Crystal Structures of Ethylenediaminecadmium(II) Tetracyanocadmate(II)-Benzene(1/2) and Ethylenediaminecadmium(II) Tetracyanocadmate(II)⋆

SHIN-ICHI NISHIKIORI and TOSCHITAKE IWAMOTO⋆⋆
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

Abstract. The crystal structure of ethylenediaminecadmium(II) tetracyanocadmate(II)-benzene(1/2), **I**, has been redetermined based on 1632 reflections collected anew for the crystal coated with epoxy resin, with a final conventional $R = 0.038$; **I** crystallizes in space group $P4_222$, with $a = b = 8.265(1)$ and $c = 15.512(3)$ Å, and $Z = 2$. Ethylenediaminecadmium(II) tetracyanocadmate(II), **II**, is concluded to be identical with the residual metal complex host of **I**, remaining after the liberation of the guest benzene molecules; **II** crystallizes from an aqueous solution containing bis- or tris-ethylenediaminecadmium(II) tetracyanocadmate(II) in space group $I4_1/acd$, with $a = b = 14.366(1)$ and $c = 23.771(4)$ Å, and $Z = 16$; refinement led to a conventional $R = 0.043$ for 1181 reflections. The bridging ethylenediamine ligand in **I** turns to a chelating one in **II**; dissociation and recombination should occur in the coordination sphere of the six-coordinate cadmium atom, when **II** is derived from **I** by the liberation of the guest molecules.

Key words: Crystal structure, Hofmann-type, en-T_d-type, metal complex, benzene inclusion compound, ethylenediamine.

1. Introduction

A great impetus to the chemistry of Hofmann-type clathrates was given by the determination of the crystal structure of Hofmann's benzene compound $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ by Powell and Rayner [1, 2]. It gave a motivation to the extension of variations of metal complex host, using metal species other than nickel(II), and also using amine or diamine in place of the ammine ligand. After the first attempt by Baur and Schwarzenbach [3], the present authors and coworkers have developed a number of inclusion compounds formed between diammine- or diaminemetal(II) tetracyanometallate(II) hosts and aromatic guest molecules [4–7]. Among them a series of clathrate compounds named en-T_d-type with a general formula $Cd(en)M(CN)_4 \cdot 2G$ (en = $C_2H_8N_2$; M = Cd or Hg; G = C_4H_5N, C_4H_4S, or C_6H_6) have been derived from the Hofmann-type $Cd(NH_3)_2Ni(CN)_4 \cdot 2G$ by replacing the pair of NH_3 ligands by an en, and the square-planar $Ni(CN)_4$ by tetrahedral $M(CN)_4$ [8–10]. The preliminarily reported structure of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ [10] demonstrated that its three-dimensional host structure is substantially similar to that presumed from the powder X-ray diffraction data [8], but the reliability index $R = 0.205$ (assuming the $P4_2/mmc$ space group) was barely acceptable for discussion of the structure in detail.

⋆ Dedicated to Professor H. M. Powell.
⋆⋆ Author for correspondence.

The clathrate liberates the guest benzene molecule gradually under ambient condition to leave a residual host metal complex $Cd(en)Cd(CN)_4$ as a fine powder. On the other hand, crystals of the metal complex $Cd(en)Cd(CN)_4$ can be grown from an aqueous solution containing $[Cd(en)_n]^{2+}$ ($n = 2-3$) and $[Cd(CN)_4]^{2-}$; its crystal structure has been reported briefly [11]. The crystallographic and spectroscopic data support that both the metal complexes have the same composition and also have identical crystal structures. This is an exceptional case of the Hofmann-type and analogous clathrates for which both the structures of the clathrate and the guest-free host metal complex are known. The present paper reports in detail on the crystal structures of the benzene clathrate and the metal complex obtained from the aqueous solution. For the clathrate, the structure was redetermined based on the reflection data collected anew for the single crystal coated with epoxy resin to prevent spontaneous decomposition during the measurement; the systematic absences of reflections were carefully reexamined. The comparative observations for the isomorphic $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$ and $Cd(en)Hg(CN)_4$ were also examined based on the powder X-ray data.

