

Article

Three-Dimensional Cadmium(II) Cyanide Coordination Polymers with Ethoxy-, Butoxy- and Hexyloxy-ethanol

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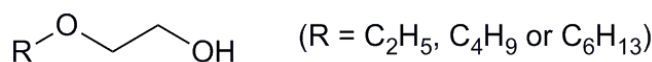
Abstract: The three novel cadmium(II) cyanide coordination polymers with alkoxyethanols, $[\text{Cd}(\text{CN})_2(\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})]_n$ (**I**), $[\{\text{Cd}(\text{CN})_2(\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{OH})\}_3\{\text{Cd}(\text{CN})_2\}]_n$ (**II**) and $[\{\text{Cd}(\text{CN})_2(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_2\}_3 \cdot 2(\text{C}_6\text{H}_{13}\text{OCH}_2\text{CH}_2\text{OH})]_n$ (**III**), were synthesized and characterized by structural determination. Three complexes have three-dimensional $\text{Cd}(\text{CN})_2$ frameworks; **I** has distorted tridymite-like structure, and, **II** and **III** have zeolite-like structures. The cavities of $\text{Cd}(\text{CN})_2$ frameworks of the complexes are occupied by the alkoxyethanol molecules. In **I** and **II**, hydroxyl oxygen atoms of alkoxyethanol molecules coordinate to the $\text{Cd}(\text{II})$ ions, and the $\text{Cd}(\text{II})$ ions exhibit slightly distort trigonal-bipyramidal coordination geometry. In **II**, there is also tetrahedral $\text{Cd}(\text{II})$ ion which is coordinated by only the four cyanides. The hydroxyl oxygen atoms of alkoxyethanol connects etheric oxygen atoms of the neighboring alkoxyethanol by hydrogen bond in **I** and **II**. In **III**, hexyloxyethanol molecules do not coordinate to the $\text{Cd}(\text{II})$ ions, and two water molecules coordinate to the octahedral $\text{Cd}(\text{II})$ ions. The framework in **III** contains octahedral $\text{Cd}(\text{II})$ and tetrahedral $\text{Cd}(\text{II})$ in a 1:3 ratio. The $\text{Cd}(\text{CN})_2$ framework structures depended on the difference of alkyl chain for alkoxyethanol molecules.

Keywords: coordination polymer; crystal structure; self-assembly; mineralomimetic chemistry; host-guest; molecular size; hydrogen bond

1. Introduction

Cadmium(II) cyanide of formula $\text{Cd}(\text{CN})_2$ and the related compounds have interesting, unique chemical properties [1–11]. Cadmium(II) cyanide is a three-dimensional porous coordination polymer, and is the clathration of various guest molecules (ex. CCl_4 [1,2], $\text{CH}_2\text{ClCHCl}_2$ [3] and Bu_2O [3]) by van der Waals force in the cavity. It is interesting that the structures of host constructed from $\text{Cd}(\text{II})$ and cyanide ions change according to the guest [1–10], and the hosts form a mineralomimetic framework. The coordination geometry of $\text{Cd}(\text{II})$ in $\text{Cd}(\text{CN})_2$ is normally tetrahedral four-coordination geometry (denoted as Cd_T) but the geometry might also be trigonal-bipyramidal five-coordination geometry (Cd_TB) or octahedral six-coordination geometry (Cd_OC) according to the influence of other ligand (ex. H_2O [6–10]). At $\text{Cd}(\text{CN})_2$ clathrates containing lipophilic guest, coordination geometries of $\text{Cd}(\text{II})$ were Cd_T , the $\text{Cd}(\text{CN})_2$ frameworks were cristobalite-like or tridymite-like structures [1–4,11]. On the other hand, the $\text{Cd}(\text{CN})_2$ clathrates with water molecule(s) coordinating to $\text{Cd}(\text{II})$ ion contained alcohol or short dialkyl-ether (alkyl group of carbon number less than 3) as a guest, and the host frameworks performed zeolite-mimetic structures [6–10]. Thus, it was

thought that the guest hydrophilic groups influence the Cd(II) coordination environment. We are interested in the effect of the coexistence of two kinds of hydrophilic groups on the Cd(II) coordination environment. Alkoxyethanol has both hydroxyl and etheric groups as shown Scheme 1. We report herein the synthesis and crystal structures of three novel cadmium(II) cyanide complexes with alkoxyethanol compounds of formulae $[\text{Cd}(\text{CN})_2(\text{Etel})]_n$ (**I**), $[\{\text{Cd}(\text{CN})_2(\text{Bucel})\}_3\{\text{Cd}(\text{CN})_2\}]_n$ (**II**) and $[\{\text{Cd}(\text{CN})_2(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_2\}_3\cdot 2(\text{Hexcel})]_n$ (**III**) (Etel = ethoxyethanol, Bucel = butoxyethanol, Hexcel = hexyloxyethanol).



Scheme 1. Structural formulae of alkoxyethanol compounds used in this work.

2. Results and Discussion

2.1. Crystal Structure

Single crystals of the complexes **I–III** were prepared by a method similar to the literature procedure [1]. Crystal data for **I–III** are listed in Table 1. In the three complexes, all cyanides bridge between two Cd(II) ions, and $\text{Cd}(\text{CN})_2$ consists of a three-dimensional framework with large cavities (Figures 1–3). From IR spectra, the peaks of $\text{C}\equiv\text{N}$ stretching (ν_{CN}) were observed at $2185\text{--}2190\text{ cm}^{-1}$. The ν_{CN} values showed a blue shift from that which was observed for terminal $\text{C}\equiv\text{N}$ of $\text{K}_2[\text{Cd}(\text{CN})_2]$ (2145 cm^{-1}), supporting a view that the $\text{C}\equiv\text{N}$ bridged between two Cd(II) ions. The exact arrangements of cyanides ($\text{Cd}-\text{NC}-\text{Cd}$ or $\text{Cd}-\text{CN}-\text{Cd}$) cannot be determined by single X-ray diffraction because these arrangements are disordered. Nishikiori et al. [6,12,13] show that arrangements of cyanides in $\text{Cd}(\text{CN})_2$ host are disordered by $^{113}\text{Cd}-\text{CP}/\text{MAS}$ NMR.

