CHEMISTRY LETTERS, pp. 1701-1704, 1990.

Novel Three-dimensional Metal-complex Host Structures of *catena*-[Propylenediaminecadmium(II) Tetra-μ-cyanonickelate(II)] and *catena*-[Propylenediaminecadmium(II) Tetra-μ-cyanocadmate(II)]

Ki-Min PARK, Masato HASHIMOTO, Takafumi KITAZAWA, and
Toschitake IWAMOTO*
Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro, Tokyo 153

Two novel metal-complex host structures, consisting of the three-dimensional linkages between square-planar tetracyanonickelate(II) or tetrahedral tetracyanocadmate(II) and propylenediamine-chelated octahedral cadmium(II), have been demonstrated for the 1,2-dichloroethane inclusion compounds.

So far small aromatic molecules such as those of pyrrole, thiophene, benzene, have been accommodated in the Hofmann-type-analogous three-dimensional metal-complex hosts involved with the ambidentate ethylenediamine (en), propylenediamine (pn), or 2-aminoethanol, whose skeletons have two methylene units and two ligating groups.[1)] Among these hosts, accommodation of aliphatic guests may be expected for Hofmann-pn-type $Cd(pn)Ni(CN)_4$ and pn-Td-type $Cd(pn)Cd(CN)_4$ hosts,[2)] since the methyl group of the pn increases lipophilic character of the cavities formed in the three-dimensional metal-complex host structures. Hence, we examined to accommodate 1,2-dichloroethane into the Hofmann-pn-type and the pn-Td-type hosts. The products, $Cd(pn)Ni(CN)_4 \cdot 0.5ClCH_2CH_2Cl$, 1, and $Cd(pn)Cd(CN)_4 \cdot ClCH_2CH_2Cl$, 2, however, revealed three-dimensional host structures different from those previously known,[2)] although the compositions of the metal-complex hosts are respectively the same to those of the Hofmann-pn-type and pn-Td-type. Contrary to the ambidentate pn in the previously-known host structures, the pn chelates to the octahedral Cd atom in the both novel structures. Moreover, the host-guest stoichiometry is different not only from the previous 2/3 but also with the difference in the tetracyanometalate(II) moiety of the host: 2/1 for the square-planar $Ni(CN)_4$ and 1/1 for the tetrahedral $Cd(CN)_4$, respectively.

The 1,2-dichloroethane inclusion compounds, 1 and 2, were prepared by the methods similar to those applied for the Hofmann-pn-type and pn-Td-type,2) but the pH of the respective mixed aqueous solutions of the host moieties were adjusted at 9.0 using citric acid. 1,2-Dichloroethane was poured under the aqueous phase. For 1 yellow, and for 2 colorless, respectively, plate-like crystals were obtained at the interface between the aqueous and organic phases by standing in a refrigerator for a few days. Anal. for 1. Found: C, 24.00; H, 2.98; N, 21.18; Cl, 8.54%. Calcd for $C_8H_{12}N_6ClCdNi$: C, 24.09; H, 3.03; N, 21.08; Cl, 8.89%. Anal. for 2. Found: C, 21.32; H, 2.75; N, 17.04; Cl, 11.80; Cd, 44.89%. Calcd for $C_9H_{14}N_6Cl_2Cd_2$: C, 21.53; H, 2.81; N, 16.75; Cl, 14.12; Cd, 44.79%.

