

The Structure of the Mineralomimetic Cadmium Cyanide–Dimethyl Carbonate Clathrate*

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Abstract. $\text{Cd}(\text{CN})_2 \cdot (\text{CH}_3\text{O})_2\text{CO}$ (**1**) contains a mineralomimetic framework of $\text{Cd}(\text{CN})_2$ analogous to the low temperature form of cristobalite. The host framework is isostructural to those of previously reported $\text{Cd}(\text{CN})_2 \cdot \text{G}$ compounds ($\text{G} = \text{CHCl}_2\text{CH}_2\text{Cl}$ **2**, $(\text{CH}_3)_2\text{CHBr}$ **3**). The dimethyl carbonate molecules in the adamantane-like cage display orientation disorder associated with the location of the carbonyl oxygen atom.

Key words. Cadmium cyanide, crystal structure, clathrate, mineralomimetic chemistry, dimethyl carbonate

Supplementary Data relating to this article are deposited with the British Library as supplementary Publication No. SUP 82204 (10 pages).

1. Introduction

A new family of structures built from Cd atoms linked by cyanide bridges, analogous to silica and silicate, opens up an immense field of study in mineralomimetic chemistry [1–15]. The ability of $\text{Cd}(\text{CN})_2$ to form inclusion compounds was first confirmed in 1988 by the discovery of the clathrate $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ [5], whose host framework $\text{Cd}(\text{CN})_2$ is isostructural with high(H)-cristobalite (high temperature form of cristobalite) [5,6,8]. Recently a theoretical study of host–guest interactions in H-cristobalite-like $\text{Cd}(\text{CN})_2 \cdot \text{G}$ clathrates has been reported [15]. Silica-mimetic polymorphism of the $\text{Cd}(\text{CN})_2$ host frameworks depend on the guest G in the $\text{Cd}(\text{CN})_2 \cdot x\text{G}$ clathrate. The H-tridymite, H-cristobalite and low(L)-cristobalite-like hosts of $\text{Cd}(\text{CN})_2$ have been obtained by using guest molecules of different properties, sizes, shapes and symmetries [5,6,8]. A quartz-like $\text{Cd}(\text{CN})_2$ host lattice has not yet been obtained. Using alcohol and ether molecules as guest allows the host framework to contain Cd atoms having coordinated water, where the guest molecules form hydrogen bonds with the water molecules coordinated to the Cd atoms [3,12–14]. We have now examined the effect on the cadmium cyanide $\text{Cd}(\text{CN})_2$ host framework of using dimethyl carbonate as guest, whose property, size, shape

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Table I. Positional Parameters and U_{eq} for $Cd(CN)_2 \cdot (CH_3O)_2CO$ (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Occupancy
<i>Host</i>					
Cd	0.3099(1)	0.3099	0	0.056(1)	
CN(11)	0.2663(11)	0.1115(11)	0.1057(8)	0.067(2)	
CN(12)	0.2390(12)	0.0104(12)	0.1550(9)	0.070(2)	
<i>Guest</i>					
C(1)	0.875(2)	0.875	0	0.15(1)	
O(1)	0.975(3)	0.816(3)	0.058(3)	0.16(1)	0.5
O(2)	0.816(4)	0.924(3)	0.113(2)	0.45(3)	
C(2)	0.718(7)	1.035(7)	0.098(4)	0.46(3)	

and symmetry are different from the previously reported guest molecules. The host structure of the clathrate obtained, $Cd(CN)_2 \cdot (CH_3O)_2CO$ (1), is isostructural with those of L-cristobalite-like $Cd(CN)_2 \cdot G$ ($G = CHCl_2CH_2Cl$ 2, $(CH_3)_2CHBr$ 3) with the tetragonal $P4_12_12$ space group [6].

2. Experimental

2.1. PREPARATION OF $Cd(CN)_2 \cdot (CH_3O)_2CO$ (1)

The dimethyl carbonate clathrate was obtained by procedures similar to those used for other silica-mimetic $Cd(CN)_2 \cdot nG$ clathrates [6]. $CdCl_2 \cdot 2.5H_2O$ and $K_2[Cd(CN)_4]$ (7 mmol each) were added to 100 mL of water. Colorless crystals were obtained by the vapor diffusion method.