Table 1. Crystal Data for **I**, **II** and **III**.

Complex	I	II	III
Empirical formula	$\text{C}_6\text{H}_{10}\text{CdN}_2\text{O}_2$	$\text{C}_{26}\text{H}_{42}\text{Cd}_4\text{N}_8\text{O}_6$	$\text{C}_{24}\text{H}_{40}\text{Cd}_4\text{N}_8\text{O}_6$
Formula weight	254.56	1012.28	986.24
Temperature (K)	253	273	90
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$\text{C}222_1$	$P2_1/c$	Pnma
a (Å)	8.1727(3)	8.9441(4)	38.0252(19)
b (Å)	15.7149(6)	15.2192(7)	8.7786(4)
c (Å)	15.3108(6)	29.4582(13)	12.0948(6)
α (°)	90	90	90
β (°)	90	91.6930(10)	90
γ (°)	90	90	90
V (Å ³)	1966.41(13)	4008.2(3)	4037.3(3)
Z	8	4	4
d_{calc} (g cm ^{−3})	1.720	1.677	1.623
μ (mm ^{−1})	2.180	2.135	2.118
$F(000)$	992	1976	1920
Reflections collected	7375	29345	20635
R_{int}	0.0142	0.0228	0.0320
Data/restraints/parameters	2909/0/115	9947/63/438	3823/343/320
GOF	1.030	1.010	1.181
$R1, wR2$ [$I > 2\sigma(I)$]	0.0164, 0.0369	0.0326, 0.0749	0.0633, 0.1312
Flack parameter [14]	0.00(3)	–	–
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.327, −0.333	0.501, 0.688	1.089, −1.559

2.1.1. Crystal Structure of $[\text{Cd}(\text{CN})_2(\text{Etelc})]_n \mathbf{I}$

For complex **I**, crystal structure is shown in Figure 1 and selected parameters are listed in Table 2. The complex **I** consists of one crystallographically independent Cd(II) ion; the Cd(II) is labeled Cd1. Cd1 exhibits five-coordination (Figure 1a). Five-coordination geometry is estimated by a simple distortion parameter τ . The τ parameter was proposed by Addison et al. [15,16]. The τ value is simply defined by $\tau = (\theta_1 - \theta_2)/60$, where θ_1 is the largest and θ_2 is second largest basal angle, a perfect square pyramid is characterized by $\tau = 0$, while $\tau = 1$ means a perfect trigonal bipyramid [15,16]. For the Cd1, τ is 0.82 from selected bond angles in Table 2. Therefore, Cd1 is slightly distorted Cd_{TB} . Around the Cd1, one hydroxyl oxygen atom O1 of Etcel ligand is located at one of the axial positions and four cyanides are located at the remaining positions, namely, another axial position (denoted as $_{\text{ax}}$) and three equatorial positions ($_{\text{eq}}$). Cd1 is located in the general position. Atoms labeled C2/N2 or C3/N3 are hybrid due to the disorder of arrangement of cyanide (Figure 1a), and due to the midpoints of $\text{C}\equiv\text{N}$ bonds on the symmetry of the lattice [1–6,12]. The values of bond lengths around Cd(II) ions decrease in the order $\text{Cd}_{\text{TB}}\text{--O} > \text{Cd}_{\text{TB}}\text{--}(\text{CN})_{\text{ax}} > \text{Cd}_{\text{TB}}\text{--}(\text{CN})_{\text{eq}}$ (Table 2). $\text{Cd}(\text{CN})_2$ framework is distorted-tridymite-like structure, and the cavities' shape is distorted [6⁵] **t-afi** tile [17,18]. The cavities of $\text{Cd}(\text{CN})_2$ network are occupied by the Etcel ligands (Figure 1b,c). Etcel ligand does not protrude from one cavity. The Etcel ligand is connected with the neighboring Etcel by hydrogen bonds between one ligand's hydroxyl oxygen atom O1 and the other's etheric oxygen atom O2 (Figure 1c and Table 2). In thermogravimetric analysis (TGA) for **I** (Figure S1), thermogravimetric (TG) and differential thermogravimetric (DTG) curves showed one-step weight loss in the range from about 100 °C to 155 °C. This supported the proposition that the Etcel ligand is crystallographically independent as shown in Figure 1a, and that the $\text{Cd}(\text{CN})_2$ cavity is uniformity as shown in Figure 1b. The absolute values of torsion angles of ethyleneglycol fragment ($\text{O--CH}_2\text{--CH}_2\text{--O}$) are values close to 60° (Table 2). Thus, the conformation of the ethyleneglycol fragment in Etcel ligand is *gauche* form. As a result, $(\text{O--CH}_2\text{--CH}_2\text{--O})_2$ eight-membered ring is constructed by the two ethyleneglycol fragments. The carbon atom (C11 or C11') binding with hydroxyl oxygen atom is disordered (Figure 1a).

