

Synthesis and Crystal Structure of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$

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Single crystals of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ have been synthesized and characterized by single-crystal X-ray diffraction. The crystallographic data are as follows: orthorhombic space group $Pnma$, $a = 12.393(2) \text{ \AA}$, $b = 14.278(5) \text{ \AA}$, $c = 7.427(1) \text{ \AA}$, $Z = 4$; $R = 0.033$, $wR = 0.042$ for 949 reflections. This material is similar to the Hofmann-type clathrates; it is structurally composed of two-dimensional sheets of alternating square planar and octahedrally coordinated metal atoms bridged by cyanide ligands. However, unlike Hofmann-type clathrates for which structures have been reported, this material does not contain ammonia, amines, or a clathrated aromatic molecule between the metal tetracyanonickelate sheets. Instead, the interlayer regions are filled by a distorted hexagonal hydrogen-bonded net of water molecules. © 1993 Academic Press, Inc.

Introduction

The Hofmann-type clathrate materials have enjoyed recurring interest since the discovery of $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ by Hofmann in 1897 (1). The main interest in these materials has stemmed from their ability to trap aromatic hydrocarbons of specific size within the cavities between the planar nickel cyanide sheets. This trapping can be quite selective; indeed, a patent has been issued for the use of this material in purifying benzene from hydrocarbon feedstocks (2).

The dominant structural feature of these materials is a two-dimensional sheet formed from square planar nickel atoms linked to an octahedral metal center by cyanide bridges; the carbon atom of the cyanide is bound to the square-planar nickel atom and the nitrogen atom to the octahedral metal center (3). The axial positions of the octahedral divalent metal center are occupied by ammonia in most of the previously studied

compounds. Extensive work was done in the late 1960s and early 1970s to investigate substitution of different metals for the square-planar and octahedral nickel centers in the original material. These studies showed that Ni, Pd, or Pt can be introduced on the square-planar site and Mn, Fe, Co, Ni, Cu, Zn, and Cd on the octahedral metal site (4). Further, the ammonia can be replaced by amines or diamines; the latter serve to covalently link the metal tetracyanonickelate layers together (4-10).

We have recently become interested in these materials and their covalently linked sheet structures for use in self-assembled multilayer syntheses analogous to the zirconium-bisphosphonate systems investigated by Mallouk for this purpose (11, 12). During our investigations of bulk Hofmann-type clathrate materials, crystals of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ suitable for X-ray crystallography were prepared, and the structure is reported here. This is the first single-crystal study of a metal tetracyanonickelate(II) hydrate which does not contain ammonia or amines, and it is the first to report the positions of the water molecules

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between the metal tetracyanonickelate(II) sheets.

Experimental

Synthesis

Crystals of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ were grown by two methods outlined below.

(1) The first method follows the procedure of Robson *et al.* (13, 14). CdCl_2 and $\text{K}_2\text{Ni}(\text{CN})_4$ in a 1 : 1 molar ratio were mixed in water to form a yellowish powder. The powder was separated and dried and 0.03 g of this sample was placed in an 80-cm pyrex tube (13-mm outside diameter) which was carefully filled with distilled water to keep the powder in the bottom of the tube. The lower end was placed in a steam bath and heated. Crystals grew as plates at the upper, cooler end of the tube over the period of days.

The tube which gave the best crystals for crystallography was also charged with 0.006 g of *trans*-1,4-diaminocyclohexane. In this case the crystals formed lower in the tube and had a long prismatic shape. These crystals did not form twins as readily as the plate-like crystals grown without the *trans*-1,4-diaminocyclohexane.

(2) Crystals can also be grown by dissolving 0.035 g of (tetrabutyl ammonium)₂- $\text{Ni}(\text{CN})_4$ in 10 ml of methylene chloride and then placing a layer of aqueous CdCl_2 (0.006 g in 10 ml of water) on top of the methylene chloride solution and leaving in a sealed vial for weeks. The crystals grow as tablets at the liquid-liquid junction.

Crystallographic data are reported for crystals grown by the first method in the presence of *trans*-1,4-diaminocyclohexane. Powder X-ray diffraction of crystals grown by the first method without the diamine and unit cell indexing of a single crystal prepared by the second route confirm that the structures of crystals prepared by these different methods are identical.

