

Accommodation of an Aliphatic Guest Molecule in Hofmann-diaminooctane-type Host. A Model Structure of a Pillared Intercalation Compound

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Abstract. *catena*-[*catena*- μ -(1,8-Diaminooctane)cadmium(II) tetra- μ -cyanonickelate(II)]-(1-hexanol)(1/1) has been prepared as the first example of an aliphatic guest clathrate of the Hofmann-type and analogous metal complex hosts. The clathrate crystallizes in the monoclinic space group $P2_1/m$, $a = 11.470(2)$, $b = 7.782(1)$, and $c = 6.945(1)$ Å, $\beta = 105.29(1)^\circ$, $Z = 1$; $R = 0.043$ for 1865 reflections. The structure presents a model of pillared intercalation compounds formed between layers of metal complex sheets pillared by α,ω -ambidentate *n*-alkane-skeletal ligands and *n*-alkyl derivative guests.

Key words. Hofmann-type clathrate, 1,8-diaminooctane, 1-hexanol, crystal structure, tetracyanonickelate, pillared intercalation compound.

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1. Introduction

Although many pillared intercalation compounds have recently been reported as new materials or media for topotactic reactions, the structural discussions appear to have been limited to the earlier models sketched by Weiss in 1958 [1] and 1963 [2]. The crystal structure of *catena*-[*catena*- μ -(1,8-diaminooctane)cadmium(II) tetra- μ -cyanonickelate(II)]-(1-hexanol)(1/1), reported in this paper, presents a model of the pillared intercalation compounds composed of metal complex layers, *n*-alkane-skeletal molecules as the pillars, and *n*-alkyl derivatives as the guests. The present 1-hexanol clathrate is the first example in which an alkyl derivative can be accommodated as the guest molecule in Hofmann-type and analogous hosts [3].

Three-dimensional host structures such as that of the present clathrate have been synthesized using the α,ω -diaminoalkanes (diam) of the skeletal carbon-chain lengths from 4 to 9 for the Hofmann-diam-type clathrates [4–10]. Single crystal structure analyses have been carried out for the aromatic guest clathrates of the Hofmann-dabn-type [5, 8] and Hofmann-dahxn-type [6, 7, 10] hosts (dabn is 1,4-diaminobutane; dahxn is 1,6-diaminohexane). The host structures of these Hofmann-diam-type clathrates are flexible enough to enclathrate the guest aromatic molecules different in size and shape to a certain degree: the bridging diam ligand takes an appropriate skeletal conformation and the two-dimensionally extended cyanometal complex network is deformed depending on the geometry of the guest

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molecule. However, to our knowledge no aliphatic molecules have been enclathrated in the Hofmann-type and analogous hosts examined previously. Since the more flexible structures were expected for the host metal complexes with the longer carbon-chain diam ligands, the syntheses of Hofmann-daotn-type (daotn = 1,8-diaminooctane) inclusion compounds were attempted for aliphatic and other bulky guest molecules [11]. The daotn was selected because diams with an even number of skeletal carbon atoms have formed stable Hofmann-diam-type clathrates, and daotn has the longest even-carbon skeleton. From the more than thirty aliphatic molecules and other species screened against the Hofmann-daotn-type host, 1-hexanol was found to form well-developed crystals suitable for single crystal diffraction experiments.

2. Experimental

2.1. SYNTHESIS

The 1-hexanol clathrate was prepared by a method similar to those previously described for other Hofmann-diam-type clathrates. An aqueous solution containing CdCl_2 , $\text{K}_2[\text{Ni}(\text{CN})_4]$, and daotn in a 1 : 1 : 2 molar ratio was prepared; each concentration of the metal salt species was kept at 0.1 mol dm^{-3} . The solution was divided into three portions, each of which was covered with 1-hexanol. Two portions of the two-phased mixture were kept at 5°C in a refrigerator and one portion was kept at room temperature for one year. One of the portions kept in the refrigerator gave bright yellow crystals of the clathrate at the interface between the aqueous and the organic phases, but the other portion kept in the refrigerator and the portion kept at room temperature did not give any visually observable crystals. For these two portions crystals of the clathrate were grown by planting seed crystals of the clathrate and allowing the solutions to stand for a few months at 5°C and room temperature, respectively. Anal. Found: C, 41.33, H, 6.74; N, 16.00%. Calcd for $\text{Cd}(\text{C}_8\text{H}_{20}\text{N}_2)\text{Ni}(\text{CN})_4 \cdot \text{C}_6\text{H}_{13}\text{OH}$: C, 41.44; H, 6.57, N, 16.11%. The clathrate contains 1 mol of the guest molecule per 1 mol of the host metal complex; the 1 : 1 composition has been observed for several Hofmann-diam-type clathrates of aromatic guests.

