J. Am. Chem. Soc. 1991, 113, 3045–3051

The Archetype for a New Class of Simple Extended 3D Honeycomb Frameworks. The Synthesis and X-ray Crystal Structures of $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^{1}/_{3}(C_6H_{12}N_4)$, $Cd(CN)_2\cdot{}^{1}/_{3}(C_6H_{12}N_4)$, and $Cd(CN)_2\cdot{}^{2}/_{3}H_2O\cdot tBuOH$ ($C_6H_{12}N_4$ = Hexamethylenetetramine) Revealing Two Topologically Equivalent but Geometrically Different Frameworks

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Abstract: This paper describes a new archetypal 3D framework with a honeycomb structure containing hexagonal channels, which provides a potentially useful model for the future construction of related materials with larger channels and with possible catalytic applications. Reaction between $Cd(CN)_2$ and hexamethylenetetramine provides two crystalline products, $Cd(CN)_2\cdot{}^{1}/_{3}(C_6H_{12}N_4)$ and $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^{1}/_{3}(C_6H_{12}N_4)$ ($C_6H_{12}N_4$ = hexamethylenetetramine), which have been studied by single-crystal X-ray diffraction. $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^{1}/_{3}(C_6H_{12}N_4)$: monoclinic, space group $P2_1/a$ (No. 14), $Z = 12$; $a = 11.358$ (2), $b = 12.619$ (2), $c = 12.366$ (2) Å; $\beta = 104.05$ (1)°; $R = 0.023$ and $R_w = 0.044$ for 4446 reflections with $I \geq 3\sigma(I)$. The extended 3D network consists of three types of Cd (6-coordinate, 5-coordinate, and intermediate between 4- and 5-coordinate) interconnected by μ_2-CN groups, μ_3-OH groups, and μ_2-$C_6H_{12}N_4$ units. A third N of each $C_6H_{12}N_4$ coordinates weakly to a Cd center that otherwise would be 4-coordinate and a fourth N is involved in H bonding to OH. $Cd(CN)_2\cdot{}^{1}/_{3}(C_6H_{12}N_4)$: orthorhombic, space group *Cmcm* (No. 63), $Z = 12$; $a = 21.274$ (4), $b = 7.782$ (1), $c = 13.272$ (5) Å; $R = 0.029$ and $R_w = 0.043$ for 1447 reflections with $I \geq 3\sigma(I)$. The structure consists of an infinite $[Cd(CN)_2]_n$ framework in which all Cd centers are coordinated by four μ_2-CN groups. The framework generates two sorts of channels running in the *b* direction; all the $C_6H_{12}N_4$ units are found in the smaller channels of roughly square cross section with all four N's coordinated to Cd's, while the larger channels of hexagonal cross section are vacant. Recrystallization of $Cd(CN)_2$ from aqueous tBuOH gives crystals of $Cd(CN)_2\cdot{}^{2}/_{3}H_2O\cdot tBuOH$, which have been studied by single-crystal X-ray diffraction: orthorhombic, space group *Amm*2 (No. 38), $Z = 6$; $a = 8.695$ (1), $b = 8.548$ (1), $c = 21.092$ (4) Å; $R = 0.033$ and $R_w = 0.044$ for 761 reflections with $I \geq 3\sigma(I)$. The $[Cd(CN)_2]_n$ network provides the first example of a new type of extended 3D structure that is particularly simple, consisting essentially of interconnected square-planar centers and tetrahedral centers in 1:2 proportions. The "square-planar" Cd's carry, in addition, two trans water ligands (which from the point of view of framework structure can be regarded as mere appendages), which project into hexagonal channels filled with disordered tBuOH. The $[Cd(CN)_2]_n$ frameworks in $Cd(CN)_2\cdot{}^{1}/_{3}(C_6H_{12}N_4)$ and $Cd(CN)_2\cdot{}^{2}/_{3}(H_2O)\cdot tBuOH$ are topologically identical (if the difference between the two ends of the cyano group is ignored) though, at first sight, geometrically very different. The geometrical relationship between the two frameworks is described in terms of sliding alternate hexagonal sheets of Cd's in the *bc* plane in $Cd(CN)_2\cdot{}^{2}/_{3}H_2O\cdot tBuOH$ in the *b* direction to generate the less regular arrangement seen in $Cd(CN)_2\cdot{}^{1}/_{3}(C_6H_{12}N_4)$.

Extended 3D framework structures consisting of rodlike units linked together in various ways may provide a new class of solids combining fundamental structural interest with potentially useful properties. They may, for example, afford zeolite-like materials with channels and cavities which, in principle, can be tailored and functionalized for specific catalytic applications.

Almost the simplest imaginable examples of this type are extended cyano–metal structures comprising interlinked MCNM rods. Prussian blue and related compounds have simple cubic arrangements of metal centers octahedrally surrounded by six cyanides, each of which forms a linear μ_2-bridge to another metal center.[1] Examples of frameworks constructed from tetrahedral metal centers linked together by linear cyanide bridges are provided by the isomorphous structures of $Zn(CN)_2$[2,3] and $Cd(CN)_2$,[3,4] which consist of two entirely independent but interpenetrating diamond-like frameworks.

Simple cyano–metal systems appear to us to have considerable value for exploratory studies of the scope for controlling the self-assembly of chosen components to yield desired 3D frameworks. As an early exercise in the deliberate manipulation of framework self-assembly we set ourselves the goal of generating a single, noninterpenetrating, diamond-like structure consisting of tetrahedral metal centers interconnected by linear cyanide bridges. One strategy explored was to attempt the construction of a negatively charged single diamond-like framework, effectively by substituting every other Zn^{2+} with Cu^+ in a $Zn(CN)_2$ array, the required counter cations being intended to make interpenetration sterically impossible. Space-filling considerations suggested that the NMe_4^+ cation would fit snugly into the adamantane-like cavities of a single framework and the overall framework charge was such that only alternate cavities would need to be occupied by cations. Under the most simple conditions, the bringing together in aqueous solution of the components Zn^{2+}, Cu^+, CN^-, and NMe_4^+ led to the spontaneous and selective self-assembly of the intended infinite array.[3] Since we embarked on these manipulative exercises with cyanide frameworks, a structure related to the one above in which CCl_4 molecules occupy the adamantane-like cavities of a single diamond-like $Cd(CN)_2$ framework has been described.[5]

Members of the family of frameworks consisting of a 3D pattern of 4-connected centers arranged in the manner of the nuclei in PtS[6] (equal numbers of square-planar and tetrahedral centers) and linked together by rods of various sorts provide especially

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0002-7863/91/1513-3045$02.50/0

attractive targets because of their intrinsic simplicity and very open channel structure. In an experiment closely similar to the generation of $[NMe_4][CuZn(CN)_4]$ above, an attempt was made to link together, via tetrahedral Cu^+ centers, the square-planar, stable, building block $Pt(CN)_4^{2-}$. The bringing together of Cu^+, $Pt(CN)_4^{2-}$, and NMe_4^+ led to the spontaneous self-assembly of the PtS-related $[CuPt(CN)_4]_n^{n-}$ framework as the NMe_4^+ derivative.[7] The present paper reports on some further manipulative exercises with cyanide frameworks.

