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A new type of mineralomimetic cadmium cyanide host framework containing methyl acetate

Takafumi Kitazawa*

Department of Chemistry, Faculty of Science. Toho University, Miyama, Funabashi, Chiba 274, Japan

The use of the methyl acetate molecule as the guest has provided a novel mineralomimetic cadmium cyanide host $Cd(CN)_2$ framework with space group *Pnma*, which is more distorted than the analogous low temperature form of cristobalite with space group $P4_12_12$. The novel clathrate $Cd(CN)_2 \cdot MeCO_2Me$ **1** crystallized in the orthorhombic space group *Pnma* with $a = 8.497(4)$, $b = 9.167(4)$, $c = 12.571(4)$ Å. The novel host framework is an example of a mineralomimetic $Cd(CN)_2$ framework which would suggest the possibility of a SiO_2 framework similar to **1**.

The wide topological similarities among crystalline cadmium cyanide, water, silica, aluminosilicate and gallophosphate has recently extended to materials chemistry. Since the first mineralomimetic behavior of the cadmium cyanide systems was reported in 1988,[1,2] cadmium cyanide clathrates with the silica-mimetic structure have stimulated considerable interest due to their variations of $Cd(CN)_2$ structures consisting of tetrahedral Cd atoms and bridged cyano ligands between Cd atoms.[3–15] The mode of host $Cd(CN)_2$ depends on the guest molecules. The H-tridymite, H-cristobalite and L-cristobalite-like hosts of $Cd(CN)_2$ have been obtained by selecting guest species with suitable properties, sizes, shapes and symmetries.[4] The dimethyl carbonate clathrate $Cd(CN)_2 \cdot (MeO)_2CO$ **2** contains a mineralomimetic framework of $Cd(CN)_2$ analogous to the low temperature form of cristobalite.[5] The effect on the cadmium cyanide $Cd(CN)_2$ host framework of using methyl acetate $MeCO_2Me$ as guest molecule, is now examined, whose properties, size, shape and symmetry are different from the previously reported dimethyl carbonate $(MeO)_2CO$. The novel mineralomimetic host structure of the clathrate obtained, $Cd(CN)_2 \cdot MeCO_2Me$ **1** of orthorhombic space group *Pnma* with $a = 8.497(4)$, $b = 9.167(4)$, $c = 12.571(4)$ Å, is more distorted than that of the L-cristobalite-like clathrate $Cd(CN)_2 \cdot (MeO)_2CO$ **2** which crystallizes in the tetragonal $P4_12_12$ space group [$a = 9.042(5)$, $c = 12.027(5)$ Å].[5]

Experimental

Preparation of $Cd(CN)_2 \cdot MeCO_2Me$ 1

The methyl acetate clathrate was synthesized by a method similar to that used for the dimethyl carbonate clathrate $Cd(CN)_2 \cdot (MeO)_2CO$ **2**.[5] $CdCl_2 \cdot 2.5H_2O$ (7 mmol) and $K_2[Cd(CN)_4]$ (7 mmol) were dissolved in 100 ml of water and the aqueous solution was filtered through a plastic membrane of 0.45 μm pore size. Colorless crystals suitable for single crystal determination were obtained by vapor diffusion after standing for a month at room temperature. The formation and decomposition of the clathrate were ascertained by IR and powder X-ray diffraction patterns. After standing for one day under the atmosphere the sample turned into neat $Cd(CN)_2$ which contains double interpenetrating frameworks.

The products lose the guest molecules readily upon exposure to air so that the above composition is based on the results of the X-ray structural analyses. The measured density of the material also supported the composition.