2.2. STRUCTURE DETERMINATION

After preliminary Weissenberg photographs were taken, a $0.25 \times 0.20 \times 0.18 \text{ mm}^3$ single crystal coated with epoxy resin was subjected to the refinement of lattice parameters and collection of intensity data on a Rigaku AFC-6A four-circle automated diffractometer using $\text{MoK}\alpha$ radiation monochromated by graphite. The crystallographic and experimental data are as follows. $\text{CdNiC}_{18}\text{H}_{34}\text{N}_6\text{O}$, formula weight 521.62; monoclinic, $P2/m$; $a = 11.470(2)$, $b = 7.782(1)$, and $c = 6.945(1) \text{ \AA}$, $\beta = 105.29(1)^\circ$, $Z = 1$; $U = 568.0(2) \text{ \AA}^3$, $d_m = 1.56(2) \text{ g/cm}^3$ by the flotation method in mesitylene-bromoform mixture, $d_x = 1.56 \text{ g/cm}^3$; $\mu(\text{MoK}\alpha)/\text{cm}^{-1} = 18.17$; scan mode: $2\theta - \omega$; scan range: $2^\circ < 2\theta < 70^\circ$; peak scan width: $1.35 + \tan \theta$; scan rate/ $^\circ\text{min}^{-1} = 4$; number of reflections observed: 2440; number of independent reflections used ($|F_0| > 3\sigma(F_0)$), $p = 1856$; number of refined parameters, $q = 96$; $R = 0.043 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$, $R_w = 0.049 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}$, and $S = 0.41 = [\Sigma w(|F_0| - |F_c|)^2/(p - q)]^{1/2}$; $w = (60/|F_0|)^2$ for $|F_0| \geq 60$, $w = 0.85$ for $60 > |F_0| \geq 30$, and $w = 0.25$ for $|F_0| < 30$.

The structure solution and the refinement of the parameters were achieved by the ordinary heavy-atom method, successive Fourier syntheses, and block-diagonal least-squares

processes. All the calculations were performed on a Hitac M-280H computer at the Computation Center of the University of Tokyo using the programs in UNICSIII [12] including ORTEP [13] and their local versions; the atomic scattering factors, including those for real and imaginary dispersion corrections, were taken from reference [14]. Among the three space groups $P2/m$, Pm , and $P2$ suggested from the Laue symmetry observed on the preliminary Weissenberg photographs, $P2/m$ was selected and used to successfully refine the structure. Before the final refinement the host structure alone had been refined to $R = 0.069$ with the anisotropic thermal parameters for all the non-hydrogen atoms and the isotropic ones fixed at 6.0 \AA^2 for the hydrogen atoms; the adjusted parameters converged into the range of Δ/σ less than 0.3. At the final stage the positional and thermal parameters of the non-hydrogen guest atoms and the thermal parameters of the doatn skeletal atoms were adjusted to $R = 0.044$ [15]. In the final difference Fourier map, peaks and holes remaining in the regions of $y/b = 0$ and 0.5 were of less than $\pm 1.0e \text{ \AA}^{-3}$.

The atomic parameters are listed in Table I; the thermal parameters are given as the equivalent isotropic parameters. Selected bond distances and angles are given in Table II.

As Figure 1 shows, the structure of the metal complex host is quite analogous to those of Hofmann-dabn-type and Hofmann-dahxn-type. The layers of the two-dimensionally extended wavy network of *catena*-[cadmium tetra- μ -cyanonickelate (II)] are bridged by the doatn ligand which makes a slanted pillar between the layers with an all-*trans* skeletal conformation. According to the $P2/m$ space group applied, the skeletal atoms of the doatn ligand and of the guest 1-hexanol are located on the mirror planes at $y/b = 0$ and 0.5, respectively. The guest 1-hexanol is accommodated in the cavity surrounded by four doatn columns between the layers. However, the thermal amplitudes of the skeletal atoms of the 1-hexanol, especially those amplitudes along the z -axis of the crystal, are so large that the apparent molecular shape is distorted considerably with respect to the skeletal bond angles and distances. The figure of 1-hexanol should be seen as the average of thermal motions of statistically distributed orientations in the cavity.

