CHEMISTRY LETTERS, pp. 723-726, 1973. Published by the Chemical Society of Japan

THE CRYSTAL STRUCTURE OF CATENA-μ-ETHYLENEDIAMINECADMIUM(II) TETRACYANOCADMATE(II) DIBENZENE CLATHRATE: $Cd(en)Cd(CN)_4 . 2C_6H_6$

Toschitake IWAMOTO
Department of Chemistry, College of General Education
The University of Tokyo, Komaba, Meguro, Tokyo 153

The crystals of $Cd(en)Cd(CN)_4 . 2C_6H_6$ belong to the tetragonal space group $P4_2/mmc$ with the dimensions a = 8.262(6) and c = 15.495(2) A (Z = 2). The three-dimensional host lattice is built of the network of Cd-CN-Cd and Cd-en-Cd linkages to form two kinds of cavities for the guest benzene molecules. The host en and the guest C_6H_6 molecules are so flexible and dynamic that precise atomic positions can hardly be determined.

As has been reported in the previous communication[1)], a novel benzene clathrate $Cd(en)Cd(CN)_4 . 2C_6H_6$ forms as colorless crystals on the boundary surface between the organic phase of neat benzene and the aqueous solution of $Cd(en)_3Cl_2$ and $K_2Cd(CN)_4$. The preliminary X-ray precession photographs of the single crystal and the powder diffraction data supported that the unit cell has the dimensions a = b = 8.27 A, c = 15.50 A, and $\alpha = \beta = \gamma = 90^\circ$. This communication will report on the crystal structure analyzed from three-dimensional X-ray data collected by counter method.

The single crystal of dimensions 0.1 x 0.2 x 0.3 mm was sealed in a thin-walled soft glass capillary with a small drop of benzene to prevent the escape of benzene from the crystal. The intensity data were collected on a Rigaku Denki computer-controlled four-circle diffractometer with Mo Kα radiation for 1445 reflections with 2θ less than 55° by $2\theta - \omega$ scanning technique. From the diffraction symmetry and the systematic absences of the hhl reflections with odd l, the space group was limited to one of the three $P4_2mc$, $P\bar{4}2c$ and $P4_2/mmc$. Among 721 independent reflections, 569 reflections had non-zero values. The structure was solved by applying the heavy atom method. At earlier stage of the refinements, the calculations had been made for the three space groups respectively. The best results were obtained for the $P4_2/mmc$. The crystallographic data are as follows:

$Cd(C_2H_8N_2)Cd(CN)_4 . 2C_6H_6$	F.W. = 545.2	tetragonal
a = 8.262 ± 0.006 A	c = 15.495 ± 0.002 A	space group $P4_2/mmc$
$D_x = 1.71$ g cm^{-3}	$D_m = 1.68$ g cm^{-3}	Z = 2

The calculations were carried out with a HITAC 5020E electronic computer at the Computation Center of the University of Tokyo by using UNICS ANSFR-2 and HBLS-IV programs.[2)] The LP correction was applied but no correction was made for absorption (linear absorption coefficient for Mo Kα, $\mu = 21.8$ cm^{-1}). The final R-index 0.205 was obtained by the block-diagonal least-squares refinements of the all non-hydrogen atoms in use of the anisotropic thermal parameters.