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

2.2. STRUCTURE DETERMINATION

A single crystal of dimension $0.30 \times 0.25 \times 0.25$ 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 (MoK_α : $\lambda = 0.71069$ Å) at 293 K. Crystal data: $Cd(CN)_2 \cdot (CH_3O)_2CO$, $M = 254.52$, $P4_12_12$ (No. 92), $a = 9.042(5)$, $c = 12.027(5)$ Å, $U = 983.3(8)$ Å³, $Z = 4$, $D_m = 1.70(1)$, $D_x = 1.72$ g cm⁻³, $\mu(MoK_\alpha) = 21.88$ cm⁻¹. 711 reflections observed, 10 restraints and 56 parameters refined: $R = 0.0355$ [$I > 2\sigma(I)$], $R_w = 0.1088$ (all data), goodness of fit (gof) = 1.072. The structure was solved using the TEXSAN software package installed on the diffractometer system [17] and refined by the full-matrix least-squares methods with the program SHELXL93 [18]. After refinement of the host framework $Cd(CN)_2$, difference maps indicated that the guest $(CH_3O)_2CO$ molecules displayed positional disorder due to the large thermal motion and pseudosymmetry of the structure. The restraints of guest atoms were

Table II. Selected distances (Å) and angles (°) for Cd(CN)₂·(CH₃O)₂CO (1)

<i>Host</i>			
Cd—CN(11)	2.234(9)	Cd—CN(12)*1	2.187(11)
CN(11)—CN(12)	1.118(12)	Cd—Cd	5.537(2)
<i>Guest</i>			
C(1)—O(1)	1.26(2)	C(1)—O(2)	1.52(2)
O(2)—C(2)	1.35(3)		
<i>Host—Guest</i>			
Cd --- O(1)*2	3.02(2)		
<i>Host</i>			
CN(11)—Cd—CN(11)*3	92.3(5)	CN(11)—Cd—CN(12)*1	109.4(3)
CN(11)—Cd—CN(12)*4	106.3(4)	CN(12)*1—Cd—CN(12)*4	127.5(6)
Cd—CN(11)—CN(12)	176.6(9)	Cd*5—CN(12)—CN(11)	178.7(9)
<i>Guest</i>			
O(1)—C(1)—O(2)	83(2)	O(1)—C(1)—O(2)*3	98(2)
O(1)—C(1)—O(1)*3	156(3)	C(1)—O(2)—C(2)	109(3)
O(2)—C(1)—O(2)*3	175(3)		

*1 : $1/2 - x, 1/2 + y, 1/4 - z;$

*2 : $-1/2 + y, 3/2 - x, -1/4 + z$

*3 : $y, x, -z;$

*4 : $1/2 + y, 1/2 - x, -1/4 + z$

*5 : $1/2 - y, -1/2 + x, 1/4 + z.$

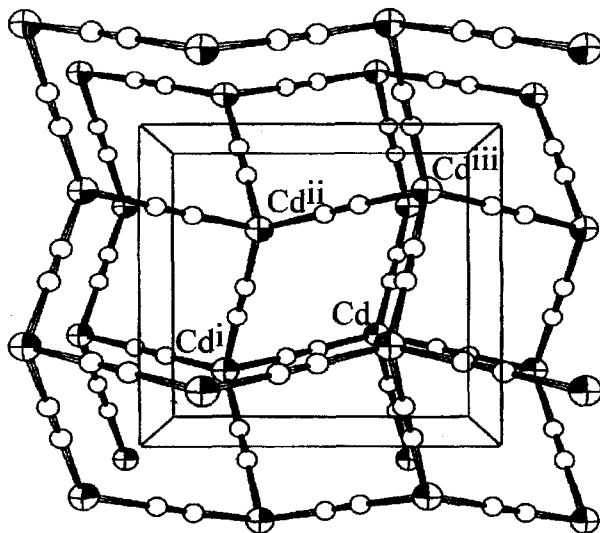


Figure 1. The host structure of Cd(CN)₂·(CH₃O)₂CO (1), viewed along the *c* axis. Cd (0.3099(1), 0.3099(1), 0); Cdⁱ (0.1901(1), 0.8099(1), 0.25); Cdⁱⁱ (0.6901(1), 0.6901(1), 0.5); Cdⁱⁱⁱ (0.8099(1), 0.1901(1), 0.75). Symmetry operations: *i* $-x + 0.5, x + 0.5, 0.25$; *ii* $1 - x, 1 - x, 0.5$; *iii* $x + 0.5, -x + 0.5, 0.75$.