Several facts suggest that the $Cd(CN)_2$ structure is not particularly stable. There is evidently considerably more empty space in the $Cd(CN)_2$ lattice than in the strictly isomorphous $Zn(CN)_2$ because the CdCNCd rod (length, 5.46 Å) is significantly longer than the ZnCNZn rod (length, 5.11 Å).[3] The average volume per atom is a "normal" 20.5 Å^3 in $Zn(CN)_2$ while that for $Cd(CN)_2$ is an "abnormally" large 25 Å^3. The relatively high thermal parameters observed for all the atoms in the X-ray structural analysis of $Cd(CN)_2$ are consistent with the notion that space is not efficiently occuped in this case.[3] In addition, while $Zn(CN)_2$ is practically insoluble in water, $Cd(CN)_2$ shows significant solubility (ca. 1.71 g mL^{-1}, 15 °C) and even has significant solubility in ethanol.[8] All of these pieces of evidence lead us to suspect that $Cd(CN)_2$ may be a material close to the borderline of stable existence and therefore may be particularly amenable to structural tinkering. The independent observation[5] of the single diamond-like $Cd(CN)_2$ framework with occluded CCl_4 supports this view. Presented below are examples of extended $[Cd(CN)_2]_n$ frameworks representing a new type of very simple 3D arrangement, which shows an interesting channel structure and which, we believe, is a significant addition to existing 3D structural archetypes.

Experimental Section

$Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ and $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$. A solution of sodium cyanide (1.00 g, 20 mmol) in water (10 mL) was added to a stirred solution of $Cd(NO_3)_2\cdot 4H_2O$ (3.09 g, 10 mmol) in water (20 mL). The milky suspension so formed was passed twice through a fluted filter paper and hexamethylenetetramine (4.02 g, 29 mmol) in water (10 mL) was added with stirring to the clear filtrate. The thick white suspension so formed was stirred for 5 min and the solid was collected, washed with water, and dried in vacuum at 100 °C. This material has composition consistent with the formulation $Cd(CN)_2\cdot{}^1/_2(C_6H_{12}N_4)$. Anal. Calcd for $C_5H_6N_4Cd$: C, 25.6; H, 2.6; N, 23.9. Found: C, 25.4; H, 2.7; N, 23.7. Highly crystalline samples of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ and $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$ were obtained from this material by the following technique, which we call "solution sublimation". We do not know whether this very simple procedure has been described and used previously, but we have found it very satisfactory for the production of crystals of a number of infinite framework materials of low solubility. The procedure is based on the principle that if a solid of poor solubility is suspended at the hotter end of a column of solvent upon which a temperature gradient is imposed, the small amount of material dissolved in the hotter solvent may be carried by convection to the colder regions where it may reprecipitate, with luck, in crystalline form. This is simply achieved by charging a small standard taper "cap" (B14 Quickfit, female) with ca. 0.2 g of the solid to be "sublimed" and attaching a B14 condenser with cold water passing through the jacket. With the assembly in a vertical position solvent is introduced down the inside of the condenser, care being taken not to disturb the solid at the bottom, until the interior of the condenser is filled. With the assembly in a vertical position the cap is then heated to just below the boiling point of the solvent and, with luck, crystals grow from the solution on the cooled walls of the condensor over a period of hours or days. When the above $Cd(CN)_2\cdot{}^1/_2(C_6H_{12}N_4)$ material is treated in this way with water as the solvent and with the cap heated on steam, crystals of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ essentially free of $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$ start to form after ~3 h. After 5–6 h a crop of essentially pure $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ can be collected. After ~6 h crystals of $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$ start to form at the expense of the initial $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$, which appears gradually to redissolve. After 24 h the "sublimate" is mainly $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$. The appearance of this hydroxy species is not surprising in view of the basicity of hexamethylenetetramine. After several days all the crystals redissolve and the white solid remaining in the cap is $Cd(OH)_2$. The two crystalline materials have very different densities (see crystallography section), and the mixture obtained at any stage in the sublimation may, after drying, be very simply and cleanly separated by adding 1,2-dibromoethane, which has an intermediate density, causing the crystals of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ to float and those of $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$ to sink. The separated solids were filtered from 1,2-dibromoethane, washed with petroleum ether (40–60 °C), and dried at 100 °C under vacuum. Anal. $(Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4))$ Calcd for $C_{12}H_{12}N_{10}Cd_3$: C, 22.7; H, 1.9; N, 22.1. Found: C, 22.7; H, 1.8; N, 22.0. Anal. $(Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4))$ Calcd for $C_{11}H_{13}N_9OCd_3$: C, 21.2; H, 2.1; N, 20.2. Found: C, 21.1; H, 1.9; N, 20.0.

$Cd(CN)_2\cdot{}^2/_3H_2O\cdot$tBuOH. Boiling tBuOH (20 mL) was added to a solution of $Cd(CN)_2$ (0.184 g) in boiling water (20 mL). The mixture was filtered while hot to remove a small quantity of precipitate and the filtrate set aside to cool and stand in an enclosed vessel. Over a period of several days brilliant colorless crystals of $Cd(CN)_2\cdot{}^2/_3H_2O\cdot$tBuOH separated. The crystals were collected, washed with 1:1 water–tBuOH, and dried in a stream of air at room temperature until a dry, free-running powder was obtained. Yield, 0.165 g. We have found it impossible to remove superficial liquid tBuOH without significant loss of tBuOH of crystallization. Anal. Calcd for $C_{5.32}H_{9.63}CdN_2O_{1.5}$ (i.e., $Cd(CN)_2\cdot 0.83C_4H_{10}O\cdot{}^2/_3H_2O$): C, 26.8; H, 4.1; N, 11.8. Found: C, 27.0; H, 4.0; N, 12.1.

X-ray Crystallography. Crystal structure analyses, using single-crystal X-ray diffraction methods were performed on $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$, $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$, and $Cd(CN)_2\cdot{}^2/_3H_2O\cdot$tBuOH. The details of the data collection and structure refinement for each compound are given in Table I. Accurate cell dimensions were obtained from the setting angles of 25 carefully centered reflections by using a least-squares procedure.[10] The intensity data were corrected for Lorentz, polarization, and absorption effects; absorption corrections[11,12a] were numerically evaluated by Gaussian integration to a precision of 0.5%. Crystallographic calculations were performed with the SHELX-76 system[11] on VAX 11/780 and VAX 11/8650 computers at the University of Melbourne. Crystallographic diagrams were obtained with the ORTEP program,[13] and with the exception of Figures 1b, 4, and 6, arbitrarily chosen isotropic thermal parameters have been employed in the representations of the atomic centers in the interests of clarity. Parameters for the atomic scattering curves of Cd were taken from ref 12b whereas for the remaining atoms those incorporated in the SHELX-76 system were used. Anomalous dispersion corrections were applied to the scattering factors of Cd. An analysis of variance at convergence for each crystal structure determination showed no special features. Specific details concerning the structure analysis of each compound are given in the following text.