X-ray Diffraction

Clear, colorless crystals were mounted on glass fibers. An unprotected crystal decomposed abruptly in the X-ray beam during data collection, but a crystal protected by a thin coat of diluted polystyrene cement remained stable. Data were collected by use of an Enraf-Nonius CAD4 diffractometer after determination of the orientation matrix and cell dimensions from the setting angles of 25 reflections in the range $6.3^\circ \leq \theta \leq 11.7^\circ$. Table I contains a summary of crystallographic information and details of data collection and structure refinement. Further details are given in the supplementary material.¹ The PHASE program incorporated in DIRDIF (15) showed the positions of the Cd and Ni atoms, the water O atom on Cd, and the two independent CN groups. Other water O atoms were located by a difference synthesis. An empirical absorption correction (DIFABS) (16) based on the isotropically-refined structure was applied. Peaks possibly corresponding to five of the six independent H atoms were apparent in the final difference synthesis. They were not included in the refined model because they had intensities ($0.3\text{--}0.5 \text{ e } \text{\AA}^{-3}$) similar to that of the stronger background peaks, and more than one set of positions for H atoms was consistent with the evident hydrogen-bond network. Inclusion of the secondary extinction parameter in the refinement gave no improvement in the residuals or standard deviations; therefore, results presented do not include a refined secondary extinction parameter. The TEXSAN program system (17), incorporating standard atomic scattering factors (18), was used in all calculations.

Results

Projections of the unit cell of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ are shown in

¹ See NAPS document No. 05031 for 17 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid.

TABLE I
 CRYSTALLOGRAPHIC DATA

Crystal data	
Formula	$\text{Cd}[\text{Ni}(\text{CN})_4] \cdot 6\text{H}_2\text{O}$
Formula weight	383.27
Crystal system	orthorhombic
Space group	$Pnma$
a, b, c	12.393(6), 14.278(5), 7.427(1) Å
V	1314(1) Å ³
Z	4
D_c	1.937 Mg m ⁻³
μ (Mo $K\alpha$)	3.07 mm ⁻¹
F_{000}	752
Data collection	
Crystal appearance	colorless prism
Crystal dimensions	0.12 × 0.15 × 0.35 mm
Diffractometer	Enraf-Nonius CAD4
Radiation, wave-length	Mo $K\alpha$, 0.71073 Å
Monochromator	graphite
Temperature	22 °C
$2\theta_{\text{max}}$	55°
Index range h, k, l	0 to 16, 0 to 18, 0 to 9
Scan mode	ω - 2θ
Scan speed (on ω)	1.6° to 5.3° min ⁻¹ after prescan
Scan width	(1.20 + 0.374 tan θ)°
Reference reflections	3, every hour
No. of independent reflections scanned	1762
Refinement	
Absorption correction	DIFABS ^a
Relative correlation factor	0.76–1.45
No. of independent reflections [$I \geq 3\sigma(I)$] (N)	949
No. of parameters (V)	79
Function minimized	$\sum w(F_o - F_c)^2$
Weighting factor, w	$1/\sigma^2(F)$
Sec. extinction parameter	Not refined
$R(F)$, $wR(F)$	0.033, 0.042
S	1.57
Max. Δ/σ , last cycle	0.02
Max., min. in final difference map	+0.58 (near Cd) to -0.63 e Å ⁻³

Note. $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $S = [\sum w(|F_o| - |F_c|)^2/(N - V)]^{1/2}$.

^a N. Walker and D. Stuart, *Acta Crystallogr. Sect. A* **39**, 158 (1983).

Figs. 1 and 2. The atomic coordinates are given in Table II, and a list of bond lengths and angles is displayed in Table III. The essential structural feature of this material is a two-dimensional square-planar net of metal atoms linked by cyanide bridges (see Fig. 2). The carbon atom of each cyanide bridge is bound to a nickel atom and the nitrogen atom to a cadmium atom. In this material, the cadmium tetracyanonickelate

sheets are not planar but have a wave (Fig. 1) which displaces the nickel atoms above and below the plane defined by the cadmium atoms and thereby doubles the unit cell in the b direction. This distortion makes the Cd–Cd distance 7.426 Å along c and 7.139 Å along b .

The sheets are arranged in the unit cell along a with adjacent sheets related by the 2_1 screw axis parallel to b . Thus, there are two layers per unit cell separated by 0.5a (6.197 Å).

The interstitial spaces between the cadmium tetracyanonickelate layers are occupied by six water molecules per formula unit which form a distorted hexagonal net. Two of the water molecules coordinate the axial positions of a cadmium atom and one water molecule has a Ni–O distance of 2.804 Å, giving nickel an effective 5 coordination. The other three waters sit in the cavities within the structure and complete the puckered hexagonal hydrogen-bonded network of water molecules; the oxygen–oxygen separation within this network is approximately 2.8 Å.