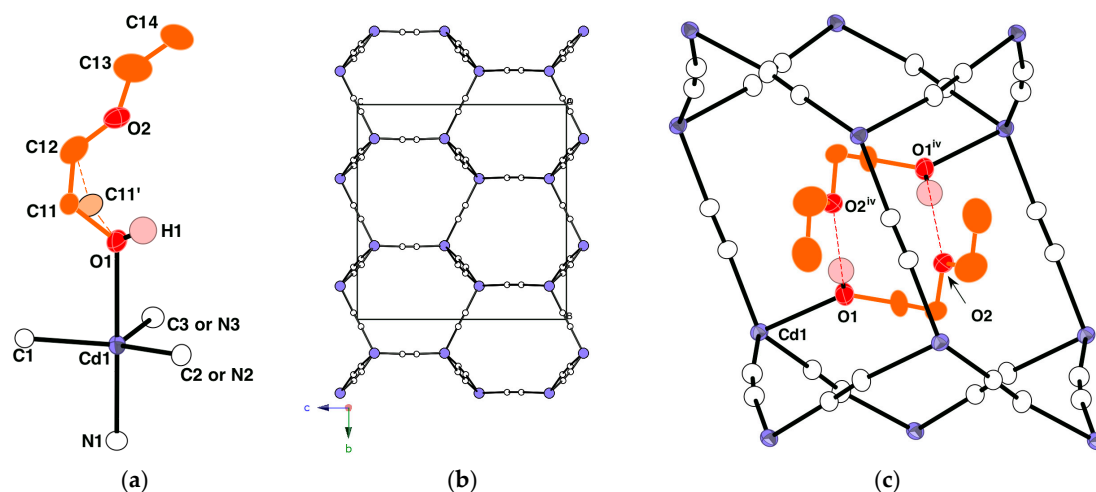


Figure 1. Crystal structure of **I**. H atoms except OH hydrogens are omitted for clarity: (a) Asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. Because arrangements of cyanides (Cd--NC--Cd or Cd--CN--Cd) are disordered, the atoms of cyanide are labeled less clearly; (b) The $\text{Cd}(\text{CN})_2$ network structure view along the a axis; (c) Hydrogen bonds between neighboring Etcel ligands in cavities of distorted-tridymite-like cadmium cyanide network of **I**. Displacement ellipsoids are drawn at the 30% probability level. The disorder part is omitted for clarity. (Symmetry codes: $\text{iv} = -x + 1, y, -z + 3/2$).

Table 2. Selected Parameters for **I**.

Cd _{TB} –O/Å	
Cd1–O1	2.5207 (19)
Cd _{TB} –(CN) _{ax} /Å	
Cd1–N1	2.3449 (19)
Cd _{TB} –(CN) _{eq} /Å	
Cd1–C1	2.197 (2)
Cd1–N2	2.2060 (18)
Cd1–N3	2.210 (2)
(CN)–(CN)/Å	
N1–C1 ⁱ	1.135 (3)
N2–C2 ⁱⁱ	1.141 (4)
N3–C3 ⁱⁱⁱ	1.135 (4)
(CN) _{eq} –Cd _{TB} –(CN) _{eq} /°	
C1–Cd1–N2	128.65 (8)
C1–Cd1–N3	116.08 (8)
N2–Cd1–N3	113.44 (8)
(CN) _{ax} –Cd _{TB} –(CN) _{eq} /°	
N1–Cd1–C1	95.06 (7)
N1–Cd1–N2	94.67 (7)
N1–Cd1–N3	93.53 (7)
(CN) _{ax} –Cd _{TB} –O/°	
N1–Cd1–O1	177.94 (7)
(CN) _{eq} –Cd _{TB} –O/°	
C1–Cd1–O1	84.83 (7)
N2–Cd1–O1	86.99 (7)
N3–Cd1–O1	84.67 (7)
Hydrogen bond/Å	
O1...O2 ^{iv}	2.774 (2)
torsion angle/°	
O1–C11–C12–O2	−68.6 (4)
O1–C11'–C12–O2	54.1 (9)

Symmetry codes: i = $x - 1/2, -y + 3/2, -z + 1$; ii = $-x, y, -z + 3/2$; iii = $x, -y + 1, -z + 1$; iv = $-x + 1, y, -z + 3/2$.

2.1.2. Crystal Structure of $[\{\text{Cd}(\text{CN})_2(\text{Bucel})\}_3\{\text{Cd}(\text{CN})_2\}]_n$ **II**

For complex **II**, crystal structure is shown in Figure 2 and selected parameters are listed in Table 3. The complex **II** contains two distinct coordination geometric Cd(II) ions; the one slightly distorted Cd_{TB} (Cd1 ($\tau = 0.76$), Cd2 ($\tau = 0.87$) and Cd3 ($\tau = 0.82$) (from Table 3)) [15,16] and the other Cd_T (Cd4) in a ratio of 3:1 (Figure 2a). Around the Cd_{TB}, one hydroxyl oxygen atom of Bucel ligand is located at one of the axial positions and four cyanides are located at the remaining positions. Cd_T is coordinated by only four cyanides. All Cd(II) ions are located on the general positions. The values of bond lengths around Cd(II) ions decrease in the order Cd_{TB}–O > Cd_{TB}–(CN)_{ax} > Cd_{TB}–(CN)_{eq} \approx Cd_T–(CN) (Table 3). This tendency is similar to **I** and Cd₅(CN)₁₀(H₂O)₄·4C₆H₁₁OH [6]. The Cd(CN)₂ framework forms zeolite-like structure and three kinds of cavities. These cavities' shapes are distorted [6⁵] **t-afi**, distorted [6².8²] **t-kaa** and distorted [4².6⁴] **t-lau** tiles [17,18], respectively (Figure 2b–d). To our knowledge, zeolite constructed by the three tiles are not reported and the framework topology is new [17,18]. The all cavities of Cd(CN)₂ network are occupied by the Bucel ligands, but the terminals of the butyl groups protrude from one cavity (Figure 2d). This is suggested below; Bucel does not coordinate to one of four Cd(II) ions because total volume of Bucel coordinating to four of four Cd(II) ions exceeds the capacity of the total cavity of the Cd(CN)₂ network. In the **t-afi** and **t-kaa** cavities, the Bucel ligand is connected with the neighboring Bucel by hydrogen bonds between one ligand's hydroxyl oxygen atom and the other's etheric oxygen atom (Figure 2d and Table 3) as case of **I**. Conformations of ethyleneglycol fragments of Bucel ligands are *gauche* form (Table 3). In TGA for **II** (Figure S2), TG and DTG curves showed three-steps weight loss in the range of about 100 °C to 180 °C. This suggests

