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Two Novel Metal-complex Host Structures Consisting of Cyanocadmate Coordination Polyhedra. Clay-like and Zeolite-like Structures

Takafumi KITAZAWA, Shin-ichi NISHIKIORI, Reiko KURODA, and Toschitake IWAMOTO*
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153

The metal-complex host of a clathrate compound $[Cd_3\{NH(CH_3)_2(CH_2)_3NH_2\}(CN)_7]\cdot C_6H_5F$ has a layered structure like a clay consisting of the linkage of tetrahedral $Cd(CN)_4$ and $Cd(CN)_3(NC)$, and octahedral $Cd(NC)_5[NH_2(CH_2)_3NH(CH_3)_2]$ coordination polyhedra. The host of another clathrate $[Cd_3(CN)_7]\cdot\{NH(CH_3)_2(CH_2)_3NH_2\}\cdot(CH_2ClCH_2Cl)$ has a three-dimensional structure like a zeolite comprised of the linkage of tetrahedral $Cd(CN)_4$ and $Cd(CN)_3(NC)$, and octahedral $Cd(NC)_6$ coordination polyhedra; the 3-(dimethylammonio)propylamine is accommodated as a cationic guest in the cavity formed in the host structure.

In the previous communication[1] we have reported a three-dimensional metal-complex host structure in $Cd[NH(CH_3)(CH_2)_3NH_2]Ni(CN)_4\cdot 0.5C_6H_{12}$, in which the N-methyl-1,3-diaminopropane behaves as a chelating ligand to the six-coordinate cadmium atom. The present investigation aimed to develop other kinds of novel three-dimensional metal-complex host structures by replacing the square-planar $Ni(CN)_4$ by tetrahedral $Cd(CN)_4$: such strategies have been successful for several metal-complex hosts originated from the Hofmann-type.[2-5] In addition, the N-methyl-1,3-diaminopropane ligand was replaced by N,N-dimethyl-1,3-diaminopropane.

Single crystals of the novel clathrates $[Cd_3\{NH(CH_3)_2(CH_2)_3NH_2\}(CN)_7]\cdot C_6H_5F$, (**1**), and $[Cd_3(CN)_7]\cdot\{NH(CH_3)_2(CH_2)_3NH_2\}\cdot(CH_2ClCH_2Cl)$, (**2**), were prepared by the method similar to that applied for the cyclohexane clathrate of the host containing the $Ni(CN)_4$ moieties:[1] N,N-dimethyl-1,3-diaminoproane, potassium tetracyanocadmate, and fluorobenzene or 1,2-dichloroethane were used in place of the N-methyl-1,3-diaminopropane, potassium tetracyanonickelate(II), and cyclohexane. Anal. **1**: Found: C, 28.78; H, 2.87; N, 18.25; Cd, 47.1%. Calcd for $C_{18}H_{20}N_9FCd_3$: C, 30.08; H, 2.80; N, 17.54; Cd, 46.93%. **2**: Found: C, 23.15; H, 2.62; N, 17.52; Cd, 46.8%. Calcd for $C_{14}H_{19}N_9Cl_2Cd_3$: C, 23.30; H, 2.65; N, 17.47; Cd 46.74%. The accommodation of each guest molecule was confirmed by IR and GC techniques.

The crystal structures of **1** and **2** were analyzed by the heavy-atom method; the intensity data were collected on a Rigaku AFC-6A four-circle automated diffractometer using graphite-monochromated Mo Kα radiation. Crystal data are:
1: $Cd_3(C_5H_{15}N_2)(CN)_7\cdot C_6H_5F$, F.W. = 718.65, triclinic $P\bar{1}$, $a/\text{Å} = 11.27(1)$, $b/\text{Å} = 15.362(8)$, $c/\text{Å} = 9.167(4)$, $\alpha/° = 107.38(4)$, $\beta/° = 113.98(5)$, $\gamma/° = 65.94(5)$, $V/\text{Å}^3 = 1306(1)$, $Z = 2$; $D_x/\text{g cm}^{-3} = 1.83$, $D_m/\text{g cm}^{-3} = 1.82(1)$; 3736 independent

reflections, R=0.048.