(a) $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$. The symmetry of the diffraction spectra obtained from crystals of this compound shows them to be monoclinic with the systematic absences being consistent with the space group as $P2_1/a$. The structure was solved by a combination of direct methods[14] and difference maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. In the latter stages of the refinement all of the hydrogen atoms were clearly discernible in the difference maps. Those of the $C_6H_{12}N_4$ molecule were incorporated into the model at their calculated position and were assigned a common isotropic thermal parameter, which was included in the refinement. The coordinates of the hydroxyl hydrogen atom together with an isotropic thermal parameter, were also included in the refinement. The assignment of C and N to the atoms of each of the cyanide groups of the asymmetric unit was tested in turn by reversing the initial assignment and repeating the least-squares refinement until convergence had been achieved. In each case there were significant differences between the values of both R and R_w obtained for the two possible assignments, and the final assignment of C and N was made on the basis of that yielding the lower values for R and R_w. In each case this resulted in the Cd–C distance being shorter than that of the

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Table I. Crystal Data Together with Details of the Data Collections and Structure Refinements for $Cd(CN)_{5/3}\cdot(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$, $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$, and $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$

compd	$Cd(CN)_{5/3}\cdot(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$	$Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$	$Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$
formula	$C_{11/3}H_{13/3}CdN_3O_{1/3}$	$C_4H_4CdN_{10/3}$	$C_6H_{34/3}CdN_2O_{5/3}$
M_r	208.2	211.2	250.6
description of crystal	colorless	colorless	colorless
crystal system	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/a$ (No. 14)	*Cmcm* (No. 63)	*Amm*2 (No. 38)
a, Å	11.358 (2)	21.274 (4)	8.695 (1)
b, Å	12.619 (2)	7.782 (1)	8.548 (1)
c, Å	12.366 (2)	13.272 (5)	21.092 (4)
β, deg	104.05 (1)		
vol, $Å^3$	1719 (1)	2197 (2)	1568 (1)
Z	12	12	6
ρ(measd), g cm^{-3}	2.417	1.916	
ρ(calcd), g cm^{-3}	2.413	1.915	1.59
cryst dimens (distance from centroid), mm	±(001) 0.100 ±(11-1) 0.152 ±(-111) 0.238 (0-10) 0.212	±(001) 0.171 ±(010) 0.043 ±(102) 0.232 ±(10-2) 0.232	±(001) 0.079 ±(100) 0.079 ±(011) 0.129 (010) 0.143
temp, K	295 (1)	295 (1)	295 (1)
radiation and wavelength, Å	Mo Kα (graphite monochromator), λ = 0.71069		
instrument	Enraf-Nonius CAD-4F diffractometer		
no. of intens control reflctns	3 every 4800 s; no significant variation	3 every 4800 s; no significant variation	3 every 4800 s; no significant variation
F(000)	1176.0	1192.0	736.0
μ, cm^{-1}	36.6	28.6	20.2
transmssn factors			
min	0.286	0.411	0.726
max	0.552	0.783	0.760
2θ limits			
min	2.0	2.0	2.0
max	60.0	60.0	55.0
hkl range			
h	$-1 \rightarrow 16$	$-1 \rightarrow 10$	$-2 \rightarrow 11$
k	$-1 \rightarrow 17$	$-1 \rightarrow 30$	$0 \rightarrow 27$
l	$-17 \rightarrow 17$	$-1 \rightarrow 18$	$-11 \rightarrow 11$
no. of reflctns measd	6516	2370	2458
no. of unique reflctns	4986	1703	1049
R_{int}	0.021	0.014	0.014
no. of reflctns used	4446 [$I \geq 3\sigma(I)$]	1447 [$I \geq 3\sigma(I)$]	761 [$I \geq 3\sigma(I)$]
no. of params	223	86	85
refinement	full-matrix least squares; functions minimized $\sum w\Delta^2$ (SHELX-76)		
weighting scheme	$w = k/[\sigma_F^2 + g\lvert F_o\rvert^2]$		
final value of *k*	1.0	1.0	1.0
final value of *g*	1.0×10^{-2}	5.0×10^{-3}	8.0×10^{-4}
Final *R* [$=\sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$]	0.023	0.029	0.033
final R_w [$=(\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2)^{1/2}$]	0.044	0.043	0.044
max shift/esd	0.007	0.004	0.24
max resid electron density, e $Å^{-3}$	1.03 [0.74 Å from Cd(1)]	0.57	0.42

Cd–N, which strongly supports the C and N assignment reported here.

(b) $\mathbf{Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)}$. A crystal of this substance sealed in a Lindemann glass tube with some mother liquor yielded diffraction data possessing the Laue symmetry *mmm*, which showed the crystals to be orthorhombic. The systematic absences were consistent with the space groups *Cmcm*, *Cmc*2, and *C*2*cm*; *Cmcm* proved to be the correct space group. The structure was solved initially in *Cmcm* by using a combination of direct methods[14] and difference maps. Anisotropic thermal parameters were assigned to the non-hydrogen atoms. All of the hydrogen atoms were evident in the difference maps calculated at the latter stages of the refinement and these were included in the model at their calculated positions together with an overall isotropic thermal parameter. The atom assignment for each atom of the cyanide groups was tested as for the previous structure with a similar convincing result. Parallel refinements were carried out in each of the two possible noncentrosymmetric space groups; neither yielded a set of *R* and R_w values significantly different from those obtained for the centrosymmetric solution. For both noncentrosymmetric refinements there was marked correlation between many of the parameters and as well the anisotropic thermal parameters of a number of atoms converged to values that were found to be nonpositive definite. On this basis, *Cmcm* was taken to be the correct space group. Finally, there were no features in any of the difference maps to indicate that the crystal contained water of solvation, a result consistent with the measured density value.

(c) $\mathbf{Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH}$. A crystal of this compound was sealed in a Lindemann glass tube with a small volume of mother liquor. The crystal proved to be orthorhombic, with the only systematic absences in the diffraction data being those required by *A* centering; these features are consistent with the space group *Ammm*, *A*222, *A*2*mm*, *Am*2*m*, and *Amm*2. A solution of the structure was obtained in each of the space groups using a combination of direct methods,[14] Patterson synthesis,[14] and difference maps; all of the solutions possessed the essential features of the Cd–CN framework reported here.

The principle differences between the models concerned the assignment of the C and N atoms of the cyanide groups and the disorder required to describe the tBuOH molecules of solvation in each of the space groups. Solutions in the space groups *Ammm*, *A*222, and *A*2*mm* converged with significantly higher values for *R* and R_w than those for *Am*2*m* and *Amm*2, and in addition, each of the former three space groups required positional disorder for the C and N atoms of the cyanide units. Although the values of *R* and R_w resulting from the refinements in *Am*2*m* and *Amm*2 were not significantly different, the space group *Am*2*m* was rejected because it yielded a result with unreasonably asymmetric Cd–O distances about the octahedral Cd center. The solution resulting from *Amm*2 on the other hand produced reasonable dimensions and was consequently adopted as the true space group. Difference maps indicated the presence of three unique tBuOH molecules, each of which displayed positional disorder; those were included in the model with appropriate site occupation factors. Because of the marked pseudosymmetry of the structure, strong correlation occurred between the parameters of some of the atoms during the course of the refinement. This caused small oscillations of a number of parameters, which resulted in shift/esd values of >0.01. The atoms of the cyanide groups were affected and for this reason the C–N bond lengths were constrained to a common value, which was included in the refinement; at convergence this value was 1.1408 (8) Å. Anisotropic thermal parameters were applied to all