2. Experimental

2.1. MATERIALS

Single crystals of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$, **I**, and $Cd(en)Cd(CN)_4$, **II**, were prepared by the methods already described [9, 11]. Polycrystalline specimens of $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$, **III**, and $Cd(en)Hg(CN)_4$, **IV**, were prepared by a similar method using $K_2[Hg(CN)_4]$ in place of $K_2[Cd(CN)_4]$. The residual metal complex hosts $Cd(en)Cd(CN)_4$, **II′**, and $Cd(en)Hg(CN)_4$, **IV′**, were prepared by keeping the benzene clathrates *in vacuo* at $100°C$ for a week [6].

2.2. STRUCTURE DETERMINATION

The crystallographic and experimental data are listed in Table I for **I** and **II**. The atomic parameters determined are listed in Tables II and III for **I** and **II**, and selected atomic distances and bond angles are in Tables IV and V, respectively. Figures 1 and 2 show the structures of **I** and **II** solved along with the atomic notations.

All the calculations for structure refinement were carried out on a HITAC 280M computer at the computation center of this University using the programs in UNICSIII [12] and their local versions; the atomic scattering factors used are those in the International Tables [13].

2.2.1. $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$, **I**

The single crystal was coated and fixed at the top of a thin glass rod with epoxy resin. Three reflections (300, 030, and 040), measured every 100 reflections during the collection of intensity data, varied their intensitites within 2%; Lp corrections were made, but absorption and extinction were not corrected for.

The space group was uniquely determined to be $P4_2 22$ from the systematic absences of $00l$ (odd l) reflections. Among the 17 hhl (odd l) reflections in the observed range, 11 showed significant intensities: the $P4_2/mmc$ space group, which had been applied previously [9], was discarded. Before the final stage of refinement, all of the non-hydrogen atoms were located on the Fourier map. Disorder was observed for the en ligand centered at 0, 0, 0, and for the

Table I.   Crystallographic parameters and experimental data

	I	II
formula	$Cd(en)Cd(CN)_4 \cdot 2C_6H_6$	$Cd(en)Cd(CN)_4$
formula weight	545.22	388.99
crystal system	tetragonal	tetragonal
space group	$P4_222$	$I4_1/acd$
$a(=b)/Å$	8.265(1)	14.366(1)
$c/Å$	15.512(3)	23.771(4)
$U/Å^3$	1059.5(3)	4906(1)
Z	2	16
$D_m/g \ cm^{-3}$	1.70(1)	2.12(1)
$D_x/g \ cm^{-3}$	1.71	2.11
systematic absences	$00l: l = 2n + 1$	$hkl: h + k + l = 2n + 1$
		$hk0: h = 2n + 1$ and $k = 2n + 1$
		$h0l: h = 2n + 1$ and $l = 2n + 1$
		$hhl: 2h + 1 \neq 4n$
diffractometer	Rigaku AFC-6A	Philips $P1$
crystal size	$0.3 \times 0.3 \times 0.4$ mm	0.3 mm diameter
temperature	ambient	ambient
radiation	$MoK\alpha (\lambda = 0.70926$ Å)	$MoK\alpha (\lambda = 0.70926$ Å)
monochromator	graphite	graphite
$\mu(MoK\alpha)/cm^{-1}$	21.8	34.2
scan mode	$3° < 2\theta < 30°$: ω scan	2θ-ω scan
	$30° \leqslant 2\theta < 70°$: 2θ-ω scan	
scan range	$3° < 2\theta < 70°$	$2° < 2\theta < 60°$
	$0 \leqslant h \leqslant 13, 0 \leqslant k \leqslant 13,$	$0 \leqslant h \leqslant 20, 0 \leqslant k \leqslant 20,$
	$0 \leqslant l \leqslant 22$	$0 \leqslant l \leqslant 33$
correction	Lp	Lp
number of observed reflections	2710	1181
number of used reflections	1632 ($|F_0| > 3\sigma(F_0)$)	1181($|F_0| > 3\sigma(F_0)$)
number of parameters	60	65
R, R_w, S	0.038, 0.038, 0.713	0.043, 0.035, 3.59
structure analysis	heavy-atom method	heavy-atom method
refinement	block-diagonal least-squares	block-diagonal least-squares
weight scheme	$|F_0| \geqslant 128 \quad w = (128/F_0)^2$	$|F_0| \geqslant 40 \quad w = (40/F_0)^2$
	$128 > |F_0| > 32 \quad w = 1.0$	$40 > |F_0| > 8 \quad w \ 1.0$
	$|F_0| \leqslant 32 \quad w = 0.25$	$|F_0| \leqslant 0.25$

