CHEMISTRY LETTERS, pp. 1035-1038, 1982.

# INCLUSION OF AROMATIC GUEST MOLECULES WITH BULKY SUBSTITUENTS IN LAYERED METAL COMPLEX HOST trans-BIS(DIMETHYLAMINE)CADMIUM(II) TETRA-catena-μ-CYANONICKELATE(II)

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A novel type of the metal complex host $Cd(NH(CH_3)_2)_2Ni(CN)_4$ derived by replacing the $NH_3$ in Hofmann-type host $Cd(NH_3)_2Ni(CN)_4$ by $NH(CH_3)_2$ includes the benzene derivatives with several bulky substituents between the layered structure, the guest molecules which have never been enclathrated into Hofmann-type and the analogous hosts.

The host of Hofmann-type clathrate $M(NH_3)_2M'(CN)_4.2G$[1,2] has a layered structure of square-meshed trans-diamminemetal(M(II)) tetra-catena-μ-cyanometallate(M'-(II)) sheets. The five- or six-membered aromatic guest molecule G is trapped between the sheets with its aromatic plane vertical to the sheets. Each guest molecule is clipped by a couple of $NH_3$ pairs protruding from the upper and lower sheets with the van der Waals contact as shown in Fig. 1. There is no room for bulky substituents in the cavity if the guest G molecule had them; only allowed are $NH_2$ and OH groups arranged vertically to the sheets. This is the reason why the selectivity of Hofmann-type host and the analogous ones is so strict that any alkyl or halo derivatives of benzene cannot be enclathrated.

By replacing the $NH_3$ ligand of the Hofmann-type $Cd(NH_3)_2Ni(CN)_4$ host by $NH(CH_3)_2$ the selectivity of the novel $Cd(NH(CH_3)_2)_2Ni(CN)_4$ host was changed drastically; methyl-, dimethyl-, trimethyl-, chloro-, bromo-, and dichlorobenzenes, methyl-, dimethyl-, and N,N-dimethylaniline, naphthalene, indene, and phenanthrene have been included in this novel host.

The novel inclusion compounds were prepared as follows. Into 40 ml of $H_2O$ 0.91 g of $CdCl_2.\frac{5}{2}H_2O$ was dissolved. The turbidity, once formed by addition of 1.04 g of $K_2[Ni(CN)_4]$, disappeared by adding 4.05 ml of $NH_2CH_2CH_2OH$. Into the yellowish transparent solution 0.9 g of tartaric acid was dissolved and 4.0 ml of 50 % aqueous solution of $NH(CH_3)_2$ was added. The aqueous solution thus prepared was covered with the organic phase of the neat liquid of guest species, or of the guest species dissolved with ethylbenzene or hexane, and kept at room temperature or at ca. 5 °C in a refrigerator for a few days. Yellow or pale yellow crystals of the inclusion compound were grown at the interface or the bottom of the aqueous phase.

The products were characterized by infrared spectroscopy, powder X-ray diffractometry, and chemical analysis. Each product showed the characteristic ir bands due to the guest species included but the bands due to the host moieties were insensitive to the change of guest species. The CN stretching band appearing at ca. 2150 $cm^{-1}$ supports the catena-μ-cyano bridging in the host structure similar to