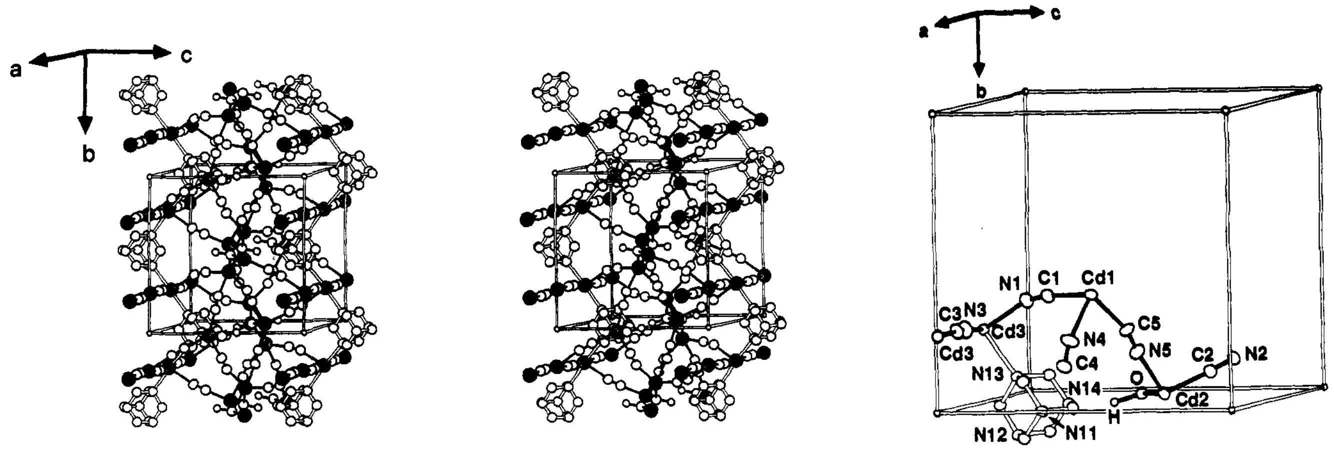

Figure 1. (a, left) Stereographic view of the structure of $\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$. The unit cell shown is centered about ($^1/_4$, $-^1/_2$, 0) and the metal atoms are indicated by filled black circles. (b, right) Atom numbering scheme for $\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$. The unit cell shown is as in (a) and the thermal boundary ellipsoids are at the 50% probability level.

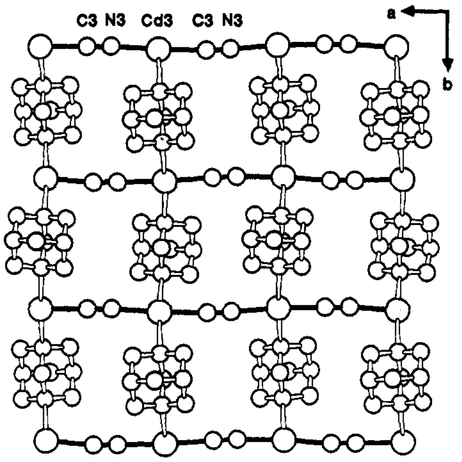

Figure 2. Structure of sheet A component of $\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$ viewed down the *c* axis. All metal atoms in sheet A are Cd(3) represented by the largest circles. The only cyanide groups present in sheet A are C(3), N(3).

non-hydrogen atoms except those of the tBuOH molecules. The C and O atoms of the tBuOH molecules were refined with a common isotropic thermal parameter applied to all the atoms of each molecule. Attempts to distinguish between the C and N atoms of the cyanide groups using the procedure in the analyses reported above were not conclusive. The cyanide atom that yielded the shorter Cd–cyanide distance was assigned as the C atom.

Results and Discussion

$\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$. Crystal data for $\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$ are given in Table I. A stereographic view of the structure including an indication of the unit cell is presented in Figure 1a and the atom numbering scheme is given in Figure 1b. Bond lengths and angles are given in Table II.

All cyano units bridge two metals. Three types of cadmium center are present. Hydroxy units are μ_3, bridging two Cd(1)'s and one Cd(2). In addition the OH is weakly hydrogen bonded to N(14) of hexamethylenetetramine (N···O 3.200 (3) Å, O–H···N angle 156.7 (2)°). All hexamethylenetetramine molecules are equivalent, being coordinated to two Cd(3)'s via N(12) and N(13) and to Cd(2) by a longer bond (2.795 (2) Å) via N(11). The environment of the remaining nitrogen N(14) has already been mentioned. Cd(1) is 5-coordinate, being bonded to two OH's; to two cyanides (via N(4) and C(5)), which bridge to two different Cd(2)'s; and to a third cyanide (via C(1)), which bridges to Cd(3). Cd(2) is intermediate between 4- and 5-coordinate, being bonded to one OH; to C(4) and N(5) of cyanides, which bridge to Cd(1)'s; and to C(2) of a cyanide, which bridges to Cd(3); the weak fifth coordinate bond is from hexamethylenetetramine N(11). Cd(3) is 6-coordinate, being bonded to two trans hexamethylenetetramine units (via N(12) of one and N(13) of the other); to C(3) and N(3) of two separate cyanides, which bridge to other Cd(3)'s; to N(2) of the cyano group, which bridges to Cd(2); and to N(1) of the cyano group, which bridges to Cd(1).

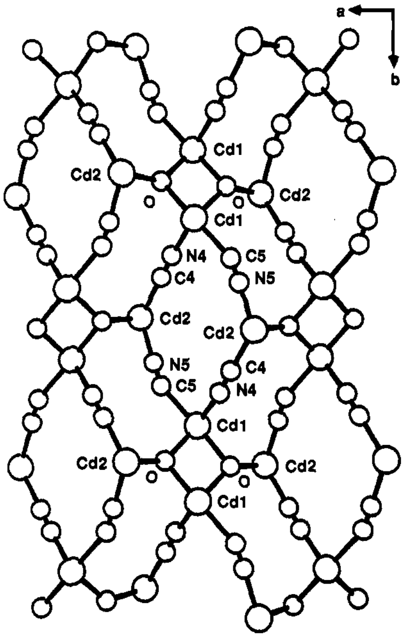

Figure 3. Structure of sheet B component of $\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$ viewed down the *c* axis. The only cyanide groups present in sheet B are C(4), N(4) and C(5), N(5). Sheets A and B are connected through the cyanide units C(1), N(1) and C(2), N(2).

The extended 3D structure is most simply described in terms of interconnected alternating sheets of the two types, A and B, shown in Figures 2 and 3, respectively. Sheets A contain an almost coplanar, approximately rectangular grid of Cd(3)'s. Within these sheets, along the *a* direction, lie almost linear chains of cyano-bridged Cd(3)'s. Metal centers in adjacent chains are bridged by hexamethylenetetramine (via N(12) and N(13)). Sheets B, which are puckered, contain Cd(1)'s, Cd(2)'s, OH's, and CN's arranged as shown in projection in Figure 3. Sheets A and B, whose mean planes lie parallel to *ab*, alternate throughout the structure and are bonded together by cyano bridges from the Cd(3)'s of sheet A to Cd(2) and Cd(1) of neighboring sheets B, by hydrogen bonding from the hexamethylenetetramine N(14) of sheets A to the OH's of sheets B, and by the weak coordinate interaction between the hexamethylenetetramine N(11) of sheets A and Cd(2) of sheets B.

