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A Novel Clay-Like Layered Host Clathrate with the Guest Molecule Accommodated in the Intralayer Cavity: The Structure of $[\{\text{Cd}(\text{imH})_2\}\{\text{Cd}(\text{H}_2\text{O})\}_2\{\text{Cd}(\text{CN})_3\}_2\{\text{Cd}(\text{CN})_3(\text{imH})\}_2\{\text{Cd}(\text{CN})_3\}_2] \cdot 2\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ (imH=imidazole)

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Cadmium cyanide and polycyanopolycadmates $[\text{Cd}_x(\text{CN})_y]^{z-}$ give a great variety of clathrate inclusion structures, as has been reported by our group and others.¹⁻³ Except for the $\text{Cd}(\text{CN})_2$ host that involves tetrahedral Cd only,¹ their multi-dimensional hosts, even for those of apparent composition $\text{Cd}(\text{CN})_2$, are constructed of the CN linkages among tetrahedral Cd(t) and octahedral Cd(o) atoms: in some cases trigonal-bipyramidal five-coordinate Cd(p) atoms are involved. The presence or absence of secondary ligand L is one of the important factors for the host to provide cavities appropriate in size and shape for guest molecules. This paper reports on the results that we have obtained clathrate of the composition $9\text{Cd}(\text{CN})_2 \cdot 4\text{C}_6\text{H}_5\text{N}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_5\text{C}_2\text{H}_5$, using imidazole (imH), a five-membered aromatic amine, as the secondary ligand. This polycyanopolycadmite inclusion structure is the first example of the clay-like layered neutral host accommodating ethylbenzene neutral guest in the intralayer cavity.

The title clathrate was prepared as single crystals by the following procedure. Into 100 mL of water, 10 mmol of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, 10 mmol of $\text{K}_2[\text{Cd}(\text{CN})_6]$, and 10 mmol of imH were dissolved successively under stirring. The solution was covered with a layer of neat phase of the ethylbenzene guest species and kept standing at ambient temperature for a few days. Colorless crystals were obtained at the interface between the organic and the aqueous phases and the bottom of the latter. The composition of clathrate and the accommodation of guest molecule were confirmed by elemental analyses, IR and GC techniques. Anal. Found for clathrate: C, 27.2; H, 2.05; N, 18.1; Cd, 50.2. Calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_8\text{O}_3\text{Cd}_9$: C, 27.6; H, 2.02; N, 18.2; Cd, 50.6%. The clathrate liberates the ethylbenzene guest molecule gradually under ambient atmosphere.

Single crystals coated with epoxy resin were subjected to the collection of the intensity data on a Rigaku AFC-5S four-circle automated diffractometer using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$); no decay was observed through monitoring three representative reflections

by every 100 interval. The crystal structure was solved using the SHELX 76^o and UNICS III^o programs. The crystal data are: $\text{C}_{26}\text{H}_{16}\text{N}_8\text{O}_3\text{Cd}_9$, $M=2000.70$, monoclinic, $P2_1$, $a=17.221(2)$, $b=8.499(3)$, $c=23.537(2) \text{ \AA}$, $\beta=105.90(1)^\circ$, $V=3313(1) \text{ \AA}^3$, $Z=2$, $D_x=2.01$, $D_m=2.00(6) \text{ gcm}^{-3}$, 10520 reflections observed, 6879 used, 376 parameters to $R=0.045$ and $R_w=0.059$.

Crystallographic diagrams were obtained using the ORTEP program.⁸ The solved crystal structure is shown in Figure 1. There are crystallographically independent two octahedral Cd atoms and three tetrahedral Cd atoms in the layer host structure. The projection of the layer along the b axis has the shape of the belt extending along the c axis with pentagonal meshes cornered by the Cd atoms. There are two set of the linear but bent linkages connected by single and coordination bonds across the belt: $\text{N}(\text{imH})\text{-Cd}(\text{t}2)\text{-(CN)-Cd}(\text{t}1)\text{-CN-Cd}(\text{o}1)\text{-NC-Cd}(\text{t}1)\text{-(CN)-Cd}(\text{t}2)\text{-N}(\text{imH})$ and $\text{O}(\text{H}_2\text{O})\text{-Cd}(\text{o}2)\text{-NC-Cd}(\text{t}3)\text{-CN-Cd}(\text{o}1)\text{-NC-Cd}(\text{t}3)\text{-CN-Cd}(\text{o}2)\text{-O}(\text{H}_2\text{O})$. Both linear arrays intercross at bis-imH-ligated Cd(o1) on the inversion center of the unit cell and inter-connected between the respective pairs of Cd(t2) and Cd(o2) on the surface of the layer. The coupled linear arrays are further interconnected to one another up and down