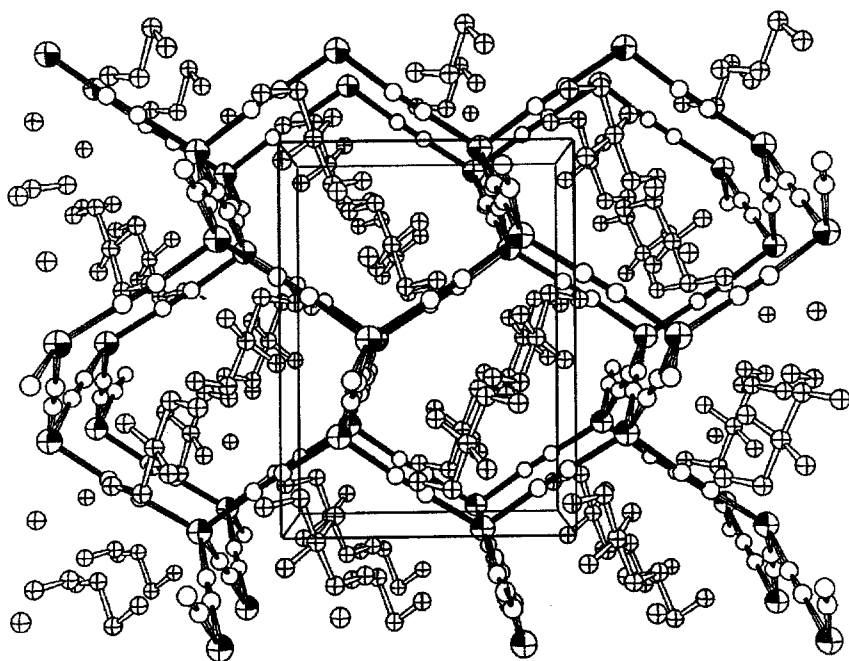


Figure 2. View of the clathrate $\text{Cd}(\text{CN})_2 \cdot (\text{CH}_3\text{O})_2\text{CO}$ (1) along the a axis.

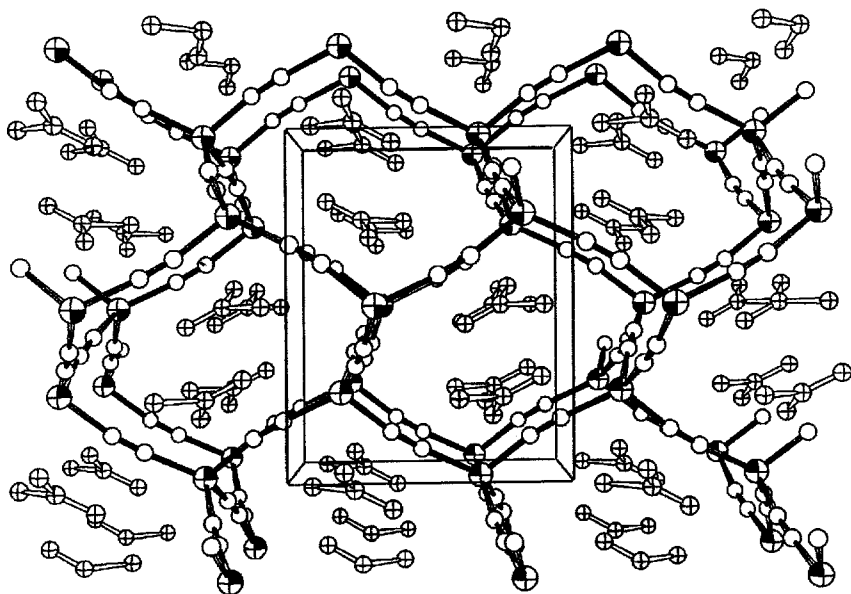


Figure 3. View of clathrate $\text{Cd}(\text{CN})_2 \cdot (\text{CH}_3)_2\text{CHBr}$ (3) along the a axis.