$\mathrm{Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)}$. Crystal data for $\mathrm{Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)}$ obtained from a crystal sealed with mother liquor in a Lindemann glass tube are given in Table I. The atom numbering

Table II. Interatomic Distances and Angles for $\mathrm{Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)}$[a]

Distances, Å			
Cd(1)–C(1)	2.231 (2)	N(2)–C(2)	1.144 (3)
Cd(1)–C(5)	2.222 (2)	N(3)–C(3)	1.155 (3)
Cd(1)–N(4)	2.450 (2)	N(4)–C(4)	1.133 (3)
Cd(1)–O$^{\mathrm{I}}$	2.185 (1)	N(5)–C(5)	1.134 (3)
Cd(1)–O$^{\mathrm{II}}$	2.396 (1)	N(11)–C(15)	1.474 (3)
Cd(2)–C(2)	2.195 (2)	N(11)–C(16)	1.458 (3)
Cd(2)–C(4)$^{\mathrm{III}}$	2.213 (2)	N(11)–C(20)	1.453 (3)
Cd(2)–N(5)	2.245 (2)	N(12)–C(17)	1.471 (3)
Cd(2)–O	2.302 (1)	N(12)–C(18)	1.473 (3)
Cd(2)–N(11)$^{\mathrm{III}}$	2.795 (2)	N(12)–C(20)	1.490 (3)
Cd(3)–C(3)$^{\mathrm{IV}}$	2.257 (2)	N(13)–C(15)	1.485 (3)
Cd(3)–N(1)	2.370 (2)	N(13)–C(17)	1.477 (3)
Cd(3)–N(2)$^{\mathrm{V}}$	2.349 (2)	N(13)–C(19)	1.490 (3)
Cd(3)–N(3)	2.275 (2)	N(14)–C(16)	1.485 (3)
Cd(3)–N(12)$^{\mathrm{IV}}$	2.481 (1)	N(14)–C(18)	1.467 (3)
Cd(3)–N(13)	2.454 (2)	N(14)–C(19)	1.470 (3)
N(1)–C(1)	1.144 (3)	N(14)···O	3.200 (3)
Angles, deg			
C(1)–Cd(1)–C(5)	110.3 (1)	C(2)–Cd(2)–O	104.6 (1)
C(1)–Cd(1)–N(4)	89.8 (1)	C(2)–Cd(2)–N(11)$^{\mathrm{III}}$	91.5 (1)
C(1)–Cd(1)–O$^{\mathrm{I}}$	120.5 (1)	C(4)$^{\mathrm{III}}$–Cd(2)–N(5)	126.8 (1)
C(1)–Cd(1)–O$^{\mathrm{II}}$	98.7 (1)	C(4)$^{\mathrm{III}}$–Cd(2)–O	91.4 (1)
C(5)–Cd(1)–N(4)	82.2 (1)	C(4)$^{\mathrm{III}}$–Cd(2)–N(11)$^{\mathrm{III}}$	79.4 (1)
C(5)–Cd(1)–O$^{\mathrm{I}}$	129.2 (1)	N(5)–Cd(2)–O	98.6 (1)
C(5)–Cd(1)–O$^{\mathrm{II}}$	94.3 (1)	N(5)–Cd(2)–N(11)$^{\mathrm{III}}$	76.9 (1)
N(4)–Cd(1)–O$^{\mathrm{I}}$	96.3 (1)	O–Cd(2)–N(11)$^{\mathrm{III}}$	163.7 (1)
N(4)–Cd(1)–O$^{\mathrm{II}}$	171.5 (1)	Cd(1)$^{\mathrm{IV}}$–O–Cd(1)$^{\mathrm{VII}}$	100.1 (0)
O$^{\mathrm{I}}$–Cd(1)–O$^{\mathrm{II}}$	79.9 (0)	Cd(1)$^{\mathrm{IV}}$–O–Cd(2)	129.8 (1)
C(2)–Cd(2)–C(4)$^{\mathrm{III}}$	129.6 (1)	Cd(1)$^{\mathrm{VII}}$–O–Cd(2)	106.3 (0)
C(2)–Cd(2)–N(5)	98.0 (1)	C(3)$^{\mathrm{IV}}$–Cd(3)–N(1)	95.0 (1)
C(3)$^{\mathrm{IV}}$–Cd(3)–N(2)$^{\mathrm{V}}$	95.9 (1)	C(16)–N(11)–C(20)	109.4 (2)
C(3)$^{\mathrm{IV}}$–Cd(3)–N(3)	176.6 (1)	C(17)–N(12)–C(18)	108.4 (2)
C(3)$^{\mathrm{IV}}$–Cd(3)–N(12)$^{\mathrm{VI}}$	89.0 (1)	C(17)–N(12)–C(20)	107.8 (2)
C(3)$^{\mathrm{IV}}$–Cd(3)–N(13)	88.0 (1)	C(18)–N(12)–C(20)	107.4 (1)
N(1)–Cd(3)–N(2)$^{\mathrm{V}}$	168.6 (1)	C(15)–N(13)–C(17)	107.7 (2)
N(1)–Cd(3)–N(3)	82.5 (1)	C(15)–N(13)–C(19)	107.7 (2)
N(1)–Cd(3)–N(12)$^{\mathrm{VI}}$	99.5 (1)	C(17)–N(13)–C(19)	107.6 (2)
N(1)–Cd(3)–N(13)	86.6 (1)	C(16)–N(14)–C(18)	108.4 (2)
N(2)$^{\mathrm{V}}$–Cd(3)–N(3)	86.8 (1)	C(16)–N(14)–C(19)	107.0 (2)
N(2)$^{\mathrm{V}}$–Cd(3)–N(12)$^{\mathrm{VI}}$	84.2 (1)	C(18)–N(14)–C(19)	107.7 (2)
N(2)$^{\mathrm{V}}$–Cd(3)–N(13)	90.2 (1)	N(11)–C(15)–N(13)	111.6 (2)
N(3)–Cd(3)–N(12)$^{\mathrm{VI}}$	89.2 (1)	N(11)–C(16)–N(14)	112.2 (2)
N(3)–Cd(3)–N(13)	94.0 (1)	N(12)–C(17)–N(13)	112.4 (2)
N(12)$^{\mathrm{VI}}$–Cd(3)–N(13)	173.4 (1)	N(12)–C(18)–N(14)	112.8 (2)
Cd(1)–C(1)–N(1)	171.2 (2)	N(13)–C(19)–N(14)	112.8 (2)
Cd(1)–N(4)–C(4)	157.5 (2)	N(11)–C(20)–N(12)	111.9 (2)
Cd(1)–C(5)–N(5)	160.5 (2)	Cd(2)$^{\mathrm{III}}$–N(11)–C(15)	108.2 (1)
Cd(2)–C(2)–N(2)	173.9 (2)	Cd(2)$^{\mathrm{III}}$–N(11)–C(16)	110.3 (2)
Cd(2)–C(4)$^{\mathrm{III}}$–N(4)$^{\mathrm{III}}$	177.3 (2)	Cd(2)$^{\mathrm{III}}$–N(11)–C(20)	111.8 (1)
Cd(2)–N(5)–C(5)	174.2 (2)	Cd(3)$^{\mathrm{VI}}$–N(12)–C(17)	105.7 (1)
Cd(3)–N(1)–C(1)	157.2 (2)	Cd(3)$^{\mathrm{VI}}$–N(12)–C(18)	117.0 (1)
Cd(3)–N(2)$^{\mathrm{V}}$–C(2)$^{\mathrm{V}}$	163.1 (2)	Cd(3)$^{\mathrm{VI}}$–N(12)–C(20)	110.1 (1)
Cd(3)–C(3)$^{\mathrm{IV}}$–N(3)$^{\mathrm{IV}}$	176.0 (2)	Cd(3)–N(13)–C(15)	109.7 (1)
Cd(3)–N(3)–C(3)	176.2 (2)	Cd(3)–N(13)–C(17)	110.1 (1)
C(15)–N(11)–C(16)	108.4 (2)	Cd(3)–N(13)–C(19)	113.8 (1)
C(15)–N(11)–C(20)	108.7 (2)		

[a] Superscripts refer to the transformations: (I) $^1/_2 + x, -^1/_2 - y, z$; (II) $^1/_2 - x, -^1/_2 + y, -z$; (III) $1 - x, -y, -z$; (IV) $-^1/_2 + x, -^1/_2 - y, z$; (V) $x, y, -1 + z$; (VI) $^1/_2 - x, -^1/_2 + y, -1 - z$; (VII) $^1/_2 - x, ^1/_2 + y, -z$; (VIII) $^1/_2 - x, ^1/_2 + y, -1 - z$.

scheme and unit cell are represented in Figure 4; Table III provides bond lengths and angles.