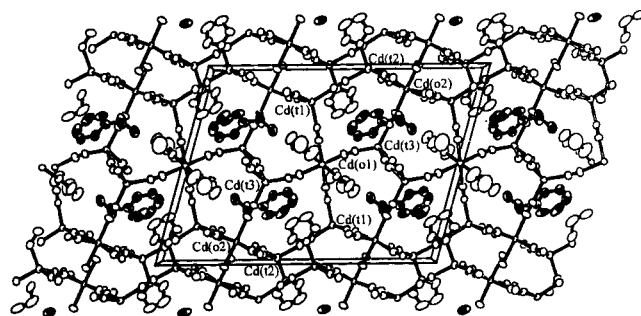


Figure 1. View of the unit cell structure of $[\{\text{Cd}(\text{imH})_2\}\{\text{Cd}(\text{H}_2\text{O})\}_2\{\text{Cd}(\text{CN})_3\}_2\{\text{Cd}(\text{CN})_3(\text{imH})\}_2\{\text{Cd}(\text{CN})_3\}_2] \cdot 2\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ along the b -axis.

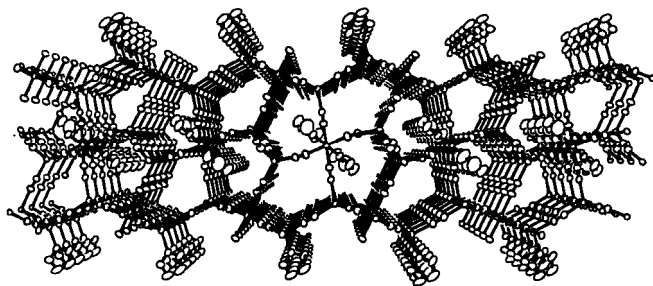


Figure 2. Host framework of $[\{Cd(imH)\}_2\{Cd(H_2O)\}_2\{Cd(CN)_2\}_2\{Cd(CN)(imH)\}_2\{Cd(CN)\}_2] \cdot 2C_6H_5CH_3$.

along the *b* axis and right and left along the *c* axis through the CN bridges from every Cd atom except for Cd(o1) to build up the layer structure, which generates polyhedral cavities inside the layer. The cavities similar to those observed in the previously reported zeolite-like three-dimensional hosts accommodate the ethylbenzene guest molecules and the imH ligands: the cavities accommodating the imH is invaded by the ethyl group of ethylbenzene and the cavities accommodating the benzene ring of ethylbenzene is invaded by the imH from adjacent layer, respectively.

As shown in Figure 2, the present host structure can be denoted as a "layered zeolite" because of the cavity formed inside the layer accommodating the guest ethylbenzene. The host structure is rather exceptional with respect to the coordination of the complementary ligand imH to both the tetrahedral Cd(t2) and the octahedral Cd(o1); in comparison with complementary ligands coordinate to Cd(o) in the precedent multi-dimensional host structures involving Cd(o) and Cd(t). The ring size of imH smaller than pyridine (py) appears to be favorable for building up the clathrate inclusion host structure because pyridine gave no-guests complexes $[Cd(py)_2Cd(CN)_2]$ with a Cd(o) : Cd(t) ratio of 1 : 1 and $[\{Cd(CN)(py)\}_2\{Cd_2(CN)_2\}]$ with the ratio of 3 : 2.^{3c} Hence, selection of secondary ligand may be a key of crystal engineering in the polycyanopolycadmiate systems.

Discrimination between C and N in a Cd(t)-CN-Cd(t) linkage is the problem we have often encountered in the X-ray crystallographic structure refinement of polycyanopolycadmates,^{1c} similar to that pointed out by Cromer for the CN linkage between Cu(I).⁹ Our empirical rule is that Cd(o) always accepts the N atom of the CN group from Cd(t) in Cd(t)-CN-Cd(o) linkage. In the present structure the CN group between Cd(t1) and Cd(t2) was refined as being in a static disorder in the orientation along the

chain unit: each of CN(1) and CN(2) was assumed to have 50% each probability of C and N.

In conclusion, a newly prepared compound with the composition $9Cd(CN)_2 \cdot 4C_6H_5N_2 \cdot 2H_2O \cdot 2C_6H_5CH_3$, has been characterized as the clathrates of the CN-bridged isopolycyanopolycadmiate hosts that involve octahedral and tetrahedral Cd atoms in a 1 : 2 ratio by single crystal X-ray diffraction method. The host of clathrate has a pylo-silicate-like layer structure the surface of which is covered by the imH at Cd(t) and H_2O at Cd(o); the guest is accommodated in the intralayer cavity along with the imH ligands coordinated at another Cd(o). Details on this clathrate will be reported later.

Supplementary Materials. Lists of refined atomic coordinates, selected bond distances and angles are available from the author.

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