Table I. Atomic parameters.

Atom	G^a	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^2$ ^b
host					
Cd	0.25	0.0	0.0	0.0	1.822(9)
Ni	0.25	0.0	0.5	0.5	2.06(2)
N(1)	1.00	-0.0558(2)	0.2199(3)	0.1907(4)	3.30(9)
C(1)	1.00	-0.0365(2)	0.3290(3)	0.3071(4)	2.60(8)
N(2)	0.50	0.1901(3)	0.0	0.2148(5)	4.2(2)
C(2)	0.50	0.2078(3)	0.0	0.4319(6)	3.4(2)
C(3)	0.50	0.3378(4)	0.0	0.5499(7)	5.5(3)
C(4)	0.50	0.3567(4)	0.0	0.7741(6)	4.1(2)
C(5)	0.50	0.4878(4)	0.0	0.8893(7)	4.6(2)
guest					
C(6)	0.50	0.460(2)	0.5	0.402(2)	25(1)
C(7)	0.50	0.382(3)	0.5	0.274(5)	40(2)
C(8)	0.50	0.264(2)	0.5	0.161(2)	16(1)
O(1)	0.25	0.298(4)	0.594(6)	0.068(5)	34(2)

^a G : multiplicity.

^b $B_{\text{eq}} = 4[\sum_i \sum_j B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j]/3$.

Table II. Selected atomic distances and angles.*

distance/Å				
Ni—C(1):	1.856(2);	C(1)—N(1):	1.153(4); N(1)—Cd:	2.354(3);
Cd—N(2):	2.294(3);	N(2)—C(2):	1.467(5); C(2)—C(3):	1.500(5);
C(3)—C(4):	1.514(6);	C(4)—C(5):	1.506(6); C(5)—C(5')	1.49(1);
O(1)—C(8):	1.11(5);	C(8)—C(7):	1.37(4); C(7)—C(6):	1.08(3);
C(6)—C(6')	1.43(2)			
angle/°				
C(1)—Ni—C(1')	91.6(2);	Ni—C(1)—N(1):	177.7(3);	
C(1)—N(1)—Cd:	154.1(3);	N(1)—Cd—N(1')	93.3(1);	
N(1)—Cd—N(2):	89.3(2);	Cd—N(2)—C(2):	121.2(3);	
N(2)—C(2)—C(3):	114.2(4);	C(2)—C(3)—C(4):	114.4(5);	
C(3)—C(4)—C(5):	113.5(5);	C(4)—C(5)—C(5')	116.0(7);	
O(1)—C(8)—C(7):	84(4);	C(8)—C(7)—C(6):	161(3);	
C(7)—C(6)—C(6')	165(3)			

* Those values related to the guest atoms, C(6), C(7), C(8), and O(1), cannot be put with great confidence. The number with prime denotes the atom generated by a symmetry operation, inversion or reflection.

Another type of disorder in the 1-hexanol clathrate arises from the statistical distribution of the head methyl and the tail hydroxyl groups. From analysis in the $P2/m$ space group, the head methyl and tail hydroxyl groups are distributed equally at both ends of the skeletal chain about the twofold axis and, in addition, the oxygen atom of the hydroxyl group is located at both sides of the mirror plane with an occupancy factor of 0.25. Formation of the hydrogen bond between the statistically distributed oxygen atom and