2: $Cd_3(CN)_7 \cdot (C_5H_{15}N_2) \cdot (C_2H_4Cl_2)$, F.W. = 721.50; orthorhombic, $Pn2_1m$, a/Å = 11.026(5), b/Å = 13.54(1), c/Å = 8.721(2), $V/Å^3$ = 1302(1), Z = 2; $D_x/g\ cm^{-3}$ = 1.84, $D_m/g\ cm^{-3}$ = 1.84(1); 2394 independent reflections, R = 0.042.

The structures solved are illustrated in Fig. 1 for **1** and Fig. 2 for **2**. The two structures are quite different to each other in spite that these compounds crystallized under the similar experimental conditions with the common stoichiometry $Cd:CN:NH_2(CH_2)_3NH(CH_3)_2:G$ = 3:7:1:1 (G = C_6H_5F or $C_2H_4Cl_2$). A layered host structure is seen in **1**, whereas the host of **2** is three-dimensional.

The metal complex layer of **1** is comprised of the linkage of the coordination polyhedra centered by three kinds of Cd atoms, Cd(a), Cd(b), and Cd(c); six of the seven cyano groups in a formula unit participate in the linkage ambidently.[6] Cd(a) is the central atom of a tetrahedral $Cd(CN)_4$ moiety, of which three N-terminals are linked to three Cd(c)'s and the last one is to a Cd(b). Cd(b) is also in a tetrahedral coordination but one of the four cyano groups is in the N-coordination from a Cd(a); two N-terminals are linked to two Cd(c)'s and an N-terminal is free from ligation but protruding to the interlayer space. Cd(c) is in an octahedral coordination with three N-terminals from three Cd(a)'s, two N-terminals from two Cd(b)'s, and the amino-nitrogen of the protonated ligand 3-(dimethylammonio)propylamine (abbrev. $dmtnH^+$). The ligand $dmtnH^+$ lays its

