

Three-dimensional Cage-like Polycyanopolycadmate Network Accommodating Werner Complexes; The Crystal Structure of $[\text{Cd}(\text{dien})_2] \cdot [\text{Cd}_2(\text{CN})_3(\text{dien})_2] \cdot [\text{Cd}_8(\text{CN})_{19}] \cdot 3\text{H}_2\text{O}$ ($\text{dien} = (\text{H}_2\text{N}(\text{CH}_2)_2)_2\text{NH}$, diethylenetriamine)

Hiroyuki Kurihara, Shin-ichi Nishikiori,* and Toschitake Iwamoto

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153

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An anionic three-dimensional network host $[\text{Cd}_8(\text{CN})_{19}]^{3-}$ enclathrates a cationic mononuclear Cd complex guest $[\text{Cd}(\text{dien})_2]^{2+}$, and a dinuclear Cd complex guest $[\text{Cd}_2(\text{CN})_3(\text{dien})_2]^+$, to form a novel inclusion compound $[\text{Cd}(\text{dien})_2] \cdot [\text{Cd}_2(\text{CN})_3(\text{dien})_2] \cdot [\text{Cd}_8(\text{CN})_{19}] \cdot 3\text{H}_2\text{O}$ ($\text{dien} = (\text{H}_2\text{N}(\text{CH}_2)_2)_2\text{NH}$, diethylenetriamine).

Polycyanopolycadmate complexes containing amines as secondary ligands often accommodate organic molecules to form clathrate compounds. A number of preparations and single crystal X-ray structure determinations of the clathrates have revealed that polycyanopolycadmate hosts are flexible enough to form various host structures in topology according to secondary ligands and guest molecules.¹ In this study, we attempt to build a polycyanopolycadmate host which accommodates Werner complex guests instead of organic molecule guests in order to seek a new possibility of polycyanopolycadmate hosts. For making a discrete Cd complex guest in a polycyanopolycadmate system, we used $\text{dien}((\text{H}_2\text{N}(\text{CH}_2)_2)_2\text{NH})$, diethylenetriamine as a ligand for the Cd complex guest. Our previous studies showed that amines and diamines, such as NH_3 , $\text{N}(\text{CH}_3)_3$, $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{NHCH}_3$ etc, tended to be onium guests in a polycyanopolycadmate host or to be assembled into a network

structure of a host.² However, dien which is known as a tridentate chelate ligand is expected to coordinate to Cd effectively to form a discrete Cd complex guest in a host network structure. This communication reports the crystal structure of an inclusion compound, $[\text{Cd}(\text{dien})_2] \cdot [\text{Cd}_2(\text{CN})_3(\text{dien})_2] \cdot [\text{Cd}_8(\text{CN})_{19}] \cdot 3\text{H}_2\text{O}$ (**1**), obtained in our preparative attempts.

An aqueous solution (100 cm^3) containing $\text{K}_2[\text{Cd}(\text{CN})_4]$, CdCl_2 (10 mmol each), and dien (8 mmol) was adjusted to pH 8.5 by adding citric acid (*ca.* 50 mg) and was kept at 10 °C in a refrigerator. After a few days, colorless single crystals of (**1**) were obtained. The postulated composition was confirmed by elemental analysis,³ and the crystal structure was determined by the single crystal X-ray diffraction method.^{4,5}

Figure 1 is a perspective view of the crystal structure of (**1**), in which an anionic three-dimensional network host accommodating two kinds of discrete cationic Cd complex guests is seen. There are four crystallographically independent Cd atoms in the host $[\text{Cd}_8(\text{CN})_{19}]^{3-}$. Two of them have tetrahedral coordination structures. The other two Cd atoms have an octahedral and a trigonal bipyramidal coordination structure. All cyanide ligands in the host work as cyanide bridges between two Cd atoms and all coordination sites of the Cd atoms are occupied by the cyanide bridges. Therefore, the