Discussion

The metal–cyanide sheets in $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ are similar to those found in the Hofmann clathrates and other materials such as $\text{Ni}(\text{CN})_2 \cdot n\text{H}_2\text{O}$ (19) and $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (20), which do not contain trapped organic molecules. All of these materials are composed of two-dimensional sheets in which a square-planar nickel, palladium, or platinum cyanide complex is bound to an octahedral metal center through the nitrogen atom of the cyanide groups (see Fig. 2). The differences between these materials arise from variations in the identity of the ligands coordinating the axial positions of the octahedral metal atoms, the stacking of the metal–cyanide layers, and the molecules trapped or clathrated within the cavities between the sheets and the axial ligands.

Three stacking arrangements for the metal tetracyanonickelate sheets were proposed by Mathey and Mazieres (19) and are

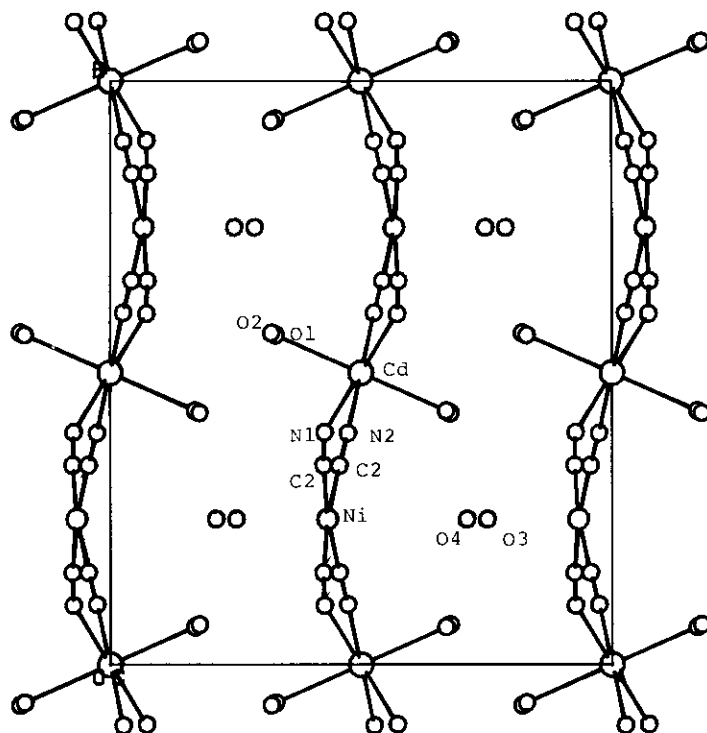


FIG. 1. Projection of the unit cell contents down the c axis.

redrawn in Fig. 3. The first, labeled L_0 , has the axial ligands of the octahedral metal center directly opposed and leads to the largest cavities within the structure. Not surprisingly, this structure is adopted by the Hofmann-type clathrates in which benzene or other aromatic molecules are trapped within the cavities. $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ with $n > 3$ also adopts this structure and the interlayer spacing is 6.10 \AA (19); the water molecules not coordinated to the octahedral metal presumably fill the cavities occupied by the organic molecule in the Hofmann-type clathrates.

Two other structural possibilities result when the axial ligands of the octahedral metal center are interdigitated. The phase labeled K by Mathey and Mazieres has the square-planar metal center arranged directly above and below the axial ligands of the octahedral metal center in the adjacent sheets. This arrangement effectively dou-

bles the unit cell dimension in the intersheet direction. To use $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ with $n = 1-3$ as an example, the interlayer distance is 5.06 \AA ; thus, the interdigitation shortens the interlayer distance by about 1 \AA in the nickel cyanide hydrates. This structure is also adopted by $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \text{biphenyl}$ (21) and $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ (22).

The second interdigitated arrangement of the axial ligands of the octahedral metal centers is labeled L_1 and has these ligands directed toward the "holes" or pores within the adjacent metal cyanide sheets. The nickel cyanide hydrates $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot n\text{H}_2\text{O}$ adopt this structure when $0 < n < 2$ (i.e., the least amount of "excess" water) and have an interlayer spacing of only 4.44 \AA .