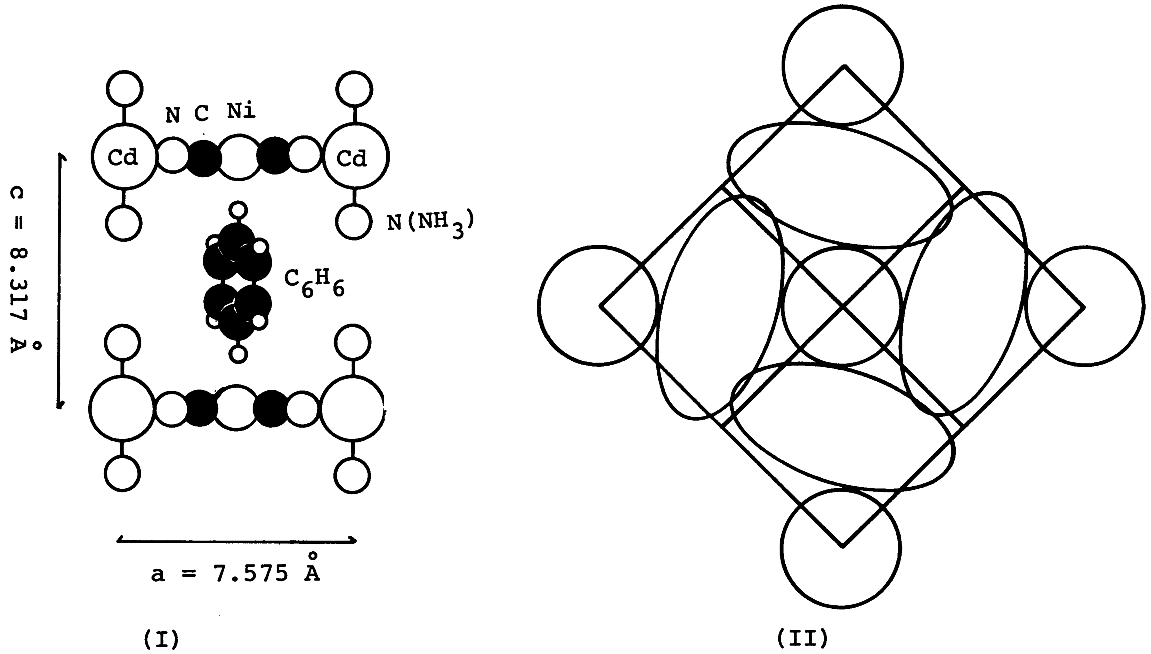
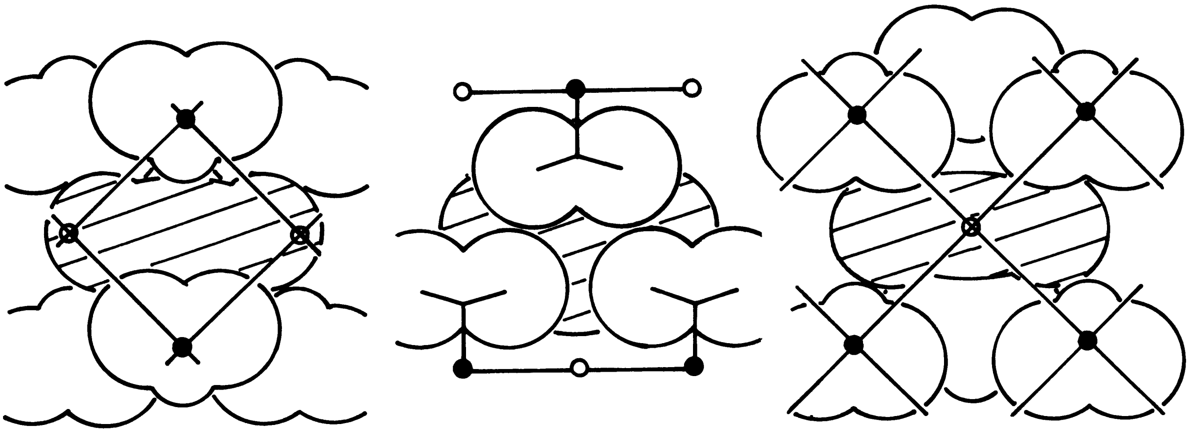


Figure 1. Illustrative structure of Hofmann-type $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ clathrate.[3] (I) Projection along b-axis of the tetragonal unit cell. Hydrogens of $NH_3$ are not shown. (II) Cross section along ab-plane. The electronic clouds of the van der Waals radii are shwon with the circle for $NH_3$ and the ellipsoid for $C_6H_6$.

Table I. The Elemental Analyses: Found/(Calcd) in %.

| | Cd | Ni | C | H | N |
|---|---|---|---|---|---|
| $CdNi(C_8H_{14}N_6)$ | 30.8 | 16.3 | 25.8 | 3.93 | 22.8 |
| | (30.76) | (16.06) | (26.30) | (3.86) | (23.00) |
| $CdNi(C_8H_{14}N_6) \cdot 0.5C_6H_6$ | 27.8 | 14.6 | 31.7 | 4.35 | 20.5 |
| | (27.79) | (14.51) | (32.67) | (4.23) | (20.78) |
| $CdNi(C_8H_{14}N_6) \cdot C_6H_5CH_3$ | 24.6 | 12.9 | 38.8 | 4.91 | 18.2 |
| | (24.57) | (12.82) | (39.38) | (4.84) | (18.37) |
| $CdNi(C_8H_{14}N_6) \cdot C_6H_5Cl$ | 23.4 | 12.2 | 30.0 | 3.90 | 19.3 |
| | (23.52) | (12.28) | 35.18) | (4.00) | (17.58) |
| $CdNi(C_8H_{14}N_6) \cdot C_6H_5Br$ | 21.6 | 11.2 | 30.1 | 3.71 | 16.9 |
| | (21.52) | (11.23) | (32.29) | (3.66) | (16.08) |
| $CdNi(C_8H_{14}N_6) \cdot 0.87\underline{o}\text{-}(CH_3)_2C_6H_4$ | 24.5 | 12.8 | 35.8 | 4.88 | 18.1 |
| $CdNi(C_8H_{14}N_6) \cdot 0.87\underline{p}\text{-}(CH_3)_2C_6H_4$ | 24.5 | 12.9 | 32.8 | 4.54 | 19.2 |
| | (24.55) | (12.82) | (39.25) | (4.99) | (18.36) |
| $CdNi(C_8H_{14}N_6) \cdot C_{10}H_8$ | 22.6 | 12.1 | 41.0 | 4.28 | 17.2 |
| | (22.77) | (11.89) | (43.80) | (4.49) | (17.02) |
| $CdNi(C_8H_{14}N_6) \cdot \underline{o}\text{-}CH_3C_6H_4NH_2$ | 24.1 | 12.5 | 37.1 | 5.25 | 19.9 |
| $CdNi(C_8H_{14}N_6) \cdot \underline{m}\text{-}CH_3C_6H_4NH_2$ | 23.9 | 12.5 | 37.4 | 5.22 | 20.4 |
| $CdNi(C_8H_{14}N_6) \cdot \underline{p}\text{-}CH_3C_6H_4NH_2$ | 23.8 | 12.4 | 36.8 | 5.26 | 19.8 |
| | (23.79) | (12.42) | (38.13) | (4.91) | (20.75) |



