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CRYSTAL STRUCTURE OF HOFMANN-DMA-TYPE BENZENE CLATHRATE BIS(DIMETHYLAMINE)CADMIUM(II) TETRACYANONICKELATE(II) - BENZENE (2/1)

Shin-ichi NISHIKIORI and Toschitake IWAMOTO*

Department of Chemistry, College of Arts and Sciences,

The University of Tokyo, Komaba, Meguro, Tokyo 153

The title clathrate $Cd(NH(CH_3)_2)_2Ni(CN)_4 \cdot \frac{1}{2}C_6H_6$ has a layered host structure of metal complex network $[CdNi(CN)_4]_\infty$ linked by the CN ligands and the benzene molecule is enclathrated in a cage-like cavity formed between the layers. The channel-like cavity, observed along with the cage-like one for the Hofmann-dma-type toluidine clathrates, is collapsed owing to the fold of the layers to minimize void space.

Hofmann-dma-type host $Cd(dma)_2Ni(CN)_4$ (dma = $NH(CH_3)_2$) exhibits the inclusion capability to a wide range of aromatic molecules in contrast to the strict guest selectivity of the Hofmann-type host $Cd(NH_3)_2Ni(CN)_4$ which is the prototype of the Hofmann-dma-type.[1] Generally, the Hofmann-dma-type host gives 1:1 clathrates with such substituted benzenes as toluene, toluidines, xylidines, halobenzenes, etc. The crystal structures of the o-, the m-, and the p-toluidine clathrates have been analyzed to demonstrate the representative structural models of the Hofmann-dma-type clathrates.[2] They are not isostructural to each other but the structure of the o-isomer is different in the way of puckering of the host metal complex network $[CdNi(CN)_4]_\infty$ from the other two. It is precarious to mention about the structure for these kinds of clathrates by analogy with the similarity in composition.

Among the novel Hofmann-dma-type clathrates, the benzene one, bis(dimethylamine)cadmium(II) tetracyanonickelate(II)-benzene (2/1), $Cd(dma)_2Ni(CN)_4 \cdot \frac{1}{2}C_6H_6$, **1**, gives the host-guest ratio of 2:1 different from those clathrates of substituted benzene guests. If **1** were isostructural to any of the three toluidine clathrates, it seemed rather curious that the benzene molecule, being smaller in volume approximately by the two substituents, $-CH_3$ and $-NH_2$, than toluidine, is

Table 1. Crystal Data

$Cd(C_2H_7N)_2Ni(CN)_4\cdot\frac{1}{2}C_6H_6$	
F.W. = 404.4	
Monoclinic, $P2_1/a$	
a/Å = 15.418(7)	
b/Å = 14.100(6)	
c/Å = 7.566(1)	
β/° = 96.56(5)	
D_m/g cm^{-3} = 1.64(1)	
D_x/g cm^{-3} = 1.65	
Z = 4	
μ(Mo Kα)/cm^{-1} = 24.4	

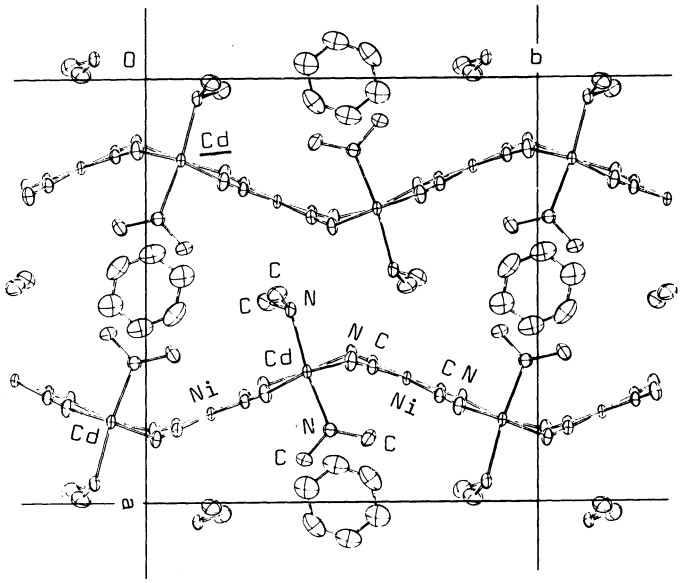
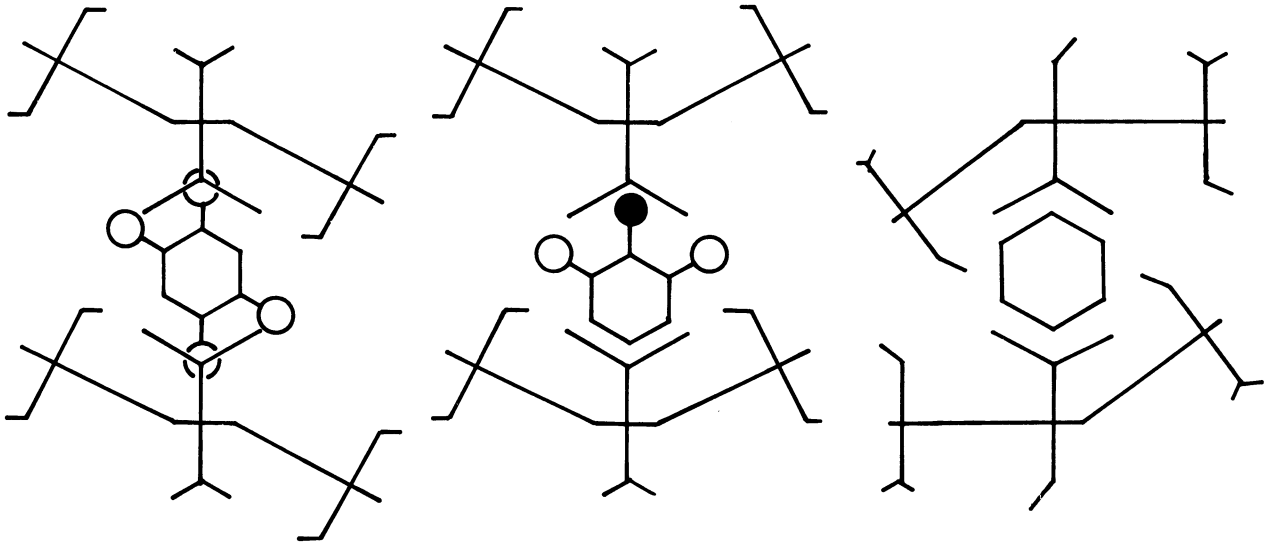