that one Bucel ligand was removed from the complex **II** having three kind of cavities (Figure 2b–d) per one-step. In Bucel ligands, part of butyl groups and of the ethylene groups are disordered. In contrast, because etheric oxygen atoms (O2, O4 and O6) of the Bucel ligand connect hydroxyl oxygen atoms (O3, O1 and O5) of the neighboring Bucel by hydrogen bond, etheric oxygen atoms are in a more strongly fixed position than the butyl groups' atoms and have small anisotropic parameters.

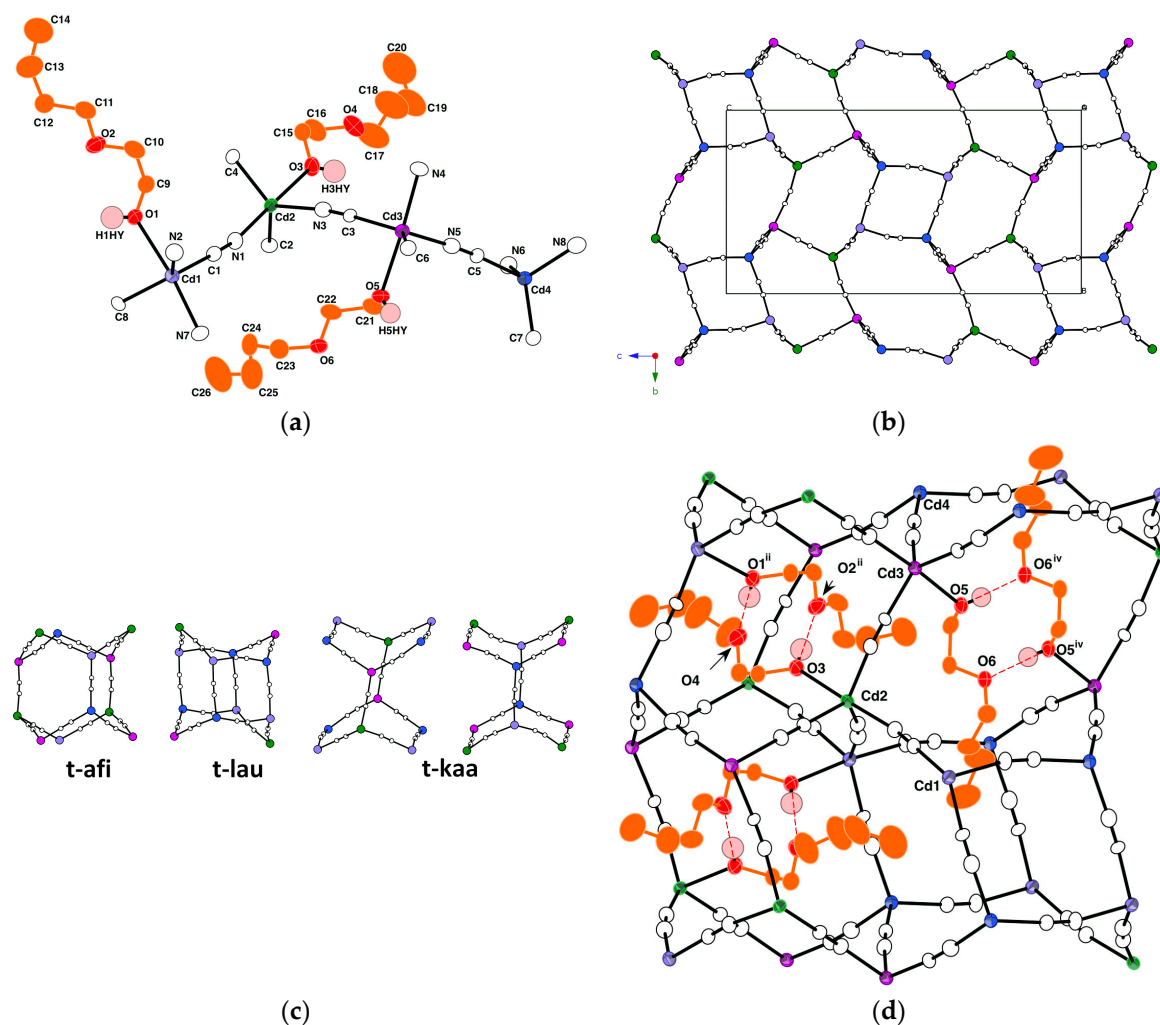


Figure 2. Crystal structure of **II**. H atoms except OH hydrogens and disorder parts are omitted for clarity: (a) Asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. Because arrangements of cyanides (Cd–NC–Cd or Cd–CN–Cd) are disordered, the atoms of cyanide are labeled less clearly; (b) The Cd(CN)₂ network structure of the view along the *a* axis; (c) [6⁵] **t-afi**, [4².6⁴] **t-lau** and [6².8²] **t-kaa** tiles; (d) Hydrogen bonds between neighboring Bucel ligands in cavities of cadmium cyanide network of **II**. Displacement ellipsoids are drawn at the 30% probability level. (Symmetry codes: ii = $-x + 1, y - 1/2, -z + 1/2$; iv = $-x + 1, -y + 1, -z$).

