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THERMAL REARRANGEMENT OF THE BRIDGING ETHYLENEDIAMINE LIGAND TO A CHELATING ONE ACCOMPANIED WITH THE LIBERATION OF THE GUEST MOLECULES FROM AN en-Td TYPE $Cd(en)Cd(CN)_4 . 2C_6H_6$ CLATHRATE

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The en ligand bridging a pair of Cd atoms in the host structure of an en-Td type $Cd(en)Cd(CN)_4 . 2C_6H_6$ clathrate was concluded to turn to a chelating ligand in the residual host metal complex $Cd(en)Cd(CN)_4$ left after releasing the guest molecules in vacuo at 100°C from the structural analysis of the $Cd(en)Cd(CN)_4$ crystal independently grown up from an aqueous solution.

Hofmann type and the analogous clathrates[1)] decompose spontaneously under ambient condition with releasing the guest molecules such as aniline, benzene, pyrrole, or thiophene. The decomposition, however, is not completely accomplished for the clathrates with three-dimensional host structure, for example $Cd(en)Cd(CN)_4 . 2C_6H_6$, built of tetrahedral tetracyanometallate moieties and ambident α,ω-diamines bridging a pair of the Cd atoms in a six-coordination. When one keeps evacuating the powdered specimen of the en-Td type $Cd(en)Cd(CN)_4 . 2C_6H_6$ clathrate at 100°C for a week, the host metal complex $Cd(en)Cd(CN)_4$ is left as colorless powder after the complete liberation of the guest benzene molecules. Anal. Found: C, 18.7; H, 2.1; N, 21.3; Cd, 57.2%. Calcd for $C_6H_8N_6Cd_2$: C, 18.52; H, 2.13; N, 21.60; Cd, 57.79%. In spite of such a long duration of evacuating and heating, the residual host appears not to suffer any thermal decomposition with regard to the constituent moieties themselves. It is our point of interest whether or not the residual host still keeps the structure with rather unusual bridging en ligand materialized in the original host structure in the presence of the guest molecules.

The structure of $Cd(en)Cd(CN)_4 . 2C_6H_6$ has been analyzed previously and shown to have a three-dimensional host frame built of the tetrahedral $Cd(CN)_4$ moieties linked by each of the N-terminals with the six-coordinate Cd, a pair of which are bridged by an ethylenediamine ligand[2]. Although it has been unable to determine the conformation of the en molecule owing to the high disorder in the crystal structure, the vibrational spectrum supports the trans conformation most plausibly[3]. On the other hand, the fact that in the Raman spectrum of the residual host a strong band is observed at 859 cm^{-1} suggests us the en ligand in the residual host taking a gauche conformation. Anyway, distortion should occur in the structure of residual host so as to reduce the vacant space left after the liberation of the guest molecules from the clathrate. In fact, the density increases from 1.86 $g\ cm^{-3}$ for the clathrate to 2.12 $g\ cm^{-3}$ for the residual host. Furthermore, the compacted residual host cannot reabsorb benzene molecules even under reflux with benzene for a few weeks.

In the course of experiments to check the preparation condition of the clathrate and bisethylenediaminecadmium complexes, we happened to discover that crystals of the metal complex $Cd(en)Cd(CN)_4$ with the same composition to that of the residual host were grown up from the aqueous solution containing $[Cd(en)_3]Cl_2$ and $K_2[Cd(CN)_4]$ in a 1:1 molar ratio at pH 9. The elementary analysis, infrared and Raman spectroscopies, powder X-ray diffractometry, and density measurement of the prepared complex gave the results completely coincident with those for the residual host complex $Cd(en)Cd(CN)_4$. Anal. Found: C, 18.3; H, 2.13; N, 21.5; Cd, 57.6%. Therefore, it was concluded that the crystals grown up from the aqueous solution have the same structure as that of the residual host. Then, the crystals were subjected to single crystal X-ray diffraction experiment to determine the crystal and molecular structure.