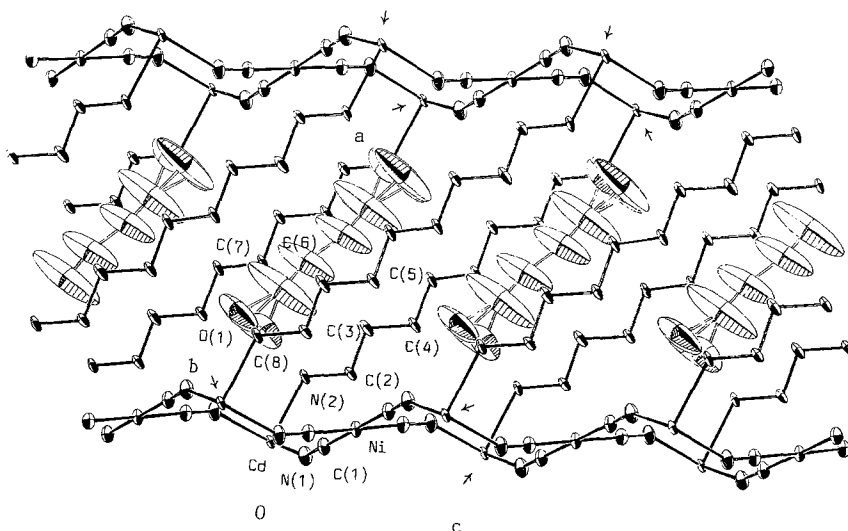


Fig. 1. ORTEP view of (1,8-diaminooctane)cadmium(II), tetra-cyanonickelate(II)-(1-hexanol)(1/1); 30% each of the probability surface for the anisotropic thermal ellipsoids. Those of the hydrogen atoms are omitted. The unit cell is cornered by the Cd atom at the origin, 0, and other seven Cd atoms indicated by arrows; those at 1, 0, 0, 0, 1, 0, and 0, 0, 1 are labeled with *a*, *b* and *c*, respectively.

the daotn amino nitrogen may be disproved from the rather long distance of 3.64(5) Å and the extremely large thermal parameter of the oxygen atom. From the infrared spectrum, the OH stretching band width of the guest 1-hexanol, *ca.* 88 cm⁻¹, was far narrower than that observed for neat 1-hexanol.

3. Discussion

Since Weiss proposed the structural model of the intercalation compounds formed between nickel(II) cyanide or clay minerals and higher alkyl derivatives in 1958 [1], the model, and later modified versions [2], has been used extensively in reviews and textbooks for the interpretations and discussions of various pillared intercalation compounds without any exemplification of single crystal structures. The present single crystal structure resembles the proposed model: the aliphatic chains of the host pillar and the guest molecule are arranged slantwise between adjacent metal complex layers. However, a distinctive feature of the present single crystal structure is the loose packing of the guest molecule in the pillared intercalation environment. In other words the aliphatic chains are not completely interlocked in parallel between the pillar and the guest in a static sense. This feature should be compared with the features of the intercalation complexes formed between nickel(II) cyanide and long carbon-chain *n*-alkylamine ligands first reported by Walker and Hawthorne [16]. The two-dimensional network of the nickel(II) cyanide is in fact that of *catena*-[nickel(II) tetra- μ -cyanonickelate(II)] analogous to the *catena*-[cadmium(II) tetra- μ -cyanonickelate(II)] network in the present structure. According to the structural model proposed for the nickel cyanide complexes, the unidentate aliphatic amines ligating to the nickel(II) are alternately interlocked in the interlayer space, but the skeletal parts of the amine behave like a 'liquid' owing to the thermal motions allowed, to a certain extent, at or above room temperature. In the present cadmium(II) structure, the alternate array of the alkyl chains of the pillar and the guest is similar to the *n*-alkyl chains of the unidentate ligands in the *catena*-[bis(*n*-alkylamine)nickel(II) tetra- μ -cyanonickelate(II)] complexes, but the 'liquid-like' behavior or disorder is observed only for the guest molecule.

Both aliphatic guest clathrates and aromatic guest clathrates of the Hofmann-diam-type have the structures of pillared intercalation compounds. In almost all the crystal structures of the Hofmann-diam-type clathrates previously determined by the single crystal X-ray diffraction method, the guest molecules are more or less in disorder owing to statistical distributions and/or thermal motions. This is true as well for the 1-hexanol guest in the present clathrate. On the other hand, the α,ω -diaminoalkane pillars, which we have described as columns because of their functions in supporting the ceiling and flooring of cyanometal networks and in compartmentalizing the cavities for guest molecules, are determined almost unambiguously. The high-entropy state of the guest molecules appears to be one of the characteristic features in the Hofmann-diam-type clathrates. This high-entropy state may also play an important role in the topotactic reactivity of the guest molecules in pillared intercalation compounds.

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