Table 1 Positional parameters and U_{eq} for $Cd(CN)_2 \cdot MeCO_2Me$ **1**

atom	x	y	z	$U_{eq}/\text{Å}^2$
host				
Cd	0.5936(1)	0.25	0.8956(1)	0.064(1)
CN(1)	0.3866(11)	0.25	0.7785(9)	0.083(3)
CN(2)	0.2864(13)	0.25	0.7180(7)	0.078(3)
CN(3)	0.5185(8)	0.4453(8)	0.9790(5)	0.079(2)
guest				
O(1)	0.323(2)	0.25	0.452(1)	0.137(4)
O(2)	0.527(3)	0.25	0.413(2)	0.33(2)
C(1)	0.416(3)	0.25	0.369(2)	0.35(3)
C(2)	0.343(5)	0.25	0.266(1)	0.49(4)
C(3)	0.601(3)	0.25	0.512(3)	0.26(2)

Table 2 Selected distances (Å) and angles (°) for $MeCO_2Me$ **1**

host			
Cd—CN(1)	2.29(1)	Cd—CN(2^{I})	2.17(1)
Cd—CN(3)	2.170(7)		
CN(1)—CN(2)	1.14(1)	CN(3)—CN(3^{II})	1.18(1)
guest			
C(1)—O(1)	1.30(3)	C(1)—O(2)	1.09(3)
O(2)—C(3)	1.40(3)	C(1)—C(2)	1.43(3)
host–guest			
Cd···O(1^{I})	2.74(1)		
host			
CN(1)—Cd—CN(1^{I})	98.75(9)	CN(1)—Cd—CN(2^{I})	99.0(4)
CN(1)—Cd—CN(3)	94.9(2)	CN(3)—Cd—CN(3^{III})	111.2(4)
CN(3)—Cd—CN(2^{I})	122.6(2)	CN(3)—Cd—CN(1^{I})	122.6(2)
CN(1)—Cd—O(1^{I})	175.4(4)	CN(3)—Cd—O(1^{I})	82.6(2)
CN(2^{I})—Cd—O(1^{I})	85.6(4)	Cd—CN(1)—CN(2)	178(1)
Cd^{IV}—CN(2)—CN(1)	179(1)	Cd—CN(3)—CN(3^{II})	177.1(9)
guest			
O(1)—C(1)—O(2)	97(2)	O(1)—C(1)—C(2)	118(3)
C(2)—C(1)—O(2)	145(3)	C(1)—O(2)—C(3)	147(3)

Symmetry operations: I $x+1/2, -y+1/2, -z+3/2$; II $-x+1, -y+1, -z+2$; III $x, -y+1/2, z$; IV $x-1/2, -y+1/2, -z+3/2$.

X-Ray structure determination

A single crystal of dimensions 0.35 × 0.30 × 0.25 mm was coated with epoxy resin in order to reduce decomposition and evaporation of the guest molecules. The collection of X-ray diffraction intensity data was carried out on a Rigaku AFC5S diffractometer (Mo-Kα radiation: $\lambda = 0.710\,69$ Å) at 293 K and a Ψ-scan absorption correction was performed. The transmission factors are between 0.88 and 1.0. Crystal data: $Cd(CN)_2 \cdot MeCO_2Me$, $M = 238.52$, orthorhombic, space group *Pnma* (no. 62), $a = 8.497(4)$, $b = 9.167(4)$, $c = 12.571(4)$ Å, $U =$

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* E-mail: kitazawa@chem.sci.toho-u.ac.jp

