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Novel Three-dimensional Host Structure Revealed in the Crystal Structure of N-Methyl-1,3-diaminopropanecadmium(II) Tetracyanonickelate(II)-Cyclohexane(2/1)

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The cavity accommodating the guest cyclohexane molecule in the title clathrate compound is topped and bottomed by the two-dimensionally extended catena-[cadmium(II) tetra-μ-cyanonickelate(II)] networks and walled by the chelate ring of the N-methyl-1,3-diaminopropane coordinate to the Cd atom and by another tetracyanonickelate(II) linkage involving the Cd atom.

We have been developing the clathrate compounds of three-dimensional host structures from the Hofmann-type $Cd(NH_3)_2Ni(CN)_4\cdot 2G$ clathrate. The Hofmann-diam-type series have been synthesized with the general formula $Cd[NH_2(CH_2)_{n}NH_2]$-$Ni(CN)_4\cdot xG$ for the α,ω-diaminoalkanes of n = 4~9 for various aromatic guest molecules G.[1-5] Their host structures are essentially of the pillared intercalation type: the two-dimensionally extended networks of cadmium(II) tetracyanonickelate(II) are bridged by the α,ω-diaminoalkane ligands. In our recent attempt to use N-substituted α,ω-diaminoalkanes in place of the α,ω-diaminoalkanes, the title clathrate compound was synthesized as the first example of accommodating an alicyclic guest. The single crystal X-ray diffraction analysis revealed a novel three-dimensional host structure.

The cyclohexane clathrate, N-methyl-1,3-diaminopropanecadmium(II) tetracyanonickelate(II)-cyclohexane(2/1), was synthesized by the method similar to those applied to the Hofmann-diam-type series. Anal. Found: C, 32.8; H, 4.46; N, 20.8; Cd, 27.8; Ni, 14.6%. Calcd for $C_{11}H_{18}N_6CdNi$ ($=Cd[CH_3NH(CH_2)_3NH_2]Ni(CN)_4\cdot\frac{1}{2}C_6H_{12}$): C, 32.59; H, 4.47; N, 20.73; Cd, 27.72; Ni, 14.47%. The crystal data are: F.W.=405.40; tetragonal, P4/mbm, a=14.209(2), c=7.876(1) Å; D_m=1.68(1) and D_x=1.69 g cm^{-3}, Z=4; graphite monochromated Mo Kα; 961 independent reflections; R=0.055. The eleven atoms constructing the host lattice in an asymmetric unit except hydrogens were refined with the anisotropic temperature factors; the atoms of the guest cyclohexane molecule were not included in the refinement.

As Fig. 1 shows, there are two kinds of square-planar tetracyanonickelate(II) moieties, centered at Ni(1) and Ni(2) respectively, in the unit cell, whereas all the Cd atoms are equivalent. The N-methyl-1,3-diaminopropane (mtn) ligates to the Cd atom as a chelating ligand in contrast to those bridging α,ω-diaminoalkanes found in other Hofmann-diam-type clathrates. The $Ni(1)(CN)_4$ is linked at each N-end to the Cd atom so as to form catena-[cadmium(II) tetra-μ-cyanonickelate(II)]

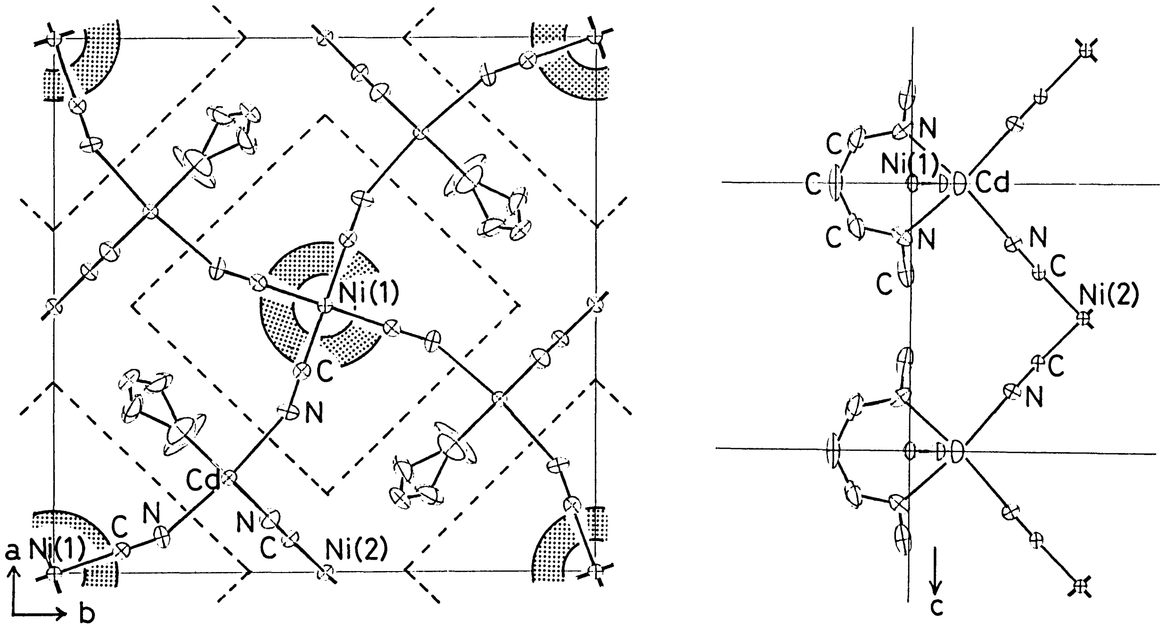

Fig. 1. Projections along the [001] (left: broken lines show the effective area of the cavity) and [110] (right: guest molecules are omitted).

network two-dimensionally extended along the ab-plane of the tetragonal unit cell. The Ni(2)$(CN)_4$ forms an X-shaped chain with the Cd atoms along the c-axis of crystal. The cavity, approximated to a rectangular box of the 7×7×5 $Å^3$ dimensions, is topped and bottomed by the Ni(1)$(CN)_4$ moieties; each side is walled by a couple of each half of the mtn-chelate rings coordinate to the Cd atoms in the top and the bottom, and by a pair of the cyanide bridges between the Ni(2) and both the Cd atoms. This type of three-dimensional structure has never been found in the Hofmann-type and related clathrates so far known previously.

The P4/mbm space group causes the structural disorder as follows: (i) the mirror planes ruling the mm site symmetry at the Cd atom give the statistically distributed mirror images of the mtn chelate ring, and (ii) the 4/m site symmetry at the center of the cavity reveals the electron densities of the guest cyclohexane molecule as a torus of a peak radius of 1.5 Å.

In spite of the multifold disorder in the structure, the host appears to be rigid enough to accommodate various kinds of organic molecules, either aromatic, alicyclic, or aliphatic, with little change in the lattice parameters so far observed by powder X-ray diffractometry. The details will be reported elsewhere.

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