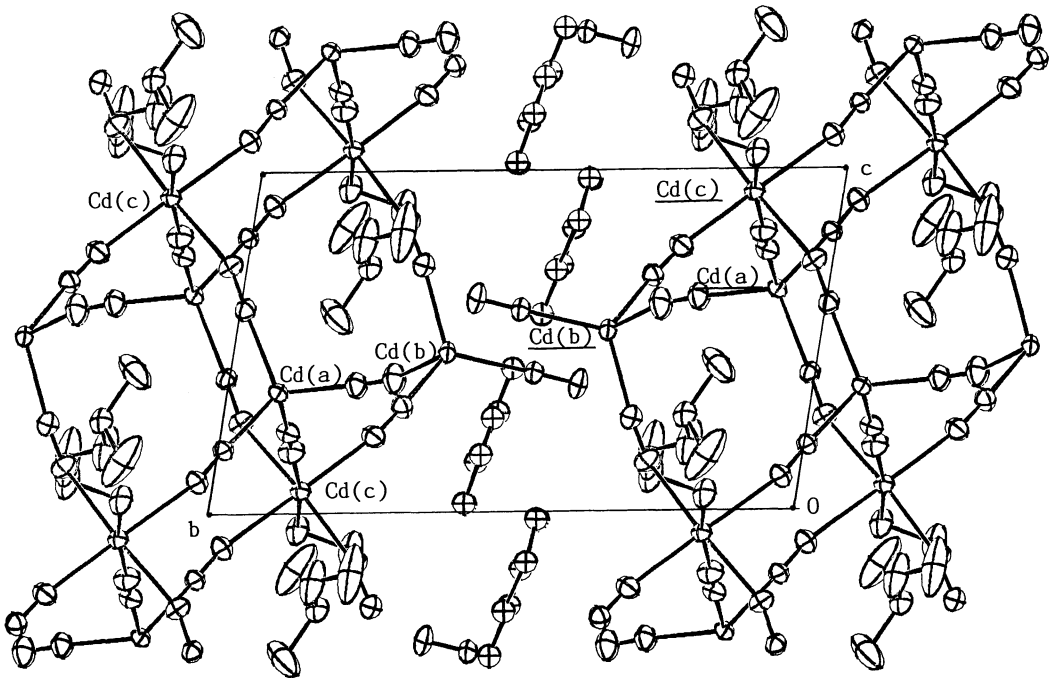

Fig. 1. Structure of $[Cd_3\{NH(CH_3)_2(CH_2)_3NH_2\}(CN)_7] \cdot C_6H_5F$, **1**; a perspective view along the a-axis. The guest C_6H_5F molecules are accommodated in the interlayer space with the aromatic plane almost parallel to the host metal-complex layers. Cd(a) at 0.70355, 0.08553, 0.64456; Cd(b) at 0.19563, 0.36546, 0.53049; Cd(c) at 0.21650, 0.15051, 0.93343; each of the equivalent atoms is shown without underline.

skeleton on the surface of the cyanometal complex layer, and the tail dimethylammonio group appears to form a hydrogen bond of the 2.80(1) Å N-N distance with the N-terminal of the cyano group protruding from the Cd(b) in adjacent layer. The cavity for the guest fluorobenzene molecule is thus formed in the interlayer space columned by the Cd(c)-dmtnH$^+$--NC-Cd(b) linkage. The whole structure as an inclusion compound resembles the layered structures of the clay minerals modified at the interlayer surfaces. Although the two-dimensional metal complex layer catena-[cadmium tetra-μ-cyanonickelate(II)] has been observed in common among the Hofmann-type and related clathrates so far we have developed in this laboratory,[3] the layer of the present structure is substantially different from the previously observed structures with the monatomic thickness.

There are also three kinds of Cd atoms, Cd(1), Cd(2), and Cd(3),[6] in the three-dimensional host structure of **2**. All the cyano ligands participate in the linkages among the polyhedra centered by the Cd atoms. Cd(1) is of a tetrahedral $Cd(CN)_4$; one of the four cyano groups is linked to another tetrahedral Cd(2) which makes a tetrahedron of $Cd(CN)_3(NC)$ type. An octahedral structure about a Cd(3) is made of six N-terminals from three each of tetrahedral Cd(1)'s and Cd(2)'s. The three-dimensional linkage of the metal complex polyhedra provides two kinds of polyhedral cavities with guest molecules; one is occupied by 1,2-dichloroethane and another by dmtnH$^+$. A remarkable difference between the present host structure and the Hofmann-type-related structures previously developed by replacing the square-planar $Ni(CN)_4$ moiety by the tetrahedral $Cd(CN)_4$, e. g. those of $Cd(NH_3)_2$-$Hg(CN)_4 \cdot 2C_6H_6$[4] and $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$,[5] is the absence of coordination from the