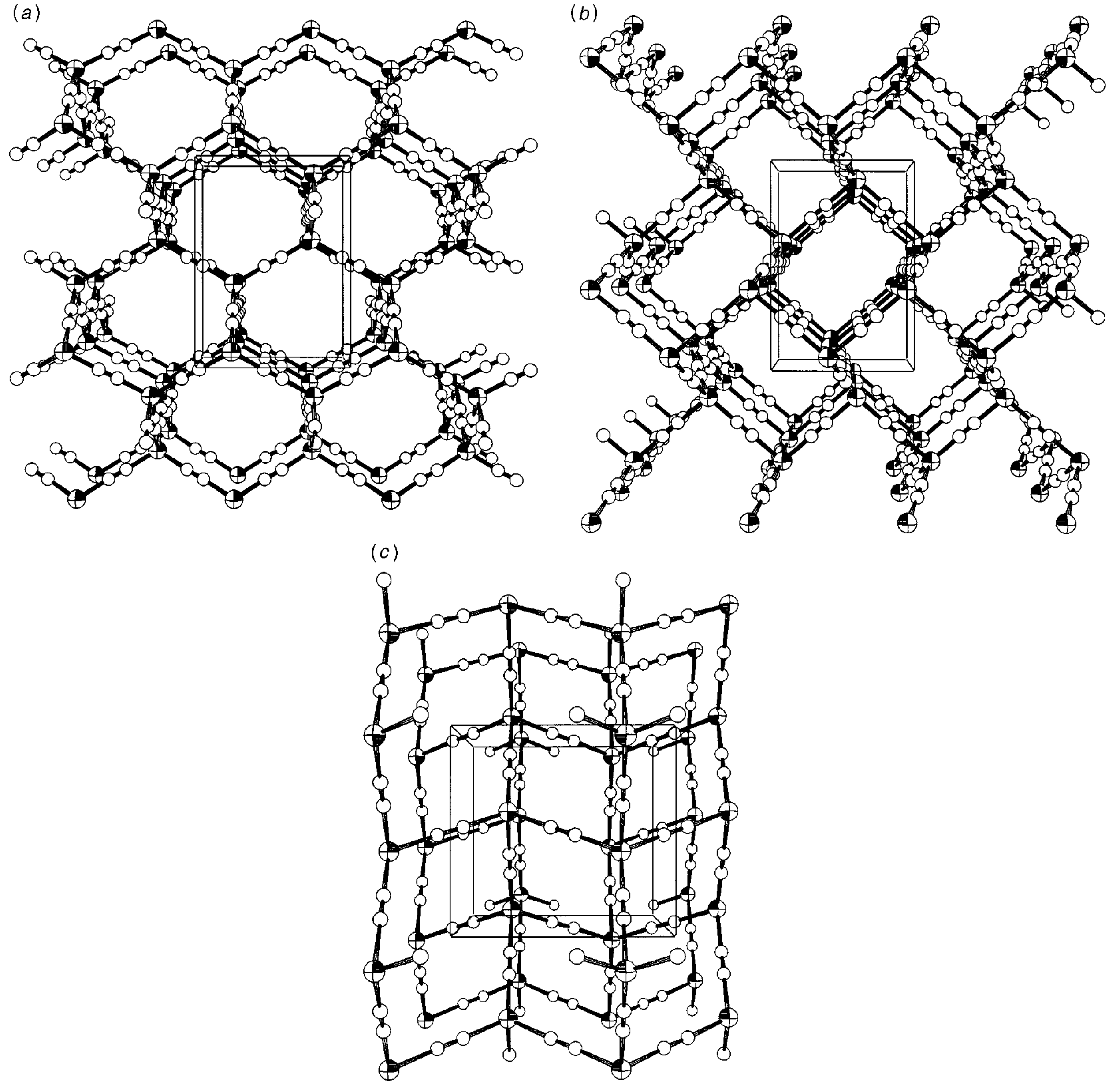

Fig. 1 The host structure of $Cd(CN)_2 \cdot MeCO_2Me$ **1**: (*a*) perspective view along the *a* axis, (*b*) along the *b* axis, (*c*) along the *c* axis