benzene molecule (G2) in the β-cavity [8] centered at 0, 0, 1/4. The benzene molecule (G1) in the α-cavity centered at 0, 1/2, 0 was uniquely located by fixing the y-coordinate of C(4) at 1/2 in order to force the G1 benzene to keep planarity. Although the electron densities of the G2 benzene skeleton appeared as a torus in the bc-plane of the crystal at $z = 1/4$, the refinement was carried out assuming that a couple of equally-distributed hexagons are overlapped with each other to satisfy the site group 222 at 0, 0, 1/4 by fixing the y-coordinate of C(5) at 0, and the z-coordinates of C(5), C(6), and C(7) at 1/4, respectively. Since any molecular groups of en ($2/m$ for the *trans*, $2m$ for the *cis*, and 2 for the *gauche* conformations) cannot be correlated with the site group 222 at 0, 0, 0, the en ligand should be statistically distributed about the a-axis of the crystal. In the refinement, the C(2)–C(2)* bond was fixed on the a-axis, and an unusually short single bond distance, 1.358(9) Å, was therefore

Table II.   Positional and equivalent-isotropic thermal parameters with estimated standard deviations in the least significant digits in parentheses for $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$

atom	weight	x/a	y/b	z/c	$B_{eq}/Å^2$
Cd(1)	0.250	0.5	0.5	0.25	2.537(7)
Cd(2)	0.250	0.5	0.0	0.0	2.26(1)
C(1)	1.000	0.499(2)	0.2913(4)	0.1597(3)	3.5(1)
C(2)	0.500	0.0822(8)	0.0	0.0	8.3(6)
C(3)	0.500	0.164(1)	0.5	0.0	7.1(5)
C(4)	1.000	0.081(1)	<u>0.5</u>[*1]	0.0739(5)	7.2(4)
C(5)	0.500	0.166(1)	<u>0.0</u>	<u>0.25</u>	5.3(2)
C(6)	0.500	0.084(2)	0.141(2)	<u>0.25</u>	5.4(3)
C(7)	0.500	−0.083(2)	0.143(2)	<u>0.25</u>	5.5(3)
N(1)	1.000	0.520(1)	0.1962(5)	0.1077(3)	3.5(2)
N(2)	0.500	0.2188(9)	0.059(1)	0.0163(8)	3.9(4)
					$B_{iso}/Å^2$
H(1)[*2]	0.500	0.21037	0.17509	−0.01565	6.0
H(2)	0.500	0.21037	0.07763	0.08507	6.0
H(3)	0.500	0.09931	−0.11450	0.03229	6.0
H(4)	0.500	0.09931	−0.01704	−0.06842	6.0
H(5)	0.500	0.29461	0.5	0.0	6.0
H(6)	1.000	0.14507	0.5	0.13451	6.0
H(7)	0.500	0.29641	0.0	0.25	6.0
H(8)	0.500	0.14976	0.25430	0.25	6.0
H(9)	0.500	−0.14768	0.25665	0.25	6.0

[*1] Artificially fixed coordinates of non-hydrogen atoms are underlined.
[*2] Positional and thermal parameters have been fixed at the listed values. H(1) and H(2) at N(2); H(3) and H(4) at C(2); H(5) at C(3); H(6) at C(4); H(7) at C(5); H(8) at C(6); H(9) at C(7).