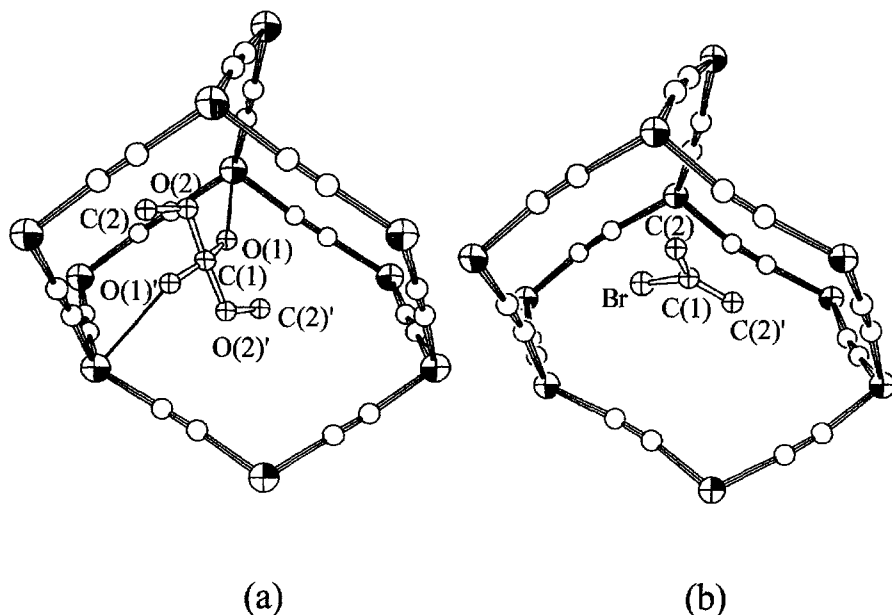


Figure 4. (a) The cavity of the the clathrate $\text{Cd}(\text{CN})_2 \cdot (\text{CH}_3\text{O})_2\text{CO}$ (**1**). The O(1) atoms are disordered. The Cd—O(1) distance is 3.02(2) Å. The C(1) atom is located on the two-fold axis of the crystal. (b) The cavity of the the clathrate $\text{Cd}(\text{CN})_2 \cdot (\text{CH}_3)_2\text{CHBr}$ (**3**). The Br and C(1) atoms are located on the two-fold axis of the crystal.

applied by the FLAT, DFIX and DELU instructions of SHELXL93. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms have not been located. Since disorder in the orientation of the cyanide group between tetrahedral Cd atoms has been found by solid state Cd NMR spectroscopy in $\text{Cd}(\text{CN})_2$ host-guest materials [13], all the relevant C and N atoms were assumed to have 50% probability of being C and N and are denoted as C.N. The disordered cyanide atoms were refined using the EXYZ and EADP constraints of SHELXL93. Crystallographic diagrams were obtained using the ORTEP program [19].

3. Results and Discussion

The refined atomic parameters are listed in Table I; the selected distances and angles are listed in Table II. The crystal structure is illustrated in Figures 1 and 2. The X-ray single crystal determination shows that the topological properties of the host framework in **1** are similar to those of L-cristobalite-like $\text{Cd}(\text{CN})_2 \cdot \text{G}$ compounds (G = $\text{CHCl}_2\text{CH}_2\text{Cl}$ **2**, $(\text{CH}_3)_2\text{CHBr}$ **3**) [6]. The cell dimensions of **1** ($a = 9.042(5)$, $c = 12.027(5)$ Å) are slightly different from those of **2** ($a = 8.978(6)$, $c = 11.934$ Å) and **3** ($a = 9.124(1)$, $c = 11.335(3)$ Å). The Cd atoms are located in special positions similar to the Si atoms of L-cristobalite. Eight cyano groups in the unit cell are placed on the general position similar to the O atoms of L-

cristobalite. Like the H-cristobalite-like framework $\text{Cd}(\text{CN})_2$, the host framework is composed of individual tetrahedral units linked to four neighboring tetrahedra by the $\text{Cd}-\text{CN}-\text{Cd}$ linkage. Clearly there is a large difference in the size of the $\text{Cd}(\text{CN})_2$ and SiO_2 tetrahedra, since organic guest species must be accommodated in the adamantane-like cavity. The $\text{Cd}-\text{CN}-\text{Cd}$ distance is ca. 5.5 Å whereas the $\text{Si}-\text{O}-\text{Si}$ distance is ca. 3.2 Å.