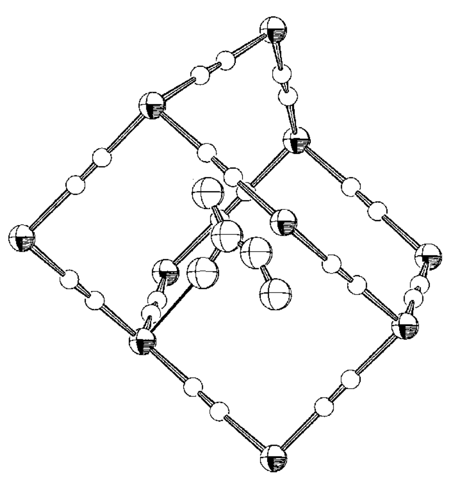

Fig. 2 The cavity of the the clathrate $Cd(CN)_2 \cdot MeCO_2Me$ **1**: the Cd—O(1) distance is 2.74(1) Å. The $MeCO_2Me$ molecule is located on the mirror plane of the crystal.

979.1(7) $Å^3$, $Z=4$, $D_m=1.60(1)$, $D_x=1.62$ g cm^{-3}, μ(Mo-Kα)$=21.85$ cm^{-1}. 1188 reflections observed, 9 restraints and 58 parameters refined: $R=0.0561[I>2\sigma(I)]$, goodness of fit (GOF)$=1.278$. The structure was solved using the TEXSAN software package installed on the diffractometer system[16] and refined by the full-matrix least-squares methods with the program SHELXL-93.[17] After refinement of the host lattice $Cd(CN)_2$, the difference map suggested that the guest $MeCO_2Me$ molecules displayed considerable positional disorder owing to the large thermal motion and pseudo-symmetry associated with the space group. Restraints of the guest atoms were applied by the FLAT, DFIX and DELU instruction cards of SHELXL-93. All the non-hydrogen atoms were refined anisotropically; hydrogen atoms were not located. Since disorder in the orientation of the cyanide group between tetrahedral Cd atoms has been found by solid state ^{113}Cd NMR spectroscopy in $Cd(CN)_2$ host–guest materials,[13,14] all the relevant C and N atoms were assumed to have 50% probability of being C and N and denoted as CN. The disordered cyanide atoms were refined using the EXYZ and EADP constraints of SHELXL-93. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See