The preliminary Weissenberg photographs indicated uniquely that the crystals belong to the tetragonal space group $I4_1/acd$ with the systematic absences of reflections hkl for $h + k + l \neq 2n$, $hk0$ for h or $k \neq 2n$, $h0l$ for h or $l \neq 2n$, and hhl for $2h + l \neq 4n$. The precise determination of lattice parameters and the collection of intensity data were carried out on a Philips four-circle automated diffractometer using MoKα radiation[4]. The crystal data are: $C_6H_8N_6Cd_2$, F. W. = 388.99, Tetragonal, space group $I4_1/acd$, $a = 14.366(1)$ and $c = 23.771(4)$ Å, $U = 4906(2)$ $Å^3$, $D_x = 2.11$ and $D_m = 2.12\ g\ cm^{-3}$, $Z = 16$.

After three-dimensional Patterson synthesis to locate the Cd atoms, the structure was solved by the heavy atom method using 1181 independent non-zero reflections. All the calculations were carried out on a HITAC 8800/8700 computer at the Computer Center of this University using the programs in UNICS[5)] and their local versions. By the successive Fourier syntheses and block-diagonal least-squares calculations, the refinement has been advanced to the stage of the conventional R = 0.047 for all the non-hydrogen atoms applied with the anisotropic thermal parameters.

Although the unit cell contains 16 formula units of $Cd(en)Cd(CN)_4$, an asymmetric unit does only one formula unit so as to make the number of crystallographically independent atoms 8. Both the Cd atoms, Cd-1 in a tetrahedral coordination and Cd-2 in a six-coordination, locate on the twofold axes of the crystal different to each other, respectively. Each of the N-terminals of cyanides extended from the Cd-1 is linked with the Cd-2, to which an ethylenediamine ligand is chelated as shown in Fig. 1. Since the whole crystal structure is too complicated to be described in this short communication, it will be reported in

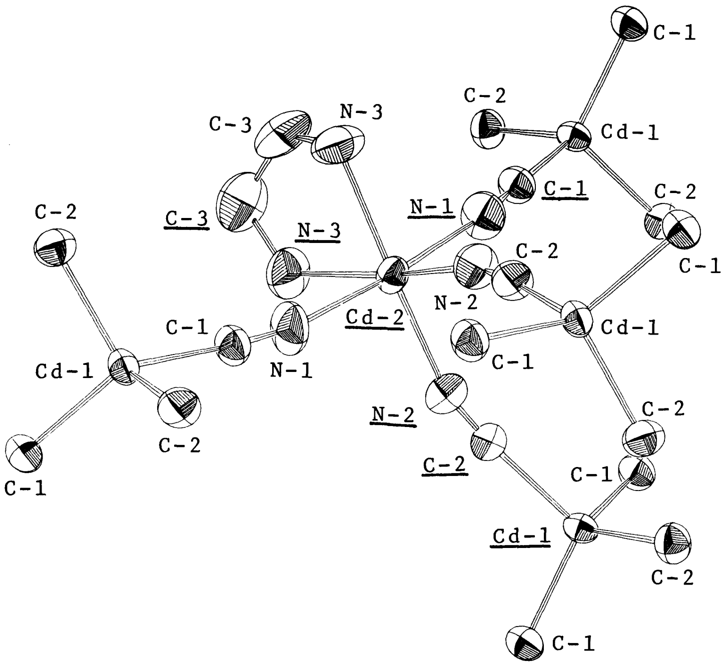

Fig. 1. An ORTEP view of the coordination structure in $Cd(en)Cd(CN)_4$. A part of the crystal structure is shown. A set of the crystallographically independent atoms are underlined. Cd-1, tetrahedral: Cd-1 at (0, 1/4, -0.02625); Cd-2, six-coordinated: Cd-2 at (0.21023, 0.03977, 1/8), (The atomic coordinates applied were the second setting in the International Tables[6)].); C-1 and C-2, C of CN; N-1 and N-2, N of CN; C-3 and N-3, C and N of en.

detail elsewhere. The result which should be noted here is the rearrangement of the en ligand from a bridging one in the original clathrate structure to a chelating one in the residual host structure left after the liberation of the guest benzene molecules. It is difficult to interpret the scheme of rearrangement from the bridging to the chelating, because the relative positions among the tetrahedral Cd-1 and the six-coordinate Cd-2 in the present crystal are quite different from those in the original clathrate host. Therefore, not only the rearrangement of en but also that of the tetracyanocadmate group should be accompanied with the liberation of the guest molecules. Although it can be expected to observe any thermal behavior indicative of these rearrangements and the liberation, a previous paper dealing with the thermogravimetry and differential thermal analysis of this clathrate reported only one step losing of the guest benzene up to 135°C7).

References and Note

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