Table 3. Selected Parameters for II.

Cd _{TB} –O/Å					
Cd1–O1	2.530(3)	Cd2–O3	2.547(3)	Cd3–O5	2.480(2)
Cd _{TB} –(CN) _{ax} /Å					
Cd1–N7	2.322(3)	Cd2–N1	2.323(3)	Cd3–N4	2.303(3)
Cd _{TB} –(CN) _{eq} /Å					
Cd1–C1	2.200(3)	Cd2–C2	2.182(3)	Cd3–C3	2.190(3)
Cd1–C8	2.185(3)	Cd2–C4	2.194(3)	Cd3–C6	2.180(3)
Cd1–N2	2.218(3)	Cd2–N3	2.212(3)	Cd3–N5	2.223(3)
Cd _T –(CN)/Å					
Cd4–C5	2.203(3)	Cd4–N6	2.229(3)		
Cd4–C7	2.176(3)	Cd4–N8	2.215(4)		
(CN)–(CN)/Å					
N1–C1	1.123(4)	N2–C2 ⁱ	1.136(4)	N3–C3	1.140(4)
N4–C4 ⁱⁱ	1.130(4)	N5–C5	1.140(4)	N6–C6 ⁱⁱⁱ	1.137(4)
N7–C7 ^{iv}	1.125(4)	N8–C8 ^v	1.137(5)		
(CN) _{ax} –Cd _{TB} –O/°					
N7–Cd1–O1	173.88(10)	N1–Cd2–O3	178.06(11)	N4–Cd3–O5	176.27(10)
(CN) _{eq} –Cd _{TB} –O/°					
C1–Cd1–O1	85.07(10)	C2–Cd2–O3	83.78(12)	C3–Cd3–O5	83.28(10)
C8–Cd1–O1	82.64(11)	C4–Cd2–O3	84.57(11)	C6–Cd3–O5	87.31(10)
N2–Cd1–O1	85.01(11)	N3–Cd2–O3	84.01(10)	N5–Cd3–O5	85.06(10)
(CN) _{eq} –Cd _{TB} –(CN) _{ax} /°					
C1–Cd1–N7	99.90(11)	C2–Cd2–N1	97.20(12)	C3–Cd3–N4	93.05(11)
C8–Cd1–N7	91.44(12)	C4–Cd2–N1	96.41(11)	C6–Cd3–N4	95.48(11)
N2–Cd1–N7	95.90(12)	N3–Cd2–N1	94.06(11)	N5–Cd3–N4	96.03(11)
(CN) _{eq} –Cd _{TB} –(CN) _{eq} /°					
C8–Cd1–C1	128.24(13)	C2–Cd2–C4	117.75(13)	C6–Cd3–C3	126.97(12)
C1–Cd1–N2	116.09(13)	C2–Cd2–N3	113.13(12)	C3–Cd3–N5	117.07(12)
C8–Cd1–N2	112.61(12)	C4–Cd2–N3	126.01(12)	C6–Cd3–N5	113.87(12)
(CN)–Cd _T –(CN)/°					
C7–Cd4–C5	110.76(12)	C7–Cd4–N6	115.46(13)	C7–Cd4–N8	111.38(13)
C5–Cd4–N6	103.02(12)	C5–Cd4–N8	110.93(12)	N8–Cd4–N6	104.89(12)
Hydrogen bond/Å					
O1...O4 ^{vi}	2.763(4)	O3...O2 ⁱⁱ	2.777(4)	O5...O6 ^{iv}	2.708(3)
torsion angle/°					
O1–C9–C10–O2	−69.5(7)	O1–C9′–C10–O2	44.6(19)		
O3–C15–C16–O4	−71.5(6)	O3–C15′–C16–O4	42(2)		
O5–C21–C22–O6	−74.2(4)				

Symmetry codes: i = $x - 1, y, z$; ii = $-x + 1, y - 1/2, -z + 1/2$; iii = $x + 1, y, z$; iv = $-x + 1, -y + 1, -z$; v = $x + 1, y - 1, z$; vi = $-x + 1, y + 1/2, -z + 1/2$.

2.1.3. Crystal Structure of $[\{\text{Cd}(\text{CN})_2(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_2\}_3 \cdot 2(\text{Hexcel})]_n$ III

For complex **III**, the crystal structure is shown in Figure 3 and selected parameters are listed in Table 4. The complex **III** contains two distinct coordination geometry Cd(II) ions; the one Cd_{OC} (Cd1) and the other Cd_T (Cd2, Cd3 and Cd4) in a ratio of 1:3 (Figure 3a). All Cd(II) ions lie on mirror plane in the cell. Around the Cd_{OC}, two oxygen atoms of water molecules are located at the *cis*-positions (Figure 3d) and four cyanides are located at the remaining positions. The water molecule (O1 or O11) is disordered (Figure 3a,d). The difference between the bond lengths of Cd1–O1 and Cd1–O11 (Table 4) indicates that the water molecule's position is not constant. Cd_T is coordinated by four cyanides. The values of bond lengths around Cd(II) ions decrease in the order Cd_{OC}–O \approx Cd_{OC}–(CN) \approx Cd_T–(CN) (Table 4). The Cd_{OC}–O bond of **III** (Table 4) is shorter than Cd_{TB}–O bonds of **I** and **II** (Tables 2 and 3). The Cd(CN)₂ framework forms zeolite-like structure and two kind of cavities. These cavities' shape are distorted [6⁴] **t-hes** and distorted [4².6².8²] **t-kdq** tiles¹⁷, respectively (Figure 3b,c). The fragment of distorted **t-kdq** tile is similar to Cd(CN)₂ framework for Cd(CN)₂(H₂O)·dmf [8]. JBW [17,18] zeolite constructed by the above two tiles are reported.