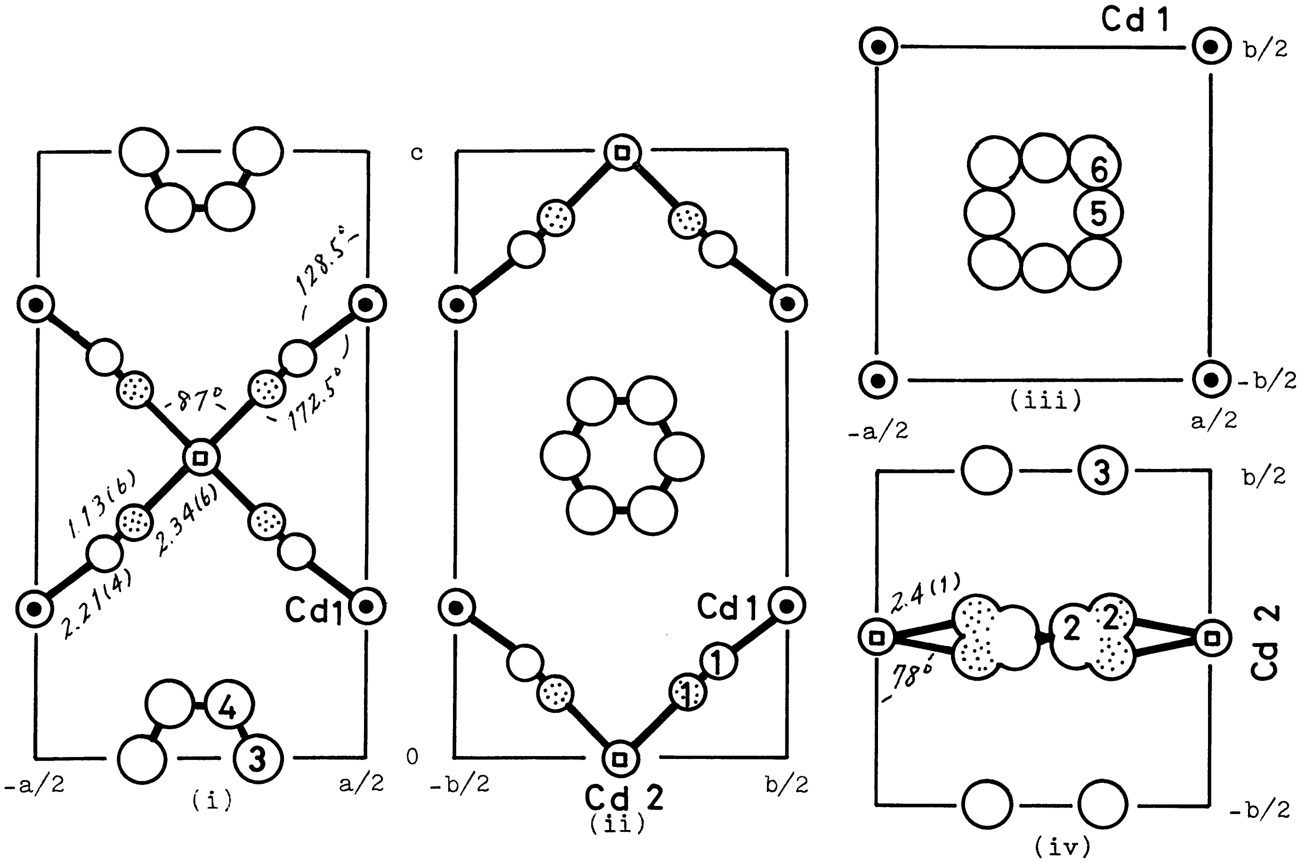


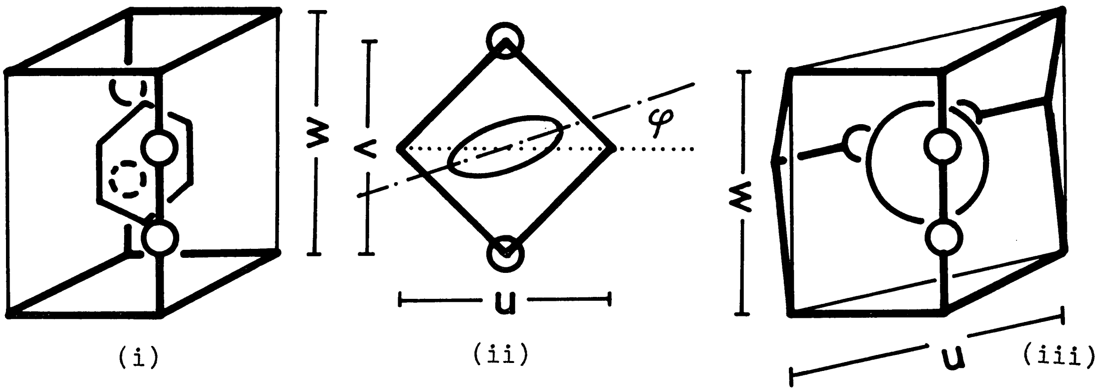
Fig. 1. The Structure of Cd(en)Cd(CN)$_4$.2C$_6$H$_6$

(i) The Section normal to the b-axis at y=b/2; x, -a/2∼a/2 and z, 0∼c.
(ii) The Section normal to the a-axis at x=a/2; y, -b/2∼b/2 and z, 0∼c.
(iii) The Section normal to the c-axis at z=c/4; x, -a/2∼a/2 and y, -b/2∼b/2.
(iv) The Section normal to the c-axis at z = 0; x, -a/2∼a/2 and y, -b/2∼b/2.
Open circle, C; shadowed circle, N; Circle with open square, Cd in hexa-coordination; circle with solid circle, tetrahedral Cd.

Table 1. The atomic coordinates.

ATOM	*1	*2	x/a	y/b	z/c
Cd 1	2 f 42m	0.125	0.500(0)	0.500(0)	0.250(0)
Cd 2	2 d mmm	0.125	0.500(0)	0.000(0)	0.000(0)
C 1	8 p m	0.5	0.500(0)	0.291(5)	0.161(0)
N 1	8 p m	0.5	0.500(0)	0.196(6)	0.109(2)
C 2	8 q m	0.25	0.101(12)	0.032(28)	0.000(0)
N 2	8 q m	0.25	0.215(16)	0.059(10)	0.000(0)
C 3	4 m m	0.25	0.171(12)	0.500(0)	0.000(0)
C 4	8 p m	0.5	0.090(8)	0.500(0)	0.088(7)
C 5	8 o m	0.25	0.155(12)	0.000(0)	0.250(0)
C 6	16 r 1	0.5	0.117(24)	0.149(31)	0.250(0)

*1 Number of positions, Wyckoff notation and point symmetry.
*2 The weight used in the calculations.