Their crystal structures were analyzed by single crystal X-ray diffraction method. The crystal data are: 1, $Cd(C_3H_{10}N_2)Ni(CN)_4 \cdot 0.5C_2H_4Cl_2$, FW = 398.78, orthorhombic, Pnma, a = 13.916(3), b = 26.638(2), c = 7.631(4) Å, V = 2829(2) $Å^3$, Z = 8, Dm/Dx = 1.87(1)/1.87, R = 0.065 for 2919 independent reflections; 2, $Cd(C_3H_{10}N_2)Cd(CN)_4 \cdot C_2H_4Cl_2$, FW = 501.98, monoclinic, $P2_1/n$, a = 8.278(2), b = 14.904(2), c = 14.477(1) Å, β = 91.24(1)°, V = 1785.7(1) $Å^3$, Z = 4, Dm/Dx = 1.86(1)/1.87, R = 0.068 for 4991 independent reflections. The intensity data were collected on a Rigaku AFC5R four-circle automated diffractometer using graphite-monochromated Mo Kα radiation.3) The ω-scan technique was applied for a 0.80×0.40×0.10 mm crystal of 1, the 2θ-ω one being for a 0.75×0.70×0.10 mm crystal of 2. The structures were solved by the heavy-atom method; the atomic parameters have been refined anisotropically for all the non-hydrogen atoms, except C atoms of the geust in 1, by the block-diagonal least-squares procedures using the programs in UNICSIII.4)

The unit cells and the cavities are illustrated in Fig. 1 for 1 and 2, respectively. The channel-like cavity extends along the crystal c-axis in 1. The cavity unit for a guest molecule is surrounded by four pn-chelated Cd atoms, each of which is in a six-coordination with the two pn-N atoms, and one each N-terminal from the two crystallographically-equivalent $Ni(CN)_4$ moieties, A, and one each N-terminal from another two crystallographically-equivalent moieties, B, as average. Moiety A makes a doubly-bridged one-dimensional linkage with the Cd atoms to form the ceiling and floor of the channel, and moiety B spans the ceiling and floor at the respective Cd atoms. The guest 1,2-dichloroethane molecule appears to take highly disordered orientation or motion in the channel-like cavity. Significant positional parameters could not be refined for the C atoms due to extremely large thermal parameters; the thermal parameters were large also for the Cl atoms (B_{eq} = ca. 9.3 and 13.4 $Å^2$).

The three-dimensional host of 2 is comprised of the cyanide linkages between the pn-chelated octahedral Cd and the tetrahedral Cd of tetracyano-