However, the **III** contains more **t-hes** tile than JBW. To our knowledge, the framework topology is new [17,18]. The Hexcel molecule does not coordinate to Cd(II) ion, and the hydroxyl oxygen atom connects the water molecule through weak hydrogen bond in the **t-kdq** cavity (Figure 3 and Table 4). In the Hexcel molecule, Weak C–H···O interaction is observed (Table 4). Two crystallographically independent Hexcel molecules exist in the crystal. TG and DTG curves (Figure S3) were observed in three steps of weight loss ranging from about 40 °C to 75 °C, from 80 °C to 205 °C, and from 205 °C to 230 °C. The first weight loss seems to trigger desorption of Hexcel molecules at the second weight loss [19]. The third weight loss seems to involve elimination of water ligands. The Hexcel molecules' atoms are disordered. In addition, because Hexcel molecules lie on the mirror plane for the cell (Figure 3a,d), the atoms are almost disordered to symmetrically mirror themselves.

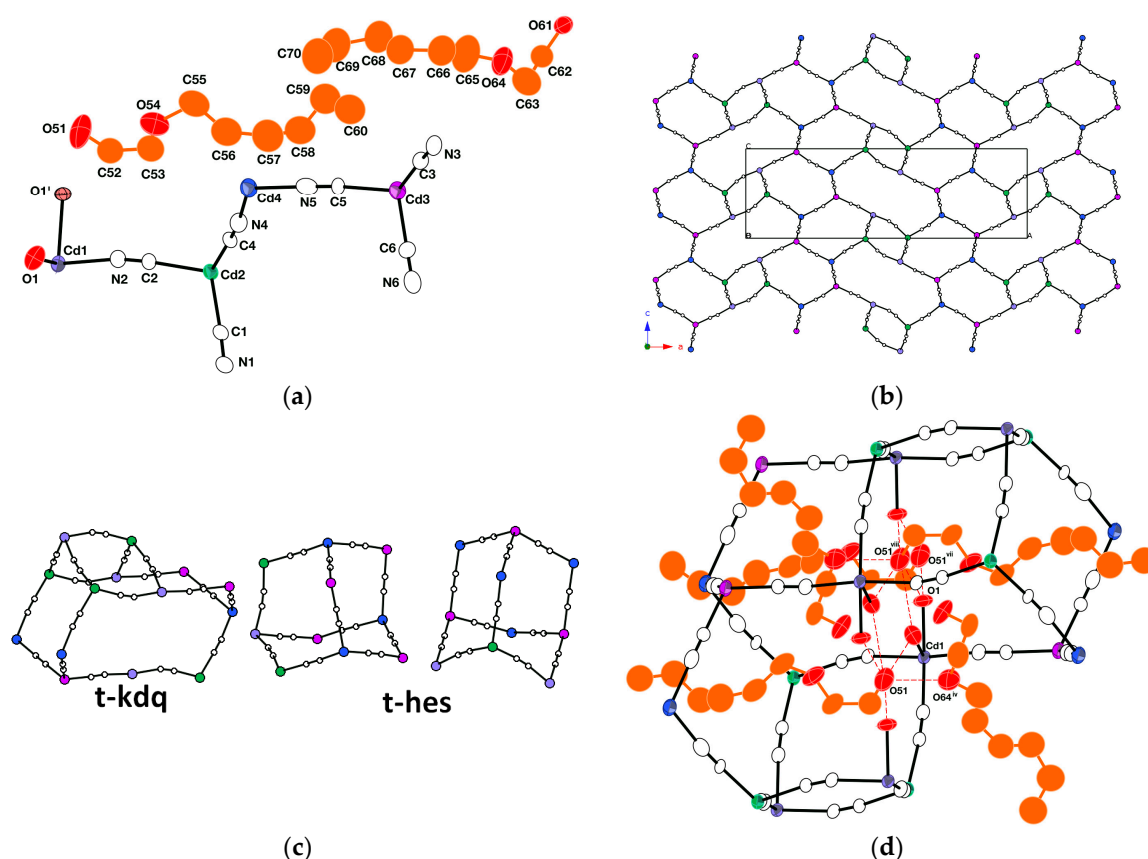


Figure 3. Crystal structure of **III**. H atoms and disorder parts are omitted for clarity: (a) Asymmetric unit of **III**. Displacement ellipsoids are drawn at the 30% probability level. Because arrangements of cyanides (Cd–NC–Cd or Cd–CN–Cd) are disordered, the atoms of cyanide are labeled less clearly; (b) The Cd(CN)₂ network structure of **III** along the *b* axis; (c) [6⁴] **t-kdq** and [4².6².8²] **t-hes** tiles; (d) Hydrogen bonds between Hexcel and water molecules in cavities of cadmium cyanide network. Displacement ellipsoids are drawn at the 30% probability level. (symmetry codes: iv = *x* + 1/2, *y*, *−z* + 3/2; vii = *x*, *y* − 1, *z*; viii = *−x* + 1, *−y* + 1, *−z* + 1).

Table 4. Selected Parameters for III.