Table III.   Positional and equivalent-isotropic thermal parameters with estimated standard deviations in the least significant digits in parentheses for $Cd(en)Cd(CN)_4$

atom	weight	x/a	y/b	z/c	$B_{eq}/Å^2$
Cd(1)	0.500	0.0	0.25	−0.02625(2)	2.60(3)
Cd(2)	0.500	0.21023(2)	0.03977(2)	0.125	2.850(9)
C(1)	1.000	0.0682(4)	−0.1358(3)	0.0714(3)	3.5(2)
C(2)	1.000	0.1046(4)	0.1795(4)	0.0284(2)	3.5(2)
C(3)	1.000	0.3846(6)	−0.0871(6)	0.1030(5)	7.8(5)
N(1)	1.000	0.1078(4)	−0.0741(4)	0.0901(3)	5.3(3)
N(2)	1.000	0.1525(3)	0.1381(3)	0.0567(2)	4.1(2)
N(3)	1.000	0.3352(4)	−0.0201(4)	0.0702(2)	5.3(3)
					$B_{iso}/Å^2$
H(1)[*1]	1.000	0.38075	0.03681	0.05724	5.0
H(2)	1.000	0.30877	−0.05353	0.03286	5.0
H(3)	1.000	0.44163	−0.04816	0.12580	5.0
H(4)	1.000	0.41903	−0.13581	0.07605	5.0