All cadmium centers are attached to four cyanides and all cyanides bridge two cadmiums. The cadmium centers are of two types. Cd(1) is in a very distorted 5-coordinate environment consisting of two cyanide C(2)'s, one cyanide C(1), one cyanide N(1), and one hexamethylenetetramine nitrogen N(12). The coordination environment of Cd(2) is distorted octahedral consisting of four cyanide N(2)'s in an approximately square arrangement together with two trans hexamethylenetetramine units bound via their N(11)'s. Cyanides are of two types, namely, Cd(2) N(2) C(2) Cd(1) and Cd(1) N(1) C(1) Cd(1). All the hexamethylenetetramine units are equivalent, acting as μ_4-bridging agents; two equivalent N(11) donors are each bound to a Cd(2) at 2.494 (4) Å and two equivalent N(12) donors are each bound somewhat weakly to a Cd(1) at 2.750 (4) Å.

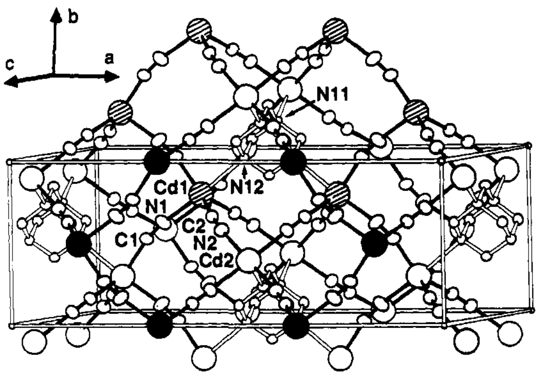

Figure 4. Structure of $\mathrm{Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)}$ and atom numbering scheme. Thermal boundary ellipsoids, at the 50% probability level, are shown only for the C and N atoms. The unit cell shown is centered about ($^1/_2$, 0.122, $-^1/_4$), its location being chosen to emphasize the hexagonal arrangement of Cd(1) atoms. Six such Cd(1) centers in the front face of the cell ($c = {}^1/_4$) are indicated by filled black circles. Six similarly arranged Cd centers from an adjacent sheet, indicated by hatched circles, are found in a plane parallel to *ab* ($c = -^1/_4$) passing through the midpoint of the cell. For clarity only selected hexamethylenetetramine units are shown. The unit cell including all hexamethylenetetramine is provided with the supplementary data.

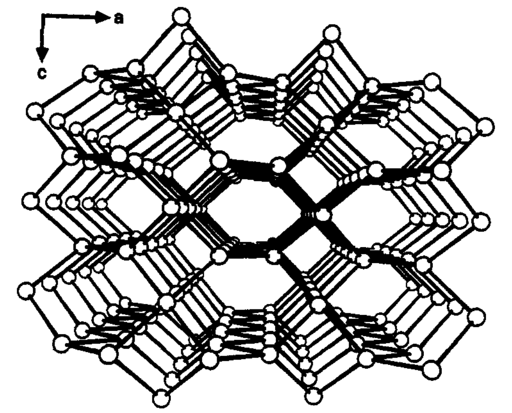

Figure 5. $\mathrm{[Cd(CN)_2]_n}$ framework of $\mathrm{Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)}$ viewed in perspective down the *b* axis. Only Cd centers are shown. All the hexamethylenetetramine units are located in the channels of roughly square cross section. The larger channels of hexagonal cross section are vacant.

Table III. Interatomic Distances and Angles for $\mathrm{Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)}$[a]

Distances, Å			
Cd(1)–C(1)$^{\mathrm{I}}$	2.166 (5)	C(1)–N(1)	1.137 (8)
Cd(1)–C(2)	2.233 (3)	C(2)–N(2)	1.132 (5)
Cd(1)–N(1)	2.302 (6)	N(11)–C(12)	1.480 (3)
Cd(1)–N(12)	2.750 (4)	N(11)–C(13)	1.483 (4)
Cd(2)–N(2)	2.313 (4)	N(12)–C(11)	1.474 (5)
Cd(2)–N(11)$^{\mathrm{II}}$	2.494 (4)	N(12)–C(12)	1.470 (3)
Angles, deg			
C(1)$^{\mathrm{I}}$–Cd(1)–C(2)	128.6 (1)	N(2)–Cd(2)–N(11)$^{\mathrm{II}}$	89.6 (1)
C(1)$^{\mathrm{I}}$–Cd(1)–N(1)	90.7 (2)	N(11)$^{\mathrm{II}}$–Cd(2)–N(11)$^{\mathrm{VII}}$	180.0 (-)
C(1)$^{\mathrm{I}}$–Cd(1)–N(12)	84.8 (2)	Cd(2)–N(2)–C(2)	167.2 (3)
C(2)–Cd(1)–C(2)$^{\mathrm{III}}$	100.0 (1)	C(12)–N(11)–C(12)$^{\mathrm{VI}}$	108.4 (2)
C(2)–Cd(1)–N(1)	98.6 (1)	C(12)–N(11)–C(13)	107.4 (2)
C(2)–Cd(1)–N(12)	84.3 (1)	C(11)–N(12)–C(12)	107.9 (2)
N(1)–Cd(1)–N(12)	175.6 (2)	C(12)–N(12)–C(12)$^{\mathrm{III}}$	108.7 (2)
Cd(1)–C(1)$^{\mathrm{I}}$–N(1)$^{\mathrm{I}}$	167.7 (5)	N(12)–C(11)–N(12)$^{\mathrm{VI}}$	112.7 (3)
Cd(1)–N(1)–C(1)	171.5 (5)	N(12)–C(12)–N(11)	112.3 (3)
Cd(1)–C(2)–N(2)	166.6 (3)	N(11)–C(13)–N(11)$^{\mathrm{III}}$	113.0 (3)
N(2)–Cd(2)–N(2)$^{\mathrm{IV}}$	180.0 (-)	Cd(2)–N(11)$^{\mathrm{II}}$–C(12)$^{\mathrm{II}}$	110.2 (2)
N(2)–Cd(2)–N(2)$^{\mathrm{V}}$	92.2 (1)	Cd(2)–N(11)$^{\mathrm{II}}$–C(13)$^{\mathrm{II}}$	113.1 (2)
N(2)–Cd(2)–N(2)$^{\mathrm{VI}}$	87.8 (1)	Cd(1)–N(12)–C(11)	107.0 (2)
N(2)–Cd(2)–N(11)$^{\mathrm{VII}}$	90.4 (1)	Cd(1)–N(12)–C(12)	112.6 (2)

[a] Superscripts refer to the transformations: (I) $^1/_2 - x, ^1/_2 + y, z$; (II) $x, -1 + y, -^1/_2 - z$; (III) $x, y, -^1/_2 - z$; (IV) $1 - x, -y, -z$; (V) $x, -y, -z$; (VI) $1 - x, y, z$; (VII) $1 - x, 1 - y, ^1/_2 + z$.