Cd _{OC} –O/Å					
Cd1–O1	2.274(12)	Cd1–O1'	2.49(2)		
Cd _{OC} –(CN)/Å					
Cd1–N1 ⁱ	2.267(8)	Cd1–N2	2.306(10)		
Cd1–N1 ⁱⁱ	2.267(8)	Cd1–N3 ^{iv}	2.285(11)		
Cd _T –(CN)/Å					
Cd2–C1	2.191(9)	Cd3–C3	2.157(13)	Cd4–N4	2.221(15)
Cd2–C1 ⁱⁱⁱ	2.191(9)	Cd3–C5	2.157(11)	Cd4–N5	2.179(13)
Cd2–C2	2.221(12)	Cd3–C6	2.151(10)	Cd4–N6 ^v	2.230(11)
Cd2–C4	2.184(12)	Cd3–C6 ⁱⁱⁱ	2.151(10)	Cd4–N6 ^{vi}	2.230(11)
(CN)–(CN)/Å					
N1–C1	1.148(11)	N3–C3	1.128(15)	N5–C5	1.162(15)
N2–C2	1.124(14)	N4–C4	1.146(16)	N6–C6	1.152(12)
O–Cd _{OC} –O/°					
O1–Cd1–O1'	87(2)				
(CN)–Cd _{OC} –O/°					
N1 ⁱ –Cd1–O1	164.9(11)	N3 ^{iv} –Cd1–O1	85.4(5)	N2–Cd1–O1'	82.4(6)
N1 ⁱⁱ –Cd1–O1	100.0(11)	N1 ⁱ –Cd1–O1'	78.3(12)	N3 ^{iv} –Cd1–O1'	93.0(7)
N2–Cd1–O1	88.0(5)	N1 ⁱⁱ –Cd1–O1'	171.5(12)		
(CN)–Cd _{OC} –(CN)/°					
N1 ⁱ –Cd1–N1 ⁱⁱ	95.2(4)	N1 ⁱ –Cd1–N3 ^{iv}	92.9(3)		
N1 ⁱ –Cd1–N2	92.5(2)	N3 ^{iv} –Cd1–N2	172.1(4)		
(CN)–Cd _T –(CN)/°					
C1–Cd2–C1 ⁱⁱⁱ	111.2(5)	C3–Cd3–C5	119.5(4)	N5–Cd4–N4	115.8(4)
C1–Cd2–C2	109.4(3)	C6–Cd3–C3	111.5(3)	N4–Cd4–N6 ^v	106.5(3)
C4–Cd2–C1	110.0(3)	C6–Cd3–C5	104.1(3)	N5–Cd4–N6 ^v	110.8(3)
C4–Cd2–C2	106.7(4)	C6–Cd3–C6 ⁱⁱⁱ	104.9(5)	N6 ^v –Cd4–N6 ^{vi}	106.0(5)
Hydrogen bond/Å					
O1...O51 ^{vii}	3.23(4)	O1'...O511	2.71(5)	O511...O1' ^{ix}	2.71(5)
O1...O51 ^{viii}	3.14(4)	O51...O64 ^{iv}	2.66(3)	C63...O61 ^{ix}	2.47(2)

Symmetry codes: i = $-x + 1, y + 1/2, -z + 2$; ii = $-x + 1, -y, -z + 2$; iii = $x, -y + 1/2, z$; iv = $x + 1/2, y, -z + 3/2$; v = $-x + 1/2, -y, z - 1/2$; vi = $-x + 1/2, y + 1/2, z - 1/2$; vii = $x, y - 1, z$; viii = $-x + 1, -y + 1, -z + 1$; ix = $x, -y + 3/2, z$.

3. Materials and Methods

3.1. Synthesis

3.1.1. Synthesis for [Cd(CN)₂(Etel)]_n I

An aqueous solution (45 mL) containing CdCl₂·2.5H₂O 2 mmol and K₂[Cd(CN)₄] 4 mmol was stirred for 30 min at room temperature. After the solution was filtered through a membrane filter, colorless crystals of I were obtained from the filtrate by vapor diffusion with Etel in refrigerator for a few days. Elemental analysis found: C; 27.97, H; 3.66, N; 11.01%. Calculated for C₆H₁₀N₂O₂Cd: C; 28.31, H; 3.96, N; 11.00%. IR(nujol mull, cm^{−1}): ν_{OH} = 3313(br), ν_{CN} = 2186(s), ν_{COC} = 1109(s).

3.1.2. Synthesis for [(Cd(CN)₂(Bucel))₃{Cd(CN)₂}]_n II

An aqueous solution (45 mL) containing CdCl₂·2.5H₂O 2 mmol and K₂[Cd(CN)₄] (molecular ratio; CdCl₂·2.5H₂O: K₂[Cd(CN)₄] = 1:1 or 1:2) was stirred for 30 min at room temperature. After the solution was filtered through a membrane filter, the filtrate was layered with Bucel. On standing at room temperature for a few days, colorless crystal of II were obtained. If the crystal was not obtained, the filtrate with Bucel was put in the refrigerator. Elemental analysis found: C; 30.72, H; 4.10, N; 11.17%. Calculated for C₂₆H₄₂N₈O₆Cd₄: C; 30.85, H; 4.18, N; 11.07%. IR(nujol mull, cm^{−1}): ν_{OH} = 3302(br), ν_{CN} = 2185(s), ν_{COC} = 1111(s).