Fig. 1. ORTEP view of $Cd(dma)_2Ni(CN)_4\cdot\frac{1}{2}C_6H_6$, 1.

enclathrated in the host of the same composition with the less extent. The fact that the powder X-ray diffraction pattern of 1 exhibits the feature different from those of the substituted benzene clathrates[1] suggested that the composition of 1 was not due to an imperfect enclathration of the guest into the isostructural host. Therefore, the structural analysis was carried out to ascertain either the host of 1 has a structure different from those of the toluidine ones or not.

The structure was analyzed based on the 2919 reflection intensities collected on a Rigaku four-circle automated diffractometer using Mo Kα radiation for a 0.20×0.20×0.20 mm^3 single crystal coated with epoxy resin in order to prevent the spontaneous decomposition at room temperature. The structure was solved by the heavy-atom method and refined to the conventional R index of 0.047. The crystal data are listed in Table 1 and the structure is illustrated in Fig. 1.

As Fig. 1 shows, the benzene molecule is enclathrated in a cage-like cavity formed between adjacent metal complex layers, each of which consists of the two-dimensionally extended $[CdNi(CN)_4]_\infty$ network similar to those observed for the host structures of the Hofmann-type and analogous clathrates containing the square-planar $Ni(CN)_4$ moieties; the dma ligands coordinate to the Cd atoms in the network in a trans configuration. The cavity, e.g. centered at $\frac{1}{2},0,\frac{1}{2}$, is surrounded by the twelve methyl groups of eight dma ligands coordinating to eight Cd atoms located at



(i) (ii) (iii)

Fig. 2. Comparison of the bending structure. (i) Benzene clathrate, 1, (ii) o-toluidine clathrate, and (iii) m- and p-toluidine clathrates. The open circles in (ii) and (iii) show the substituents statistically distributed. For the details see Fig. 1 in Ref. 2.

x = 0.1920, y = 0.0895, z = -0.0133 and the equivalent positions in both the unit cells sharing the point $\frac{1}{2},0,\frac{1}{2}$. Eight of the twelve methyl groups are those of the dma's protruding from the Cd atoms at x, y, z; x, y, 1+z; 1-x, -y, -z; and 1-x, -y, 1-z; the remaining four are each one of those dma's protruding from the four Cd atoms at $\frac{1}{2}$+x, $\frac{1}{2}$-y, z; $\frac{1}{2}$+x, $\frac{1}{2}$-y, 1+z; $\frac{1}{2}$-x, $-\frac{1}{2}$+y, -z; and $\frac{1}{2}$-x, $-\frac{1}{2}$+y, 1-z. The Cd atom at x, y, z is underlined in Fig. 1. Thus, the benzene molecule is tightly enclathrated in the cage-like cavity surrounded by twelve methyl groups in total. This cage structure is substantially similar to that designated as cavity A in each crystal structure of the three toluidine clathrates.[2] The essential difference between the crystal structure of 1 and those of the toluidine ones is brought about by the difference in the place and the direction of bending which occurs in the metal complex network. The bending, which causes the fold of the network, occurs at the joints between a Cd atom and two terminal nitrogens of a pair of the approximately coplanar $Ni(CN)_4$ moieties. In the structure of 1, it occurs at one side of each Cd atom along the crystal b-axis; at another side the Cd atom is almost coplanar with a pair of $Ni(CN)_4$ moieties linked with the terminal nitrogens. This way of bending makes the fold of the metal complex layers so as to collapse the channel-like cavity designated as cavity B in the structures of the toluidine

clathrates. Since cavity B is formed in a 1:1 ratio to cavity A in the crystal structures of the toluidine clathrates with the formula $Cd(dma)_2Ni(CN)_4 \cdot CH_3C_6H_4NH_2$, the number of guest molecules in the benzene clathrate decreases to a half that in the toluidine ones: the composition of 1 becomes $Cd(dma)_2Ni(CN)_4 \cdot \frac{1}{2}C_6H_6$.

In the toluidine clathrates, the bending occurs at both sides of every other Cd atom along the crystal a-axis which corresponds to the b-axis in 1. As shown by the simplified models in Fig. 2, the direction of bending in the o-isomer clathrate is same at both sides, but that in the m- and the p-isomer ones is opposite. The reason why the direction differs from each other in the host structures of these clathrates can be interpreted in terms of the effect of substituents attached to the benzene ring of the guest enclathrated in cavity A on the fold of the metal complex network. The presence of substituent near the dma ligand protruding from the Cd atom above or beneath the cavity A appears to govern the direction. Taking the statistical distribution of the substituent in the structures of the toluidine clathrates into account, the bending of the metal complex layer occurs outwards from the cavity in order to make room for the substituents. On the other hand, inward bending occurs at the side where the substituents are absent. Since a benzene molecule has no bulky substituents, the host metal complex layer always bends inwards to the cavity so as to enclose the guest molecule with minimal void space.

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