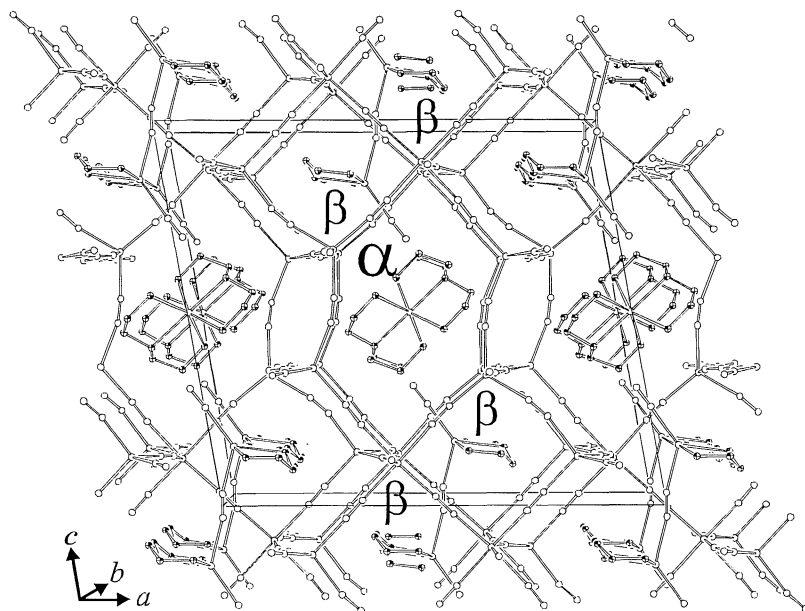


Figure 1. A perspective view of the unit cell (**1**), a ball-and-stick drawing.

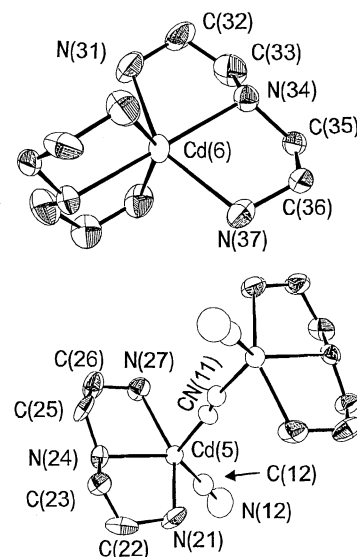


Figure 2. The structure of guest complex cations; mononuclear guest $[\text{Cd}(\text{dien})_2]^{2+}$ (top), and dinuclear guest $[\text{Cd}_2(\text{CN})_3(\text{dien})_2]^+$ (bottom).

network structure of the host is built of Cd atoms and cyano bridges, and does not contain dien as a secondary ligand.

Figure 2 shows the structures of the two cationic Cd complex guests. One is a mononuclear complex $[\text{Cd}(\text{dien})_2]^{2+}$, and another is a dinuclear complex $[\text{Cd}_2(\text{CN})_3(\text{dien})_2]^+$. The Cd atom of the mononuclear complex has an octahedral configuration coordinated by two diens at meridional sites. The Cd atom is located on a two-fold axis of the C2 space group of the crystal, so that the two diens are equivalent. The dinuclear structure of the other Cd complex guest $[\text{Cd}_2(\text{CN})_3(\text{dien})_2]^+$ is formed with a cyanide ligand bridging two mononuclear Cd complex parts. The Cd atom of the mononuclear part has a pentacoordinated structure with a tridentate dien, a unidentate cyanide ligand and the cyanide bridge. Therefore, the structure of the dinuclear complex is abridged to $[\text{NC}(\text{dien})\text{Cd}-\text{CN}-\text{Cd}(\text{dien})\text{CN}]^+$. A two-fold axis of the space group runs through the middle point of the cyanide bridge, so that the two mononuclear parts are equivalent each other and the cyanide bridge is in a structural disordered state.

A cavity trapping the mononuclear complex guest (α -cavity, See Figure 1) has a dodecahedral shape formed with four hexagonal faces and eight quadrilateral faces having corners of Cd atoms and sides of cyanide bridges. A cavity trapping a mononuclear part of the dinuclear complex guest (β -cavity) has an octahedral shape formed with two hexagonal faces and six quadrilateral faces. Two adjacent β -cavities trap one dinuclear complex guest. The cyanide bridge of the dinuclear complex guest runs through the center of the octahedral face at the border of the two β -cavities. The cavity array of $-\alpha-\beta-\alpha-\beta-$ is seen along the c axis. Along the array the cavities border on each other with their hexagonal faces, and the open windows at the center of the hexagonal faces form a tunnel with 6.0-9.9 Å diameter running through the network host. In the tunnel, the mononuclear complex, which has a spherical shape of *ca.* 10 Å diameter, and the long-shaped dinuclear complex are arrayed alternately and linked each other with two chains of hydrogen bonding as shown in Figure 3. One chain is the linkage of $\text{N}(12)\dots\text{N}(37)-\text{Cd}(6)-\text{N}(37)^{\#}\dots\text{N}(12)^{\#}$. N(12) is the terminal atom of a unidentate cyanide ligand of the dinuclear complex guest. The unidentate cyanide ligand gets into α -cavity through the hexagonal face at the border between the α and the β cavity. N(12) is linked with a hydrogen bond to N(37) which belongs to dien of the mononuclear complex guest. The other chain is