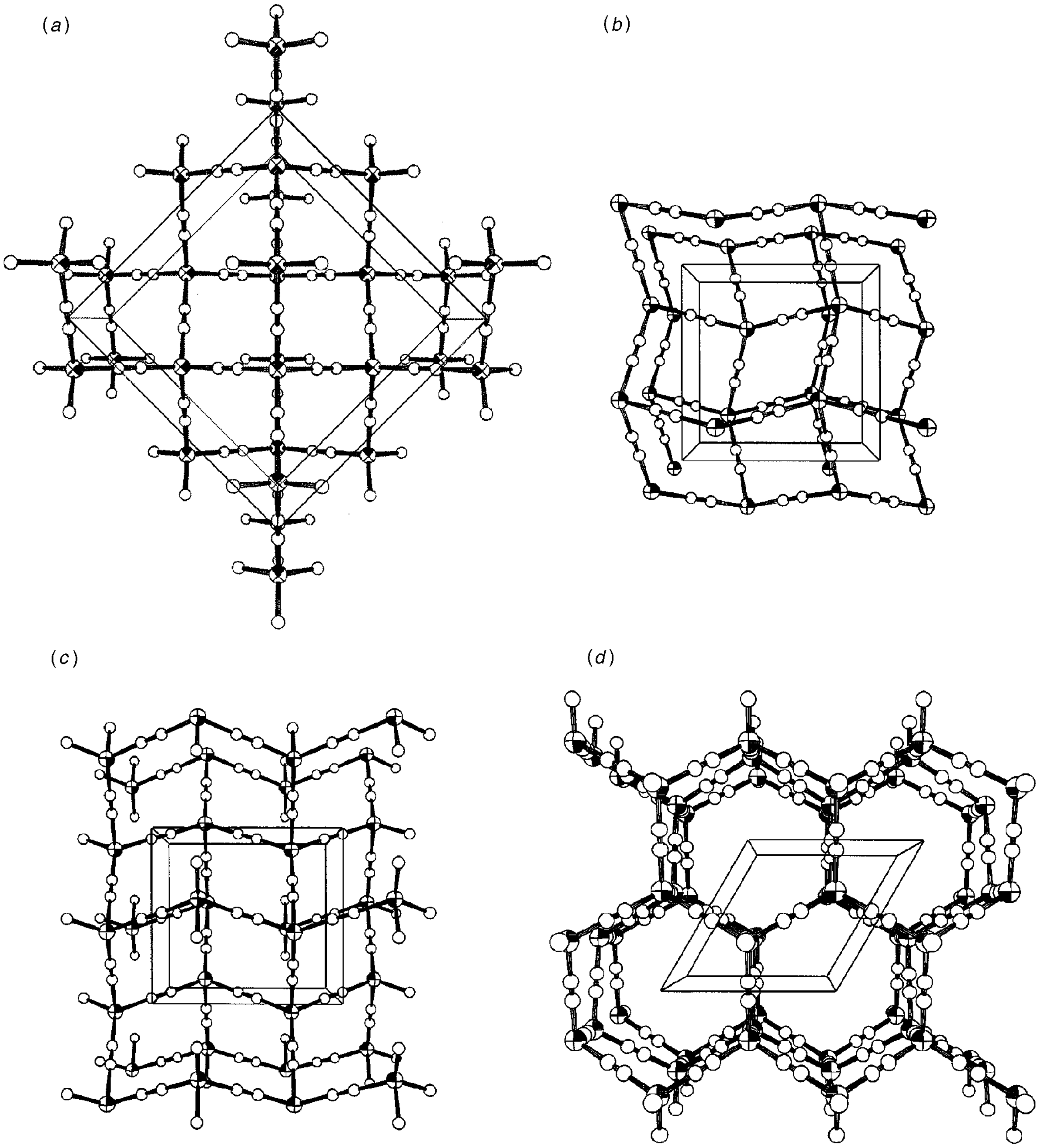

Fig. 3 Structure of $Cd(CN)_2$ host frameworks viewed along the *c* axis: (*a*) H-cristobalite-like (*Fd*3*m*) type; (*b*) L-cristobalite-like ($P4_12_12$, $Z=4$) type; (*c*) distorted-cristobalite-like (*Pnma*) type; (*d*) H-tridymite-like ($P6_3/mmc$) type

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Results and Discussion

The refined atomic parameters are listed in Table 1 and selected distances and angles are listed in Table 2. The crystal structure is illustrated in Fig. 1 and 2. The X-ray single crystal determination shows that the host framework of **1** is composed of individual tetrahedral units linked to four neighboring tetrahedra by Cd—CN—Cd linkages. The topological properties of the host framework in **1** are similar to those of cristobalite SiO_2. While the Si—O—Si distance is *ca.* 3.2 Å, the Cd—CN—Cd distance is *ca.* 5.5 Å analogous to previously reported $Cd(CN)_2 \cdot n$G clathrates and related compounds.[1–14]

The space group of **1** is orthorhombic (*Pnma*) while SiO_2 in the space group *Pnma* has not been found. The Cd atom is located on the crystallographic mirror plane. In the host framework there are two crystallographically independent bridged cyano groups. Groups CN(1) and CN(2) are located on the mirror plane. The center of CN(3) is an inversion center, so that, based on the X-ray result alone, this group must be 1 : 1 disordered.