One representation of the extended 3D $\mathrm{[Cd(CN)_2]_n}$ framework, viewed along the *b* axis, is given in Figure 5, in which two sorts

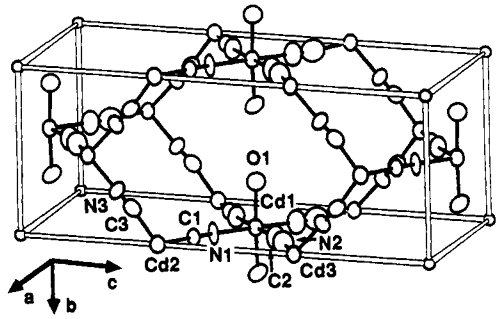

Figure 6. Unit cell of $Cd(CN)_2 \cdot {}^2/_3H_2O \cdot tBuOH$ and atom numbering scheme. The thermal boundary ellipsoids are at the 50% probability level. tBuOH, which is disordered, is omitted for clarity. The Cd(1) indicated at the midpoint of the bottom face lies at the origin.

Table IV. Interatomic Distances and Angles for $Cd(CN)_2 \cdot {}^2/_3H_2O \cdot tBuOH^{a,b}$

	Distances, Å		
Cd(1)···Cd(2)	5.566 (1)	Cd(1)···Cd(3)	5.602 (1)
Cd(2)···Cd(3)^{I}	5.548 (2)	Cd(2)^{IV}···Cd(3)^{I}	14.083 (3)
Cd(1)···Cd(1)^{II}	8.548 (1)	Cd(1)–N(1)	2.281 (7)
Cd(1)–C(2)	2.170 (9)	Cd(2)–C(1)	2.161 (7)
Cd(2)–C(3)	2.170 (8)	Cd(3)–N(2)	2.326 (8)
Cd(3)–N(3)^{III}	2.244 (7)	Cd(1)–O(1)	2.330 (5)
	Angles, deg		
N(1)–Cd(1)–C(2)	89.9 (3)	N(1)–Cd(1)–N(1)^{V}	92.5 (3)
N(1)–Cd(1)–O(1)	91.4 (3)	N(1)–Cd(1)–C(2)^{V}	177.6 (3)
C(2)–Cd(1)–C(2)^{V}	87.7 (3)	C(2)–Cd(1)–O(1)	88.6 (3)
O(1)–Cd(1)–O(1)^{V}	176.1 (5)	C(1)–Cd(2)–C(3)	109.1 (2)
C(1)–Cd(2)–C(1)^{VI}	111.8 (3)	C(3)–Cd(2)–C(3)^{VI}	108.5 (4)
N(2)–Cd(3)–N(3)^{III}	110.9 (2)	N(2)–Cd(3)–N(2)^{VI}	114.9 (3)
N(3)^{III}–Cd(3)–N(3)^{VII}	96.7 (3)	Cd(1)–N(1)–C(1)	173.3 (7)
N(1)–C(1)–Cd(2)	177.0 (7)	Cd(1)–C(2)–N(2)	172.9 (8)
C(2)–N(2)–Cd(3)	173.5 (8)	Cd(2)–C(3)–N(3)	172.8 (8)
C(3)–N(3)–Cd(3)^{I}	178.7 (7)		

[a] Superscripts refer to the transformations: (I) $x, -{}^1/_2 + y, -{}^1/_2 + z$; (II) $x, -1 + y, z$; (III) $x, {}^1/_2 + y, {}^1/_2 + z$; (IV) $x, -{}^1/_2 + y, {}^1/_2 + z$; (V) $-x, -y, z$; (VI) $1 - x, -y, z$; (VII) $x, -{}^1/_2 - y, {}^1/_2 + z$. [b] C–N distances constrained to a common value (1.1408 (8) Å); see text.

of channels can be seen, one of hexagonal cross section, the other of square cross section. The hexamethylenetetramine units are all found in the smaller square channels while the larger hexagonal channels are vacant. Inspection of the relative sizes of the two sorts of channels in Figure 5, bearing in mind that molecules as bulky as $C_6H_{12}N_4$ can be accommodated in the smaller ones (admittedly by forming coordinate bonds to the cadmiums lining the channel), emphasises how remarkable it is that the larger channels do not contain water, the solvent from which the crystals grew. An earlier preliminary X-ray examination of a dry crystal of $Cd(CN)_2 \cdot {}^1/_3(C_6H_{12}N_4)$ mounted in air had indicated the presence of these channels. The complete X-ray analysis described here on a crystal kept moist throughout and sealed with mother liquor in a Lindemann glass tube was carried out with the express purpose of checking the possibility that the crystals had initially grown with water in the channels, which was subsequently lost. The results leave no doubt the hexagonal channels are vacant. We have observed similar behavior to this with $[N(CH_3)_4][CuZn(CN)_4]$[3] and $[N(CH_3)_4][CuPt(CN)_4]$,[7] both of which were crystallized from aqueous solution, the first having large vacant adamantane-like cavities, the second, vacant channels of large square cross section.

$Cd(CN)_2 \cdot {}^2/_3H_2O \cdot tBuOH$. Crystal data are given in Table I. The orthorhombic unit cell and atom numbering scheme are presented in Figure 6; structural parameters are given in Table IV. A brief preliminary description of this structure has already been published.[9]

All cadmium centers are attached to four cyanides and every cyanide bridges two cadmiums. There are minor deviations from linearity within the CdCNCd systems. Three types of cadmium center are present. Cd(1) has an octahedral coordination environment consisting of two cis cyanide nitrogens, two cis cyanide carbons, and two trans water ligands. Cd(2) and Cd(3) are in nonregular tetrahedral environments of four cyanide carbons and four cyanide nitrogens, respectively. Bond distances are unexceptional and the assignments of cyanide carbons and nitrogens (Experimental Section) are consistent with the general view that in structures involving MCNM interactions the MC bonds tend to be shorter than the MN bonds.

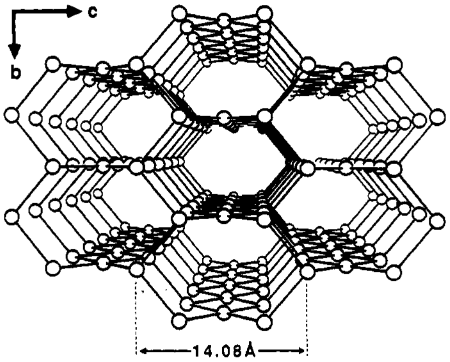

Figure 7. Perspective view of $[Cd(CN)_2]_n$ framework in $Cd(CN)_2 \cdot {}^2/_3H_2O \cdot tBuOH$ down the *a* axis. Only the Cd centers are shown.