Curiously, $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ adopts this L_1 arrangement of the $\text{Cd}(\text{H}_2\text{O})_2\text{-Ni}(\text{CN})_4$ sheets but with an interlayer spac-

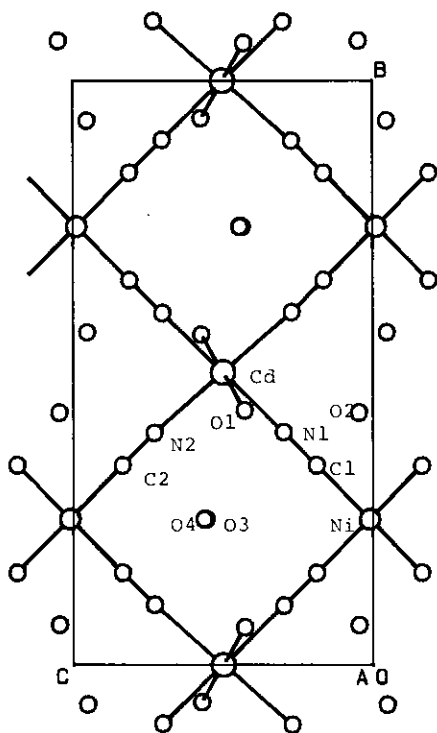


FIG. 2. Projection of a single cadmium-nickel-cyanide sheet and its associated water molecules down the a axis.

ing of 6.2 \AA , which is longer than the L_0 nickel cyanide hydrates ($n > 3$) in which no interdigitation of the water molecules bound to the axial sites of the octahedral metal

TABLE II
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Atom	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Cd	0.5	0.5	0.5	1.74(2)
Ni	0.4335(1)	0.25	0.0111(2)	1.74(4)
O(1)	0.6702(3)	0.4352(3)	0.4280(6)	2.8(2)
O(2)	0.6787(4)	0.4313(4)	0.0465(7)	3.8(2)
O(3)	0.7522(7)	0.25	0.9436(11)	4.4(4)
O(4)	0.7117(7)	0.25	0.5633(11)	4.5(4)
N(1)	0.4273(5)	0.3984(4)	0.2977(8)	3.0(3)
N(2)	0.4739(5)	0.3969(4)	-0.2706(8)	3.1(3)
C(1)	0.4252(6)	0.3419(4)	0.1875(8)	1.9(2)
C(2)	0.4570(6)	0.3416(5)	-0.1638(9)	2.1(3)

TABLE III
BOND LENGTHS (\AA) AND ANGLES (DEG)

Cd-O(1)	2.365(4)	Ni-C(2)	1.866(7)
Cd-N(1)	2.274(6)	N(1)-C(1)	1.149(8)
Cd-N(2)	2.275(6)	N(2)-C(2)	1.138(8)
Ni-C(1)	1.857(7)	Ni··O(4 ^h)	2.804(8)
Hydrogen bonds			
O(1)··O(2 ^h)	2.814(6)	O(2)··O(3 ^h)	2.849(7)
O(1)··O(2)	2.836(7)	O(3)··O(4)	2.860(12)
O(1)··O(4)	2.875(6)		
Symmetry code			
(i) $x, y, 1+z$;		(ii) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$;	
(iii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$;		(iv) $x, y, -1+z$	
O(1)-Cd-O(1)	180	C(1)-Ni-C(2)	90.2(2)
O(1)-Cd-N(1)	87.4(2)	C(1)-Ni-C(2)	174.2(3)
O(1)-Cd-N(2)	92.5(2)	C(2)-Ni-C(2)	89.0(4)
N(1)-Cd-N(1)	180	Cd-N(1)-C(1)	158.0(7)
N(1)-Cd-N(2)	91.5(2)	Cd-N(2)-C(2)	175.4(6)
N(2)-Cd-N(2)	180	Ni-C(1)-N(1)	175.5(8)
C(1)-Ni-C(1)	89.9(4)	Ni-C(2)-N(2)	178.3(7)

center occurs. This arrangement appears unexpected until one realizes that the six water molecules per formula unit form a puckered hexagonal hydrogen-bonded net between the $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4$ sheets. This hydrogen-bonded array provides the structural strength to keep the layers apart and gives an explanation for the sensitivity of the crystals to mild heating; removal of water results in a structural collapse which turns the crystals to powder. A nickel cyanide hydrate compound with the corresponding stoichiometry $(\text{Ni}(\text{CN})_2 \cdot 3\text{H}_2\text{O})$ has been reported, but no structural data for this compound accompany this report (19).

The distortion or wave that develops in the $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4$ sheets of the compound reported here (doubling the unit cell along b) appears to be a feature of many similar compounds in which the cavities between the layers are incompletely filled by clathrated molecules. Thus, if the clathrated molecule is small (like water) or if the axial ligands on the octahedral metal are large, the cavities are inadequately filled and the sheets distort from planar geometry. Examples of other compounds with puckered metal cyanide sheets include $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, (20) and $\text{Cd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_2\text{Ni}(\text{CN})_4 \cdot \text{C}_4\text{H}_5\text{N}$ (23).

