line shape. The motion of the cyclohexanol OD may be much more complex possibly involving reorientation of the OD about the C-O bond together with a motion of the whole cyclohexanol molecule. These few ^{13}C and 2H NMR results should be regarded as preliminary, but they provide a hint of the complexity of the motions of the water and cyclohexanol. A thorough study of the dynamics could constitute an extremely interesting paper. Indeed, there may be analogous motions in solid cyclohexanol; from a 1H NMR study¹⁷ it was suggested that in one solid phase of $C_6H_{11}OH$ the COH unit is fixed and the C_6H_{11} unit rotates about the C-O bond.

Conclusion

This work is an excellent example of the complementary use of X-ray diffraction and solid-state NMR techniques, revealing

**Figure 8.** 2H NMR line shapes of $Cd_5(CN)_{10}(D_2O)_4 \cdot 4C_6H_{11}OD$ at various temperatures.

structural details in a material possessing both static and dynamic disorder. While the X-ray results provide information on the long-range order of the system, this must, by the nature of the technique, give a spatially averaged picture over the disorder present. The NMR results then provide a detailed picture of local structures without this averaging. The NMR also reveals dynamic processes which may or may not be evident from the X-ray results.

In the course of developing new materials with framework structures, many compounds that can accommodate guest molecules have been synthesized. In the next stages of this development, one desirable goal is to control the orientation and movement of guest molecules in a cavity in order to realize functions such as catalytic action, guest-host reaction, guest-guest reaction, and so on. In the previously known cadmium cyanide type clathrates, although the host complexes have large cavities, the guest molecules which occupy the cavities are either in a disordered state or are undergoing a large amplitude motion, and there seems to be no significant interaction between the host and the guest molecule. In contrast, the host structure of the new material $Cd_5(CN)_{10}(H_2O)_4 \cdot 4C_6H_{11}OH$ has not only a large cavity for accommodating a guest molecule but also a site where it interacts with the guest molecule by hydrogen bonding. This material thus points the way to formulating new materials with the desired properties, by making appropriate modifications to the cadmium cyanide complex.

Supplementary Material Available: Table S-I, listing final coordinates and isotropic temperature factors, Table S-II, listing anisotropic temperature factors (2 pages); Table S-III, listing observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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