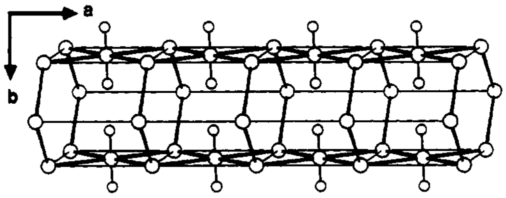

Figure 8. Side view of a single hexagonal channel (with axis parallel to *a*) in $Cd(CN)_2 \cdot {}^2/_3H_2O \cdot tBuOH$. Only Cd and O (of H_2O) atoms are shown.

One view of the extended 3D $[Cd(CN)_2]_n$ framework (along the *a* axis) is presented in Figure 7. In planes parallel to *bc* are sheets of cadmium atoms (Cd(2) and Cd(3) in equal numbers) arranged in a hexagonal pattern resembling the arrangement of carbon atoms in the sheets of graphite, but somewhat elongated in the *c* direction. The hexagonal sheets are stacked in such a way that all the cadmium centers are found on lines parallel to the *a* axis. This generates infinite linear channels of large hexagonal cross section running perpendicular to the sheets. In Figure 7 we are looking directly down the channels; in Figure 8 is provided a side-view of one channel. Hexagonal groups of three Cd(2) and three Cd(3) (which alternate within the group) perpendicular to the channel axis and appearing at intervals of 8.695 (1) Å (the unit cell edge *a*) define the dimensions of the channel and can be clearly seen in Figures 7 and 8. The largest Cd···Cd diagonal within a hexagonal group is 14.08 Å. The face-to-face Cd(1)···Cd(1) separation across the channel is 8.548 (1) Å. Molecules of tBuOH disordered over a number of crystallographic sites occupy the channels into which project water molecules coordinated to Cd(1).

To the best of our knowledge the structure of $Cd(CN)_2 \cdot {}^2/_3H_2O \cdot tBuOH$ provides the first example of a new type of 3D 4-connected net of appealing simplicity comprising tetrahedral and square-planar centers in 2:1 proportions. We consider this new 3D pattern to possess some fundamental significance in the area of the geometry of extended structures, deserving a place in the company of such classical, structural archetypes as NaCl, CsCl, diamond, etc. We have put forward the proposition that a number of simple 3D structures (e.g., diamond, Lonsdaleite, PtS, α-polonium) can be regarded as prototypes or models on the basis of which related but more elaborate frameworks of great structural interest and potential usefulness can be designed and deliberately constructed. The 3D net described here could possibly be put to similar use as the basis for the design and construction of a whole family of unusual materials, e.g., solids in which the planar ribbons of edge-shared square units apparent in Figures

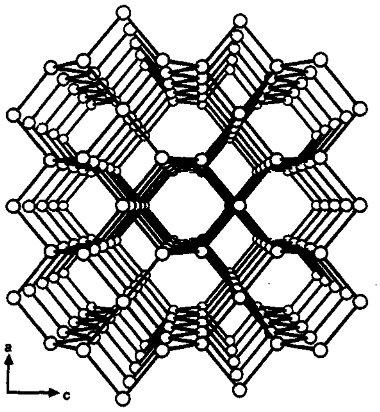

Figure 9. Perspective view of $[Cd(CN)_2]_n$ framework in $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ down the *b* axis. Only Cd centers are shown.

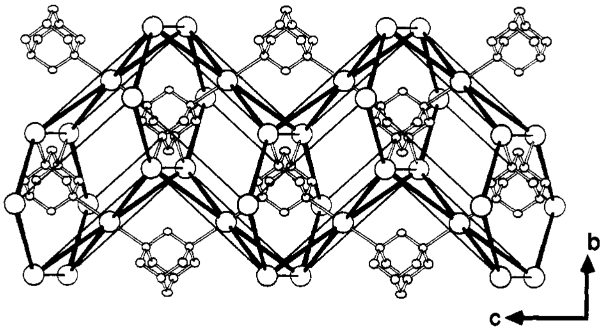

Figure 10. Side view of a single zig-zag hexagonal channel in $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ analogous to the single linear channel in $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$, a similar side view of which is shown in Figure 8. Comparison of the two reveals their geometrical interrelationship and how the deformation allows each hexamethylenetetramine unit to coordinate to four Cd centers.

7 and 8 have been replaced by banks of coplanar porphyrins or similar platelike building blocks; such materials may have extraordinary chemical and physical properties.

Geometrical and Topological Relationship of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ and $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$. The infinite 3D $[Cd(CN)_2]_n$ frameworks of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ and $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ appear at first sight to have little in common. However, if one sets aside the difference between the two ends of a cyanide unit and focuses attention on the cadmium centers and their connectivities it is apparent that the two are topologically identical. The geometrical relationship of the two frameworks becomes apparent after comparison of the views along the *b* axes, which are represented in Figures 5 and 9. The apparently close similarity revealed here is somewhat misleading because the counterpart in Figure 5 of the coplanar strips of edge-shared squares running in the *a* direction in Figure 9 is pronouncedly corrugated (dihedral angle between one $Cd(Cd)_4$ plane and each of its two near-neighbors, 83.1°); viewed from above, as it is in Figure 5, this corrugation is appreciated only after close inspection. Two questions immediately arise: what sort of geometrical transformation is required (in principle) to convert the framework in $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ into the topologically equivalent but geometrically much less regular one in $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ without breaking any connections and what has happened in the second of these to the large linear hexagonal channels apparent along the *a* direction in the first? The geometrical relationship between the two framework structures can be appreciated by comparing the unit cell of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ in Figure 4 with two unit cells of $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ (Figure 6) sharing a *bc* face. If one imagines sliding the sheet containing the six Cd's in the shared *bc* face in this latter case in the $-b$ direction, while holding unmoved the sheets of Cd's in the front and back faces and while maintaining all Cd···Cd connections, one generates the framework arrangement found in Figure 4. The relationship of the two frameworks can be very clearly seen by considering the consequences to the linear hexagonal channels of $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ of the shearing described above. Sliding alternate hexagonal sheets in opposite directions along the *b* axis transforms the linear channels of $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ seen in side view in Figure 8 into the zig-zag channel seen from a similar angle in Figure 10. This distortion of the framework allows all four nitrogen donors of each hexamethylenetetramine unit to form coordinate bonds to metal centers, two to Cd(2)'s (2.494 (4) Å) and two weaker bonds to Cd(1)'s (2.750 (4) Å).

Acknowledgment. It is with special pleasure that we acknowledge support from the Selby Scientific Foundation.

Registry No. $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$, 131729-27-6; $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$, 131729-28-7; $Cd(CN)_2\cdot{}^2/_3H_2O\cdot t\text{-}BuOH$, 127105-34-4.

Supplementary Material Available: Figure S1 depicting the unit cell of $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$ showing all the $C_6H_{12}N_4$ units and Tables S-I and S-IIa,b listing thermal parameters, non-hydrogen atom and hydrogen atom coordinates for $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$ and Tables S-III and S-IVa,b listing similar data for $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$, and Table S-Va,b listing the atomic coordinates and thermal parameters for $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ (8 pages); Tables S-VI–S-VIII listing observed and calculated structure factors for $Cd(CN)_{5/3}(OH)_{1/3}\cdot{}^1/_3(C_6H_{12}N_4)$, $Cd(CN)_2\cdot{}^1/_3(C_6H_{12}N_4)$, and $Cd(CN)_2\cdot{}^2/_3H_2O\cdot tBuOH$ (44 pages). Ordering information is given on any current masthead page.