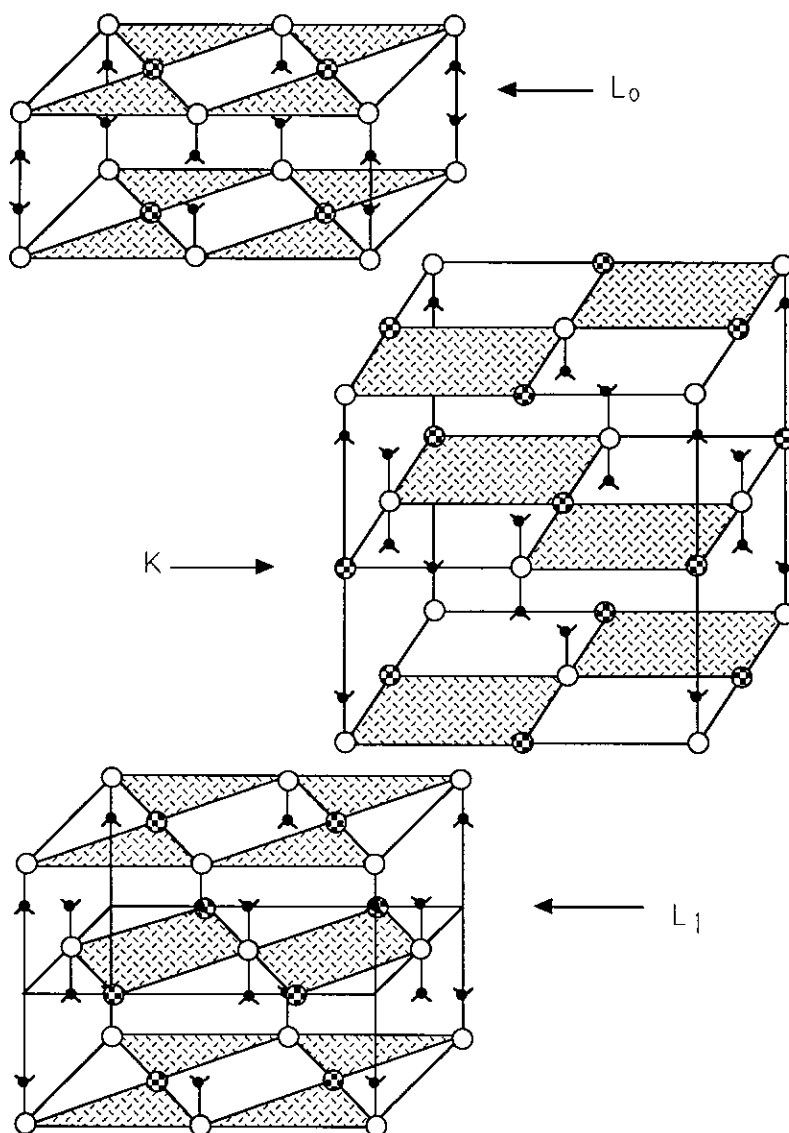


FIG. 3. Three different stacking sequences of the metal tetracyanonickelate sheets labeled according to the designations of Ref. 19. Symbol designations: octahedral metals, open circles; nickel atoms, patterned circles; water molecules, filled circles.

The crystallization of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ in the presence of diamines requires further study. It is odd that the *trans*-1,4-diaminocyclohexane is not incorporated into a structure that is known to accept diamines as bridging ligands between the cadmiums of adjacent sheets (e.g., $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$). Also, the crystal

morphology is profoundly affected by the presence of the diamine: prismatic crystals are obtained when the material is crystallized from a solution containing diaminocyclohexane, whereas in the absence of the diamine a tabular habit results. Evidently, the diamine is modifying the kinetic competition between growth of the metal cyanide

sheets and growth perpendicular to the sheets in this material, thus changing the crystal habit. More studies need to be done to elucidate the role of the diaminocyclohexane and to identify which diamines serve to modify the crystal shape and which if any are incorporated into the structure as interlayer bridges.

Conclusions

The synthesis and structure of $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ are reported. While related to known Hofmann-type clathrate materials, the single-crystal structural determination reported here is the first such study of a metal tetracyanonickelate sheet material which does not contain ammonia, amines, or a clathrated aromatic molecule. The structure solution also locates the oxygen of the interlayer waters for the first time and indicates that this material contains a hydrogen-bonded array of water in the interlayer region which gives a greater separation of the cadmium tetracyanonickelate layers than is seen in other nickel cyanide hydrate materials.

Acknowledgments

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