(LA) (A) (UA)

Figure 2. Structural model of the novel inclusion compound. Electronic clouds based on the van der Waals radii are shown for dimethylamine and guest (hatched). View of the layered structure (A), view of the (A) from the lower side (LA), and view of the (A) from the upper side (UA). Solid circle, Cd; open circle, Ni; the cyanide bridge is shown as the solid line.

that in Hofmann-type and the analogous hosts. Typical examples of the elemental analyses are listed in Table I; the values for the host metal complex are those obtained for the residual host left after evacuating the toluene compound at 80 °C. Except the benzene compound, the ratio of the guest to the host appears to be about 1:1. The guest content in the two xylene compounds was somewhat lower (0.87:1) based on the values of the metal content determined on the bench-top of our laboratory for the freshly prepared specimens by chelatometry. The apparently stoichiometric compositions in Table I were estimated on the basis of the values of the metal content rather than those of the C, H, and N, which were determined in another place4) for the specimens reserved in sealed tubes for a few days after the preparation. Therefore, the compositions should be the limiting ones for the saturated inclusion of the guest molecules into the host.

The powder X-ray diffraction patterns of these compounds can be classified into three groups, I, II, and III, according to their characteristic features. The compounds of the *o*-isomers belong to group I, whereas those of the *p*-isomers and other guests belong to II. The benzene compound, III, is different not only in the composition but also in the feature of diffraction pattern from the other compounds. Precise assignments of the diffraction patterns have not yet been possible, but the basal spacings, assignable to the distance between the metal complex sheets intercalating the guest molecules, have been found out for some of the compounds as follows: $C_6H_5CH_3$, 9.23 Å; $C_6H_5Cl$, 9.17 Å; $C_6H_5Br$, 9.24 Å; *p*-$(CH_3)_2C_6H_4$, 9.23 Å; and $C_{10}H_8$, 9.50 Å.

Based on these observations the structure of these novel inclusion compounds can substantially be illustrated as shown in Fig. 2. The host metal complex is thought of being isomorphic to that of Hofmann-type host with respect to the alternate array of the six-coordinate Cd and square-planar $Ni(CN)_4$ in a two-dimensionally extended sheet. Both sides of the sheet are covered with the hydrophobic methyl groups of the dimethylamine ligands coordinating to the Cd atom in the sheet. The guest molecules are trapped between the sheets with the van der Waals contact. The cavity has a tunnel-like character rather than the cage-like one in Hofmann-type and the analogous hosts; generally an inclusion compound with tunnel-like cavity is apt to be non-stoichiometric. The affinity of these guest molecules to the novel host is caused from the hydrophobic interaction with the methyl groups covering the metal complex sheets. The π-electron system of the guest molecule appears to play an important role in this interaction because any aliphatic and alicyclic molecules have not yet been known to be included in this host.

The residual host $Cd(NH(CH_3)_2)_2Ni(CN)_4$ gave the powder X-ray diffraction pattern assigned to the tetragonal system with a = 10.64 Å and c = 13.66 Å. The dimensions correspond to the unit cell containing four formula units and suggest the structure which consists of doubly-layered four meshes of the metal complex sheets. The interlayer distance should be a half of the c dimension, 6.83 Å. When trimethylamine was used in place of dimethylamine, any inclusion compounds were not obtained but a metal complex $Cd(N(CH_3)_3)_2Ni(CN)_4$ precipitated. Its powder X-ray diffraction pattern was assigned to the tetragonal system with a = 10.65 Å and c = 13.96 Å; the values are similar to those for the residual host complex $Cd(NH(CH_3)_2)_2Ni(CN)_4$. In the case of the trimethylamine complex, the methyl groups on the respective metal complex sheets appear to be interlocked by each other without any intercalated aromatic molecules.

With regard to the benzene compound $Cd(NH(CH_3)_2)_2Ni(CN)_4\cdot\frac{1}{2}C_6H_6$, the structure may not be similar to those of the other inclusion compounds. In this case, by analogy with Hofmann-pn-type $Cd(NH_2CH(CH_3)\text{-}CH_2NH_2)Ni(CN)_4\cdot\frac{3}{2}C_6H_6$[5], three of the four cavities may be occupied by the methyl groups of the dimethylamine ligands and the remaining one by a benzene molecule, if the host structure is similar to that of Hofmann-type. Single crystal structure analyses of these compounds are in progress.

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(Received April 28, 1982)