The host structure of the clathrate, $Cd(CN)_2 \cdot MeCO_2Me$ **1** [orthorhombic (*Pnma*) $a=8.497(4)$, $b=9.167(4)$, $c=12.571(4)$ Å] differs from that of the L-cristobalite-like clathrate $Cd(CN)_2 \cdot (MeO)_2CO$ **2** [tetragonal ($P4_12_12$) $a=9.042(5)$, $c=12.027(5)$ Å].[5] The tetrahedral $P4_12_12$ host lattice in **2** ($Z=4$) is transformed into the orthorhombic *Pnma* setting in **1** ($Z=4$). The deformation of the host framework is due to the guest methyl acetate, whose symmetry is lower than that of dimethyl carbonate. However, the orthorhombic *Pnma* host framework of **1** contains a crystallographically mirror plane while the tetrahedral $P4_12_12$ host framework of **2** does not. Since the cubic *Fd*3*m* host framework in H-cristobalite-like structures such as $Cd(CN)_2 \cdot CMe_4$ has mirror planes,[2,4,8] the orthorhombic *Pnma* host framework of **1** can be considered to retain the mirror plane upon distortion from the cubic $Fd\bar{3}m$ host framework. The tetrahedral $P4_12_12$ host lattice in $Cd(CN)_2 \cdot Pr^iCN$ **3** [$a = 12.483(7)$, $c = 12.719(3)$ Å, $Z = 8$] is also more distorted than that of **2**.[4] The distortion mode of host framework in **1** is also different from that of **3**. While the Cd atoms in **1** are located on the mirror plane of *Pnma*, those in **3** are displaced at the general positions of $P4_12_12$.

As shown in Fig. 2, the guest methyl acetate is accommodated in the adamantane-like cavity, and participates in weak bonding between its carbonyl O atom and the host Cd atom. The adamantane-like cavity volumes of **1** and **2** are 122 and 123 Å^3 respectively, which are approximately one-eighth the volume of the unit cell. While the size of the $MeCO_2Me$ molecule is smaller than that of $(MeO)_2CO$ the methyl acetate clathrate has a slightly smaller adamantane-like cavity. The carbonyl O atom of **2** is distributed statistically about the two-fold axis of the crystal,[5] whereas that of **1** is fixed on the mirror plane of the crystal. The guest $MeCO_2Me$ molecules located on the crystallographic mirror plane display considerable disorder. The very large temperature factors of the atoms and the unusual geometries are related to the disorder of the guest molecules. As to the size and shape of the cavity, planar conformations, thermal motions and polarities are other factors to be considered.

The interaction between the Cd and O(1) of the guest $C{=}O$ group with a $Cd{-}O(1)$ distance of 2.74(1) Å is associated with the formation of the more distorted mineralomimetic $Cd(CN)_2$ framework. The distance $Cd{-}O(C{=}O)$ in **1** is shorter than that in **2** [3.02(2) Å] and suggests the Cd is five-coordinate. Coordination of the guest molecule as a fifth ligand from the cavity to the host Cd atom has previously been found in cadmium cyanide clathrate systems.[4,13]

The present work also shows the remarkable flexibility of cadmium cyanide clathrates. The guest $MeCO_2Me$ with lower symmetry allows formation of the novel mineralomimetic $Cd(CN)_2$ framework with space group *Pnma*. $Cd(CN)_2 \cdot n$G clathrates have been classified into at least five types: $P6_3/mmc$ ($Z = 4$),[4] $Fd\bar{3}m$ ($Z = 8$),[2,4,8] $P4_12_12$ ($Z = 4$),[4,5] $P4_12_12$ ($Z = 8$),[4] and *Pnma* ($Z = 4$) (Fig. 3). Possibilities remain to form new mineralomimetic cadmium cyanide clathrates other than of these five types.

Conclusion

The new host framework with space group *Pnma* has been obtained by selecting suitable guest molecules. To my knowledge, SiO_2 frameworks similar to **1** have not been found until now. The formation of the *Pnma* type $Cd(CN)_2$ framework would indicate the formation of a novel type SiO_2 framework which has not been obtained. The result is an example that mineralomimetic chemistry using $Cd(CN)_2$ can potentially feedback to the field of natural or/and synthetic mineral structures. The kinetics of the reaction of guest loss together with concomitant phase changes remain to be explored.

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