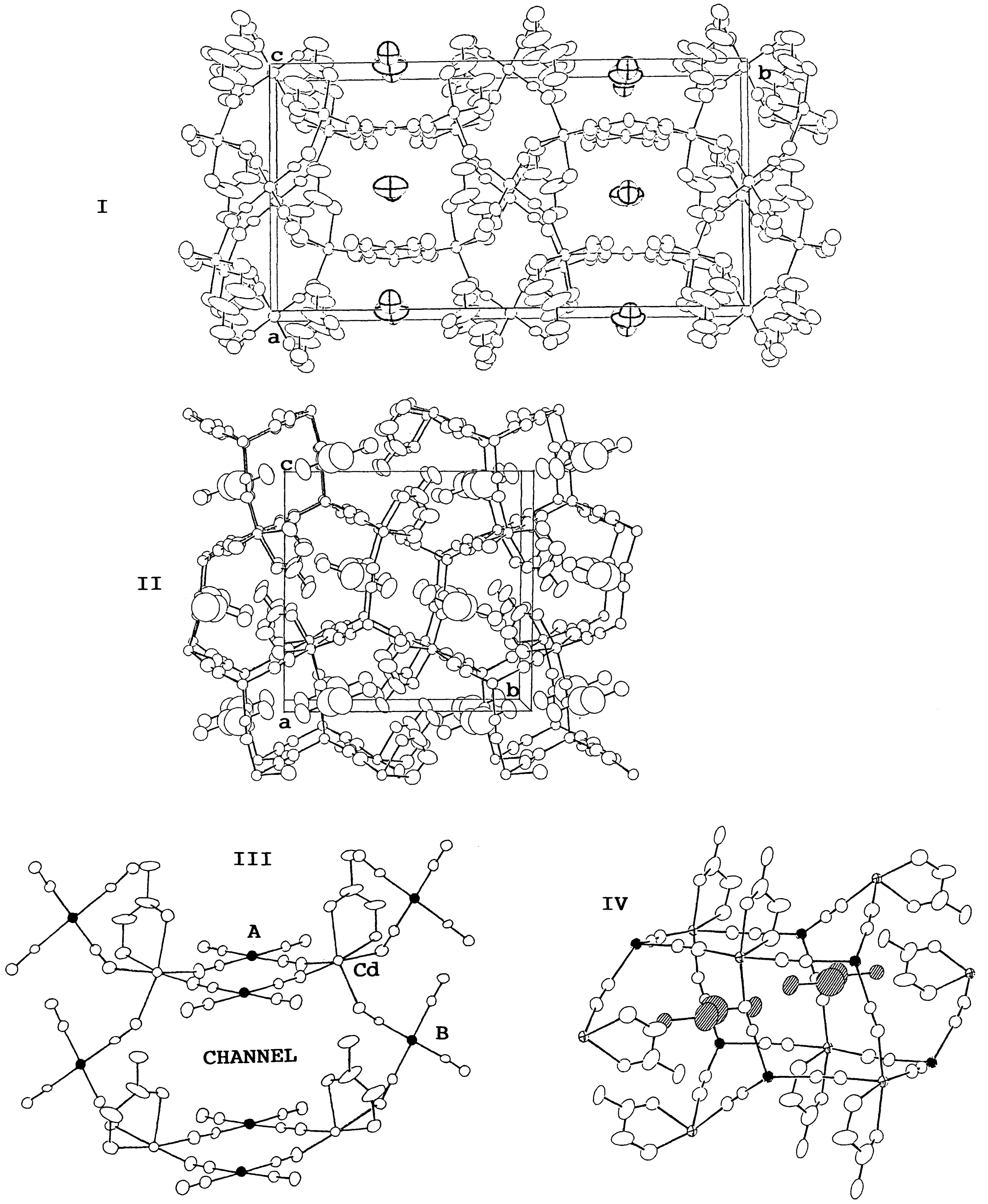

Fig. 1. Perspective views of the unit cell of 1 (I: along the c-axis), and 2 (II: along the a-axis), and those of the channel-like cavity in 1 (III) and of the cage-like one in 2 (IV). In III, solid ellipsoid: square-planar Ni; in IV, shadowed: the guest molecules; solid ellipsoid: tetrahedral Cd.

cadmate(II). A pair of the guest 1,2-dichloroethane molecules are accommodated in the cage-like cavity cornered with fourteen Cd atoms, eight of them being the pn-chelated octahedral Cd atoms. At the both sides of the cavity the corners are not linked with cyanide groups but each of the chelated pn ligands plays a role of the wall separating cavities one and another. The thermal amplitudes are large enough for the Cl atoms of the guest (ca. 10–20 $\mathring{A}^2$ in B_{eq}) and for the C atoms of the pn (ca. 10–14 $\mathring{A}^2$) to suggest the thermal motion of the guest associated with that of the pn-chelate ring.

These structures exemplify a structure isomerism of the metal complexes involved with multidentate ligands which can behave as either chelating or bridging ones.

Any host structures of the en-analogs have not yet been known, although the en-chelated and cyanide-bridged structures of $Cd(en)Ni(CN)_4$ and $Cd(en)Cd(CN)_4$ have been known as the residual hosts left after liberation of the guest molecules from the respective en-bridged host inclusion compounds accompanied with collapse of cavities.[5,6] Hence the methyl group of the pn ligand appears to contribute to the formation of the inclusion structure owing to its lipophilic character, although the results differ from those expected initially.

References

1) T. Iwamoto, "The Hofmann-type and Related Inclusion Compounds," in "Inclusion Compounds Vol. 1," ed by J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London (1984).
2) S. Nishikiori, T. Iwamoto, and Y. Yoshino, Bull. Chem. Soc. Jpn., 53, 2236 (1980).
3) The authors are indebted to Dr. Hikaru Ichida of the Department of Chemistry, Faculty of Science of this University for the use of the diffractometer.
4) The authors have deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.
5) T. Kitazawa, Y. Mizushima, J. Shiraha, R. Taguchi, A. Katoh, T. Hasegawa, S. Nishikiori, and T. Iwamoto, J. Incl. Phenom., in press.
6) S. Nishikiori and T. Iwamoto, J. Incl. Phenom., 3, 283 (1985).

(Received July 4, 1990)