[*1] Positional and thermal parameters have been fixed at the listed values. H(1) and H(2) at N(3); H(3) and H(4) at C(3).

apparently observed with the thermal ellipsoid expanded along the *bc*-plane of the crystal. This situation was not improved by releasing the fixation of the C(2)—C(2)* bond from the *a*-axis. The anisotropic thermal parameters were applied for the six atoms of the host constituents and the two C atoms, C(3) and C(4), of the G1 guest molecule, the isotropic parameters being applied for the C atoms, C(5–7), of the G2 guest. The hydrogen atoms were located at calculated positions and their isotropic thermal parameters were fixed at 6.0 Å^2; the positional
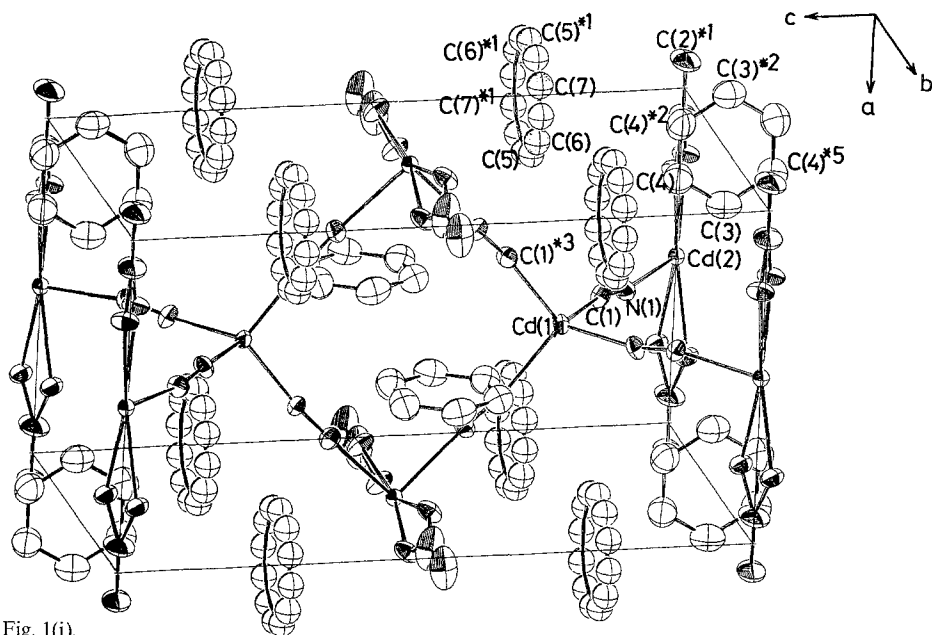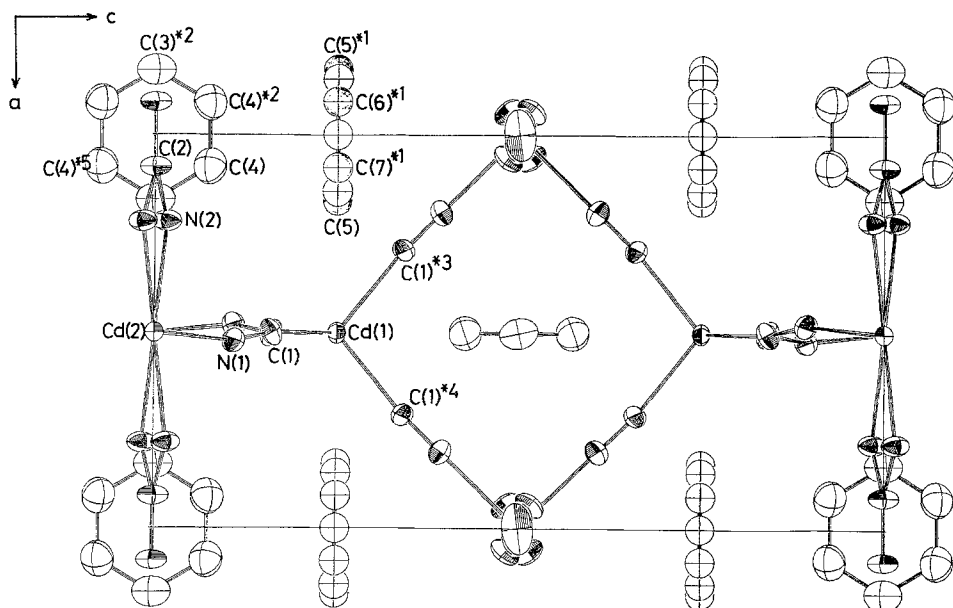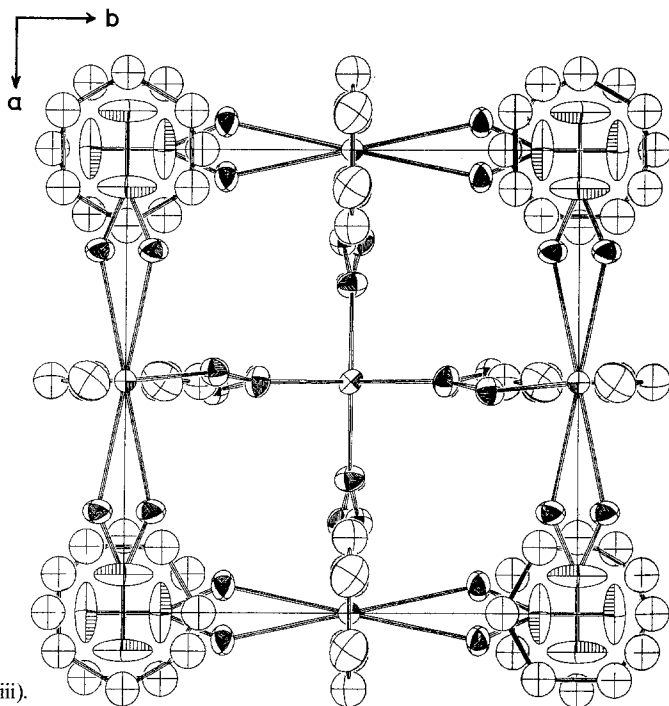