3.1.3. Synthesis for $[\{\text{Cd}(\text{CN})_2(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_2\}_3 \cdot 2(\text{Hexcel})]_n$ **III**

An aqueous solution (45 ml) containing $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ 2 or 1 mmol and $\text{K}_2[\text{Cd}(\text{CN})_4]$ (molecular ratio; $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} : \text{K}_2[\text{Cd}(\text{CN})_4] = 1:1$ or $1:2$) were stirred for 30 min at room temperature. After the solution was filtered through a membrane filter, the filtrate was layered with Hexcel. On standing at room temperature for a few days, colorless crystals of **III** were obtained. Elemental analysis found: C; 28.93, H; 3.92, N; 11.30%. Calculated for $\text{C}_{24}\text{H}_{40}\text{N}_8\text{O}_6\text{Cd}_4$: C; 29.23, H; 4.09, N; 11.36%. IR(nujol mull, cm^{-1}): $\nu_{\text{OH}} = 3388(\text{br})$, $\nu_{\text{CN}} = 2190(\text{s})$, $\nu_{\text{COC}} = 1117(\text{s})$.

3.2. Single Crystal X-ray Diffraction

The structural characterization for **I** and **III** were determined by the single crystal X-ray diffraction using a BRUKER APEXII SMART CCD area-detector diffractometer (Bruker, Madison, WI, USA) with monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) under the temperature controlled N_2 gas flow. The structural characterization for the **II** was determined by the single crystal X-ray diffraction using a BRUKER SMART CCD area-detector diffractometer (Bruker, Madison, WI, USA) with monochromated Mo-K α under the temperature controlled N_2 gas flow. The diffraction data were treated using APEX2 [20] and SAINT ver.7.23A [21] for **I** and **III**, and using SMART [22] and SAINT ver.6.22 [23] for **II**. Absorption data were performed using SADABS [24]. Their structures were solved by direct method, expanded using Fourier techniques, and refined by full-matrix least-square refinement.

For **I** and **II**, H atoms for hydroxyl group were located in difference syntheses and refined isotropically. The remaining H atoms were placed at calculated positions, and allowed to ride on the parent atom. For **II**, the (0 0 2) reflection affected by the beamstop was omitted from the final refinement.

For **III**, H atoms for water molecules were mixed that were located in difference syntheses, and that were placed at calculated positions. The remaining H atoms were placed at calculated positions. All H atoms were allowed to ride on the parent atom. The (2 0 0) reflection affected by the beamstop was omitted from the final refinement.

The overall structural solution was performed using SHELXTL [25]. Torsion angles and hydrogen bonds of all complexes were searched using SHELX [25] and PLATON [26]. CCDC 1472511–1472513 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

We synthesized and crystallographically characterized for novel tridymite-like or zeolite-like cadmium(II) cyanide coordination polymers with alkoxyethanol; $[\text{Cd}(\text{CN})_2(\text{Etel})]_n$ (**I**), $[\{\text{Cd}(\text{CN})_2(\text{Bucel})\}_3\{\text{Cd}(\text{CN})_2\}]_n$ (**II**) and $[\{\text{Cd}(\text{CN})_2(\text{H}_2\text{O})_2\}\{\text{Cd}(\text{CN})_2\}_3 \cdot 2(\text{Hexcel})]_n$ (**III**). In **I** and **II**, hydroxyl oxygen atoms of alkoxyethanol molecules coordinate to the Cd(II) ions, the Cd(II) ions exhibit slightly distort trigonal-bipyramidal coordination geometry. In **II**, there is also tetragonal Cd(II) ion which is coordinated by only the four cyanides. On the other hand, In **III**, hexyloxyethanol molecules do not coordinate to the Cd(II) ions, and two water molecules are located at the *cis*-positions of octahedral Cd(II) ion.

Cadmium(II) cyanide clathrates with dialkyl-ether guests are reported that the host with short dialkyl-ether guest are $\text{Cd}_8(\text{CN})_{16}(\text{H}_2\text{O})_6$ (Guest: Et_2O or *i*- PrO_2O) or $\text{Cd}_3(\text{CN})_6(\text{H}_2\text{O})_2$ (Guest: Pro_2O), [9] and that the host with Bu_2O guest is $\text{Cd}(\text{CN})_2$ [3]. This work reveals that Etel and Bucel molecules coordinate to Cd(II) ion, and that Hexcel molecule does not coordinate to Cd(II) ion. However, the Hexcel molecule may cause water molecules to coordinate to Cd(II) ion. Thus, the polar group of guest molecule may support the proposition that water molecule coordinates to Cd(II) ion in $\text{Cd}(\text{CN})_2$ network, or that the molecule itself coordinates to Cd(II) ion in the network. However, the lipophilic group of the guest molecule may decrease the coordination effects. From the above, it is guessed that short-alkyl alcohol molecules such as propanol coordinate to Cd(II) ion of

$\text{Cd}(\text{CN})_2$. However, until now, it has been reported that $\text{Cd}(\text{II})$ ions of $\text{Cd}(\text{CN})_2$ are coordinated by not the short-alkyl alcohol molecules but water molecules [6,7,10]. In the case of **I** and **II**, it is suggested that the hydrogen bonds (Figures 1c and 2d) between two alkoxyethanol molecules assist alkoxyethanol molecules coordinating to $\text{Cd}(\text{II})$ ions. In other words, it is suggested that the alkoxyethanol dimer $(\text{RCH}_2\text{CH}_2\text{OH})_2$ serves as a template for $\text{Cd}(\text{CN})_2$ frameworks. Complex **II** contains two kinds of coordination geometries of the $\text{Cd}(\text{II})$ ions by total capacity of the $\text{Cd}(\text{CN})_2$ framework. The coordination geometries of $\text{Cd}(\text{II})$ ions and $\text{Cd}(\text{CN})_2$ framework structures depended on the difference of alkyl chains for alkoxyethanol molecules.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/6/9/103/s1>, Figure S1: TG and DTG plots of **I**, Figure S2: TG and DTG plots of **II**, Figure S3: TG and DTG plots of **III**, CdCN2_Rcel.cif: Crystal analysis data for complexes **I–III**.

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