(i) (ii) (iii)

Fig. 2. The Illustration of the Cavities and Their Dimensions.
(i) Rhombohedron (the α-cavity) or rectangular box.
(ii) Projection of (i) along w axis.
(iii) Biprismatic cage (the β-cavity).

Table 2. Comparison of the volume of cavity.

HOST	u	v	w	φ	VOLUME
$Mn(NH_3)_2Ni(CN)_4$	7.432 A	7.432 A	8.335 A	26°	230.2 A^3
$Ni(NH_3)_2Ni(CN)_4$	7.242	7.242	8.277	23	217.1
$Cu(NH_3)_2Ni(CN)_4$	7.345	7.345	8.260	26	222.8
$Cd(NH_3)_2Ni(CN)_4$	7.575	7.575	8.317	31	238.6
$Cd(en)Ni(CN)_4$	7.675	7.675	8.056	5	237.3
$Cd(en)Cd(CN)_4$ α	7.748	8.262	8.262	0	264.4
β	8.262	7.748	8.262	0	264.4

The crystal structure is illustrated in Fig. 1. There are two kinds of Cd atoms, Cd 1 and Cd 2, in the host lattice. Cd 1 is that of the tetrahedral $Cd(CN)_4$ and Cd 2 is in a hexa-coordination with four N atoms of four $Cd(CN)_4$ moieties and two N atoms of two catena-μ-en ligands, which make an infinite -en-Cd-en-Cd-en- linkage along the a or b axis of crystal. The $Cd(CN)_4$ moiety suffers a distortion from a regualr tetrahedron along the c-axis of crystal so that the Cd-C-N-Cd linkage is bent by ca. 7.5° at the C atom unlike the linear Cd-C-N-Cd found in $Cd(CN)_2$. The distortion is apparently caused from the en bridging between Cd 2 atoms, the length of which determines the a dimension of unit cell. However, the value of a = 8.262 A, i. e., the length of Cd-en-Cd bridge, is longer by ca. 0.2 A than that observed for the Cd-en-Cd bridge in $Cd(en)Ni(CN)_4.2C_6H_6$ 3). Therefore, it can be said that the host lattice is in a balance between the bridging force of en in the Cd-en-Cd linkage and the reactive force of $Cd(CN)_4$ moiety against the distortion from a regular tetrahedron. The atomic coordinates of the en molecule have been determined only with the large standard deviations from the least-squares calculations by assuming each set of the atomic positions possible in the $P4_2/mmc$ space group. Those values listed in Table 1 are the best among the examined ones. The en molecule appears to take a trans configuration in the xy-plane at z = 0 where a couple of the possible orientations are in a statistically random distribution.

The rotation model, which has been rationalized in the crystal structure of $Cd(en)Ni(CN)_4.2C_6H_6$[3], was rejected on the Fourier maps and from the least-squares calculations.

The host lattice provides two kinds of cavities, α and β, to the guest benzene molecules; the shape of the α-cavity is approximated to a rhombohedron and that of the β-cavity is a biprismatic cage. The both cavities have approximately the same volumes. The α-cavity is similar in shape to that in $Cd(en)Ni(CN)_4.2C_6H_6$ and to those in the Hofmann-type $M(NH_3)_2Ni(CN)_4.2C_6H_6$ clathrates[4] if the two NH_3 molecules are replaced by an en molecule. However, with regard to the volume the α-cavity (and the β-cavity) is considerably larger than those cavities in the other clathrates as is compared in Table 2 along with the illustration of the dimensions in Fig. 2. In these bulky α- and β-cavities, the guest benzene molecules may have a freedom of motion in a certain extent. In fact, their atomic positions could not be uniquely fixed but with the extremely large standard deviations and the unusual interatomic distances; the molecular shape of benzene in the β-cavity is quite unusual.

The present results, the best among the calculations made for all the possible sets of atomic positions including those for the en molecule in accordance with the $P4_2/mmc$ space group and the stoichiometry, claim that the en, the benzene in the α-cavity, and that in the β-cavity are apparently placed in the xy-plane at $z = 0$, the xz-plane at $y = b/2$, and the xy-plane at $z = c/4$, respectively. These positions with the rather high point symmetries may be resulted from the average of vehement thermal motions of the en and the benzene molecules. Therefore, the structure in Fig. 1 would be seen as the most probable model of $Cd(en)Cd(CN)_4.2C_6H_6$.

References

1) T. Iwamoto and D. F. Shriver, Inorg. Chem., 11, 2570 (1972).

2) Crystallographic Society of Japan, 5020 UNICS, The Universal Crystallographic Computation Program System (1967).

3) T. Miyoshi, T. Iwamoto and Y. Sasaki, Inorg. Chim. Acta, 6, 59 (1972).

4) T. Iwamoto, T. Nakano, M. Morita, T. Miyoshi, T. Miyamoto and Y. Sasaki, ibid., 2, 313 (1968).

(Received May 14, 1973)