Fig. 1(i).

Fig. 1(ii).

Fig. 1(iii).

Fig. 1. Structure of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$, I. Hydrogen atoms are omitted; thermal ellipsoids with 30% probability. The twelve carbon atoms with the isotropic spheres in β-cavity centered at 0, 0, 1/4 (and the equivalent positions) are those of a pair of benzene skeletons distributed statistically. (i) A view of unit cell. (ii) Projection along b-axis. (iii) Projection along c-axis.

and thermal parameters of the hydrogen atoms were not adjusted but included in the calculation of F_c values. At the final stage of refinement, three reflections, 200 ($F_0 = 136$, $F_c = 221$), 112 (132, 214), and 004 (127, 193), were omitted, assuming that these reflections were greatly influenced by the secondary extinction effect. The shifts of parameters at the final cycle of least-squares calculation was not larger than 27% of their estimated standard deviations; the difference Fourier map remained a vague peak with the density of *ca.* 1.0 e Å^{-3} around the G2 guest molecule [14].

2.2.2. $Cd(en)Cd(CN)_4$, II

The systematic absences of reflections as listed in Table I predicted the space group $I4_1/acd$ uniquely. Parameters refined were the positional and the anisotropic thermal ones for all non-hydrogen atoms. The hydrogen atoms were located at calculated positions with the isotropic thermal parameter fixed at 5.0 Å^2; these parameters were not refined but included in the calculation of F_c values. The shifts of parameters in the final cycle were not larger than 10% of their estimated standard deviations [14].
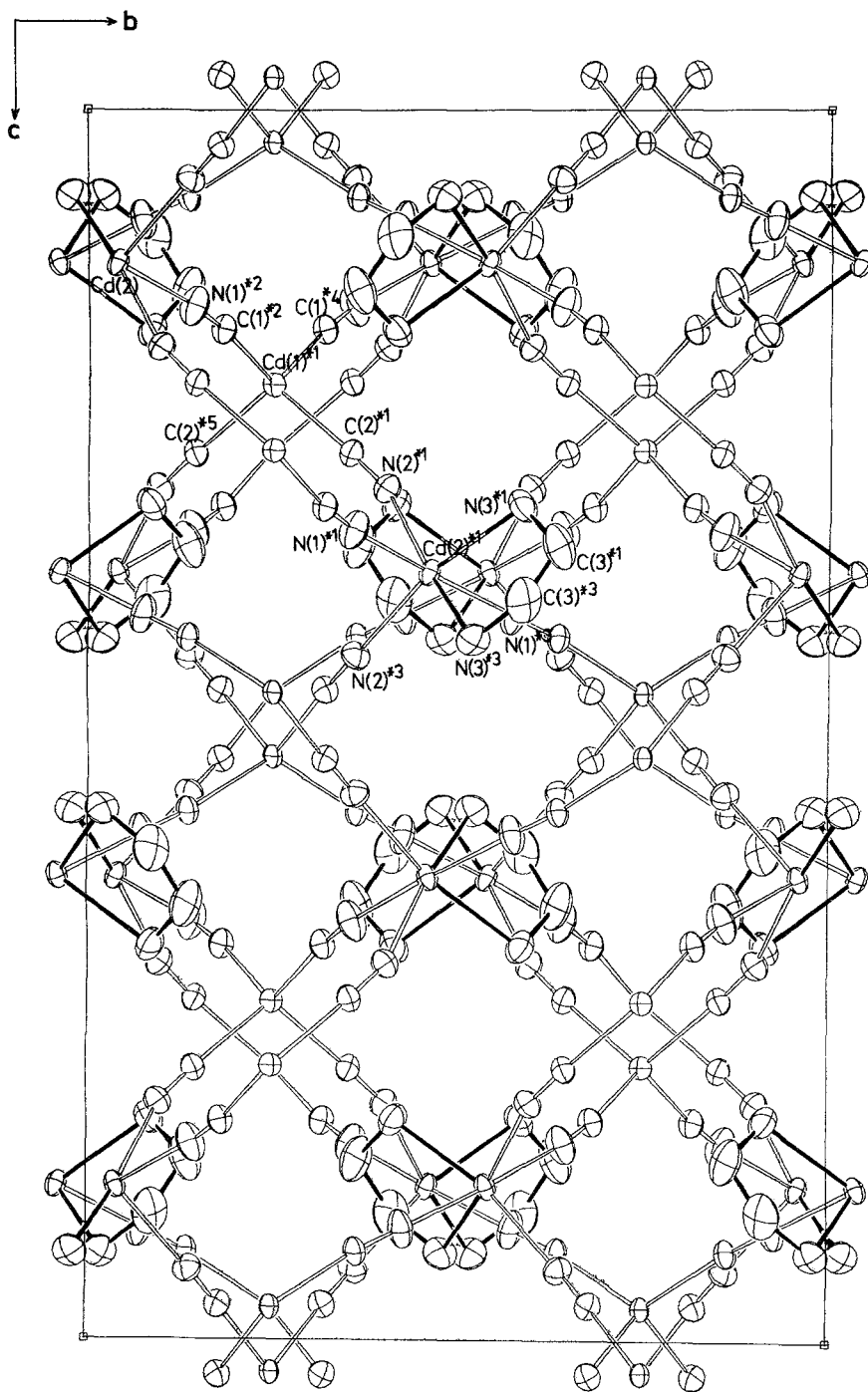