The topological relation between the H- and L-cristobalite-like framework $\text{Cd}(\text{CN})_2$ is similar to that between the two cristobalite SiO_2 structures [16]. The H and L-cristobalite-like inclusion compounds $\text{Cd}(\text{CN})_2 \cdot \text{G}$ crystallise in the space group $Fd\bar{3}m$ and $P4_12_12$, respectively. According to Ref. 16, in order to compare the two structures, the conventional P cell of space group $P4_12_12$ on L-cristobalite-like clathrates is transformed to an unconventional C cell which corresponds to the F cell of $Fd\bar{3}m$. In space group $P4_12_12$ the Cd atoms are in Wyckoff position $4a..2$ with the coordinate $x, x, 0$ ($x = 0.3099(1)$; **1**, $0.2963(2)$; **2**, $0.3179(3)$; **3**). The parameters $x = 0.3099$, 0.2963 and 0.3179 of the P cell change to $x = 0.0599$, 0.0463 and 0.0679 in the C cell. If x is 0, the special position of the C cell assumes the same coordinate triplets as special position $\bar{4}3m$ in space group $Fd\bar{3}m$ where the Cd atoms of the H-cristobalite-like host framework are located. These different x parameters reflect the distortion of the host framework. The tetrahedral Cd atom of clathrate **1** is rather distorted ($\text{CN}(11)-\text{Cd}-\text{CN}(11)$; $92.3(5)^\circ$ and $\text{CN}(12)-\text{Cd}-\text{CN}(12)$; $127.5(6)^\circ$).

When compared to H-cristobalite-like $\text{Cd}(\text{CN})_2$, L-cristobalite-like $\text{Cd}(\text{CN})_2$ has a much less open structure. The adamantane-like cavity volume of the H-cristobalite-like $\text{Cd}(\text{CN})_2$ clathrate is ca 130 \AA^3 , which is approximately one-sixteenth of the volume of the unit cell. The distorted adamantane-like cavity volumes of the L-cristobalite-like $\text{Cd}(\text{CN})_2$ are 123 \AA^3 (**1**) 120 \AA^3 (**2**) and 118 \AA^3 (**3**), which are approximately one-eighth of the volume of the unit cell.

The guest $(\text{CH}_3\text{O})_2\text{CO}$ molecules in the distorted adamantane-like cavity display considerable disorder. The C(1) atom is located at a special position. The carbonyl oxygen O(1) atom is distributed statistically about the two-fold axis of the crystal. The significantly large temperature factors of the O(2) and C(2) atoms and the unusual geometries are related to the disorder of the $(\text{CH}_3\text{O})_2\text{CO}$ molecules. These crystal data cannot discriminate between static disorder and dynamic disorder. Spectroscopic methods, such as solid state $^2\text{H-NMR}$, will be helpful in investigating the dynamic behavior of the $(\text{CH}_3\text{O})_2\text{CO}$ molecules [20].

In the L-cristobalite-like clathrate series, $(\text{CH}_3\text{O})_2\text{CO}$ molecules require a larger cavity than the $\text{CH}_2\text{ClCHCl}_2$ and $(\text{CH}_3)_2\text{CHBr}$ molecules. The shape, size and conformation of $(\text{CH}_3\text{O})_2\text{CO}$, $\text{CHCl}_2\text{CH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{CHBr}$ are associated with the formation of L-cristobalite-like $\text{Cd}(\text{CN})_2$. However, this work also suggests that selection of the L-cristobalite-like host is delicate. The inclusion mode of $(\text{CH}_3\text{O})_2\text{CO}$ molecules is different from those of the $\text{CH}_2\text{ClCHCl}_2$ and $(\text{CH}_3)_2\text{CHBr}$ molecules (Figures 2 and 3). As shown in Figure 4, the two C—Me bonds of the $(\text{CH}_3)_2\text{CHBr}$ point toward the tripod consisting of one Cd atom and

three cyanide groups, whereas the two O—Me bonds of the $(\text{CH}_3\text{O})_2\text{CO}$ extend to the hexagonal channel built up of six Cd atoms. The different mode of the $(\text{CH}_3\text{O})_2\text{CO}$ molecules is related to the interaction between the Cd and O(1) of the guest C=O group with the Cd—O(1) distance of 3.02(2) Å (Figure 4b). A planar configuration and a thermal motion of the $(\text{CH}_3\text{O})_2\text{CO}$ are other factors to be considered. Much remains to be explored in the mineralomimetic chemistry of cadmium cyanide clathrates.

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