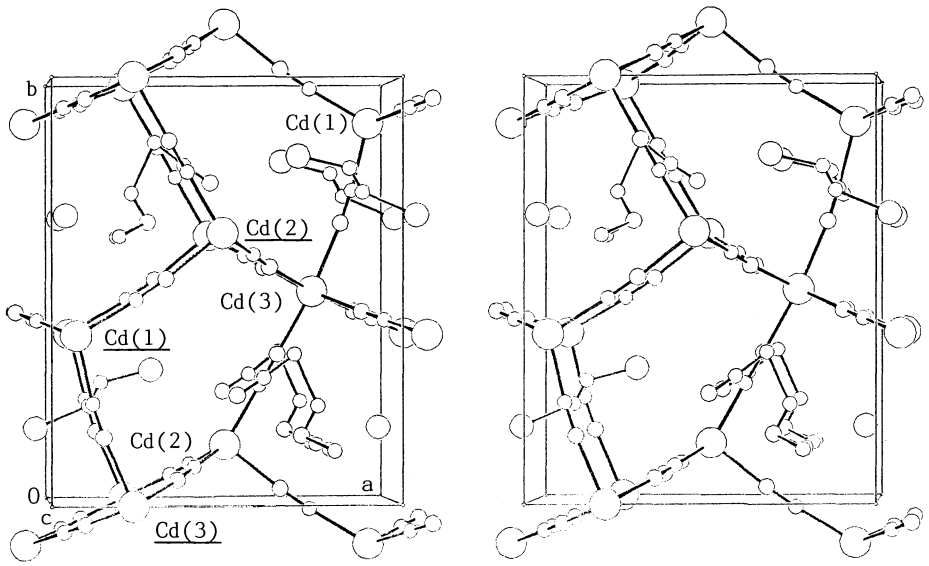

Fig. 2. Structure of $[Cd_3(CN)_7]\cdot\{NH(CH_3)_2(CH_2)_3NH_2\}\cdot(CH_2ClCH_2Cl)$, **2**; a stereo view along the c-axis. One of the guests CH_2ClCH_2Cl is accommodated in the cavity centered at ca. 0.132, 0.252, 0.5 (and the equivalent position), another guest $NH(CH_3)_2(CH_2)_3NH_2^+$ being in that at ca. 0.66, 0.24, 0 (and the equivalent position). Cd(1) at 0.06945, 0.39745, 1; Cd(2) at 0.48655, 0.63528, 1; Cd(3) at 0.23234, 0.00000, 1; each of the equivalent atoms is shown without underline.

amino nitrogen. Although the host is anionic, the host structure is like those of zeolites: coordination polyhedra make polyhedral cavities.

The formation of either the structure of the clay-like type 1 or the zeolite-like type 2 for other guest molecules appears to be critically dependent on pH of the aqueous solution containing the host components. As a general tendency type 1 structure is preferential to type 2 structure at the higher pH within the range of pH 8 - 9; the discrimination between type 1 and type 2 has been based on the feature characteristic of the layered structure for type 1 observed in the powder X-ray diffraction patterns. Benzene, 1,1,2-trichloroethane, 1,1,1-trichloroethane, and 2-chlorobutane have given both type 1 and type 2 clathrates depending on the pH value. However, at the present stage, only type 1 structure clathrates have been obtained for the guest molecules as follows: fluorobenzene, chlorobenzene, bromobenzene, acetophenone, cyclohexane, cis-1,2-dichloroethylene, chloroform, bromoform, carbon tetrachloride, 1,1,1-trichloro-2,2,2-trifluoroethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, 2-cyanopropane. Guests which have given only type 2 structure are: 1,2-dichloroethane, ethylbenzene, benzyl alcohol, toluene, 1,2-dibromoethane, dichloromethane, dibromomethane, trans-1,2-dichloroethylene, cyanomethane, methanol, bromoethane, ethanol, cyanoethane, 1-cyanobutane, propan-2-one, butan-2-one, pentan-3-one. Since the crystal structures have not yet been determined for the inclusion compounds of the above-mentioned guest molecules except **1** and **2**, possibilities remain to have novel structures other than that of **1** or **2**.

Much attention has been paid to inclusion compounds of clay and zeolite minerals as the media of separation and topotactic reaction. The present artificially synthesized host structures are potential reaction media, as their versatilities are expected owing to accommodation ability of various guest molecules different in function, size and shape. The details will be reported elsewhere.

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6) Cd-C(CN) and Cd-N(CN) bond lengths are from 2.18 - 2.24 Å and 2.30 - 2.38 Å for **1**, and 2.20 - 2.24 Å and 2.28 - 2.38 Å for **2**, respectively. Details of the structures will be reported elsewhere.

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