
Communications to the Editor


A Novel Clay-Like Layered Host Clathrate with the Guest Molecule Accommodated in the Intralayer Cavity: The Structure of [{Cd(imH)\textsubscript{2}}\{Cd(H\textsubscript{2}O)\}\{Cd(CN)\}\{Cd(CN)\}(imH)\{Cd(CN)\}\{Cd(CN)\}\{imH}\} 2C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{5} (imH=imidazole)

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Cadmium cyanide and polycyanopolycadmates [Cd(CN)\textsubscript{x}, y] give a great variety of clathrate inclusion structures, as has been reported by our group and others.\textsuperscript{12} Except for the Cd(CN)\textsubscript{1} host that involves tetrahedral Cd only,\textsuperscript{13} their multi-dimensional hosts, even for those of apparent composition Cd(CN)\textsubscript{5}, are composed 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 9Cd(CN)\textsubscript{3}, 4C\textsubscript{6}H\textsubscript{5}N\textsubscript{2}H\textsubscript{2}O \cdot 2C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{5} using imidazole (imH), a five-membered aromatic amine, as the secondary ligand. This polycyanopolycadmate 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 CdCl\textsubscript{2}, 2.5H\textsubscript{2}O, 10 mmol of K,[Cd(CN)\textsubscript{5}], 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 C\textsubscript{56}H\textsubscript{5}N\textsubscript{10}O\textsubscript{1}Cd\textsubscript{12}; 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-\textit{K}\alpha radiation (\(\lambda =0.71069\) \textsc{\textit{\AA}}); no decay was observed through monitoring three representative reflections by every 100 interval. The crystal structure was solved using the SHELX 76 and UNICS III\textsuperscript{1:i} programs. The crystal data are: C\textsubscript{56}H\textsubscript{5}N\textsubscript{10}O\textsubscript{1}Cd\textsubscript{12}, M=2000.70, monoclinic, \(P2_1/c\), \(a=17.221(2), b=8.499(3), c=23.537(2)\textsc{\textit{\AA}}, \beta=105.90(1)^\circ, U=33133(1)\textsc{\textit{\AA}}^3, Z=2, D_{c}=2.01, D_{c}=2.00(6)\textsc{\textit{g cm}^{-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.\textsuperscript{11} 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: N(imH)-Cd(t2)-O-H\textsubscript{2}O)-Cd(o2)-NC-Cd(t3)-CN-Cd(o1)-NC-Cd(t3)-CN- and O(H\textsubscript{2}O)-Cd(o2)-NC-Cd(t3)-CN-Cd(o1)-NC-Cd(t3)-CN-Cd(o2)-O(H\textsubscript{2}O). Both linear arrays intercross at bis-imH-linked Cd(o1) on the inversion center of the unit cell and interconnected 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 [{Cd(imH)\textsubscript{2}}\{Cd(H\textsubscript{2}O)\}\{Cd(CN)\}\{Cd(CN)\}(imH)\{Cd(CN)\}\{Cd(CN)\}\{imH\} 2C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{5} (imH=imidazole) along the \(b\) axis.
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 ligands coordinate to Cd(o) in the previously reported zeolite-like three-dimensional hosts involving octahedral and tetrahedral Cd atoms in a 1:2 ratio by single crystal X-ray diffraction method. The host of clathrate has a pyro-silicate-like layer structure the surface of which is covered by the imH from adjacent layer, respectively.

In conclusion, a newly prepared compound with the composition \( 3\text{Cd} \text{(CN)} \cdot 4\text{C}_6\text{H}_5\text{N}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_4\text{C}_6\text{H}_4 \) has been characterized as the clathrates of the CN-bridged isopolycyanopolycadmate 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 pyro-silicate-like layer structure the surface of which is covered by the imH at Cd(t) and H\( _2\text{O} \) 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.

**References**