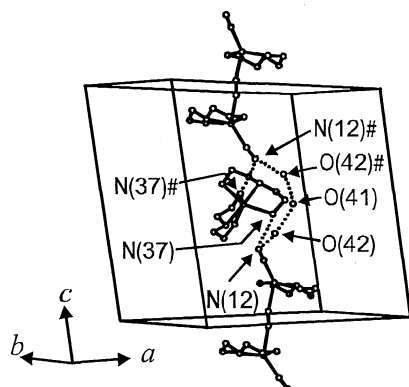


Figure 3. The double 1D-chain of the guest complex cations, dotted lines show hydrogen bonds, the symbol # means the key to symmetry operation of $-x+1, y, -z+1$.

formed with the linkage of $\text{N}(12)\dots\text{O}(42)\dots\text{O}(41)\dots\text{O}(42)^{\#}\dots\text{N}(12)^{\#}$. O(41) and O(42) are oxygen atoms of water molecules trapped in α -cavity together with the mononuclear complex guest.

It is apparent that inclusion compounds composed of a metal complex host and a metal complex guest bring new possibilities to the fields of the material science. Our study has presented one example of a polycyanopolycadmite host which accommodates Cd complex guests. This example has given us the recognition that polycyanopolycadmite hosts had a large ability of forming network structures according to size and shape of guests, again. Each of the Cd complex guests has a larger size compared with sizes of organic guests used in our studies so far.² And, the shape of the dinuclear complex is unique from a view point of a molecular geometry. The accommodation of the Cd complex guests by (1) shows the structural flexibility of polycyanopolycadmite hosts, which generates wide inclusion phenomena. As for the polycyanopolymetalate structures containing dien, two mixed metal systems, $[\{\text{Cu}(\text{dien})\}_2\cdot\text{Fe}(\text{CN})_6]\cdot 6\text{H}_2\text{O}$ and $[\{\text{Cu}(\text{dien})\}_3\cdot\{\text{Fe}(\text{CN})_6\}_2]\cdot 6\text{H}_2\text{O}$, had been already reported.⁶ In a sense, they are similar to (1). However, an advantage of polycyanopolycadmite is that polycyanopolycadmite have larger structural flexibility, whose reputation has been already established by recent many papers^{1,2} including this report. Next step is to develop methods to control the state of a metal complex guest. Our study indicated the selection of the ligand for a metal complex guest is an important factor. Along this sense, preliminary experiments are in progress. Their results will be reported elsewhere.

References and Notes

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- Anal. Found: C, 19.87; H, 2.54; N, 20.89%. Calcd. for $\text{C}_{38}\text{H}_{58}\text{Cd}_{11}\text{N}_{34}\text{O}_3$: C, 20.06; H, 2.57; N, 20.93%.
- Crystal data: $\text{C}_{38}\text{H}_{58}\text{Cd}_{11}\text{N}_{34}\text{O}_3$, $M = 2275.58$, monoclinic, C2, $a = 20.150(3)$, $b = 10.299(4)$, $c = 17.849(4)$ Å, $\beta = 99.88(2)^\circ$, $V = 3649(2)$ Å³, $Z = 2$, $D_m = 2.07(1)$, $D_x = 2.07$ g cm⁻³, $R(F) = 0.042$, $wR(F^2) = 0.104$ and $\text{GOF} = 1.07$ for 389 parameters using 4544 ($> 3\sigma(F_o)$) reflections. The crystal structure was solved by the direct method using SHELXS86⁵, and was refined anisotropically using SHELXL93.⁵ A difficulty of discrimination between C and N of cyanide bridges appeared in the refinement process. There are twelve crystallographically independent cyanide ligands in the crystal. The atoms of eight cyanide ligands were assigned from bond distances between Cd and the coordinating atom, but the atoms of two cyanide ligands were not. Another two cyanide ligands are in a structural disordered state caused by the space group. Each atom of the last four cyanide ligands was treated as a hybrid atom which consists of a 50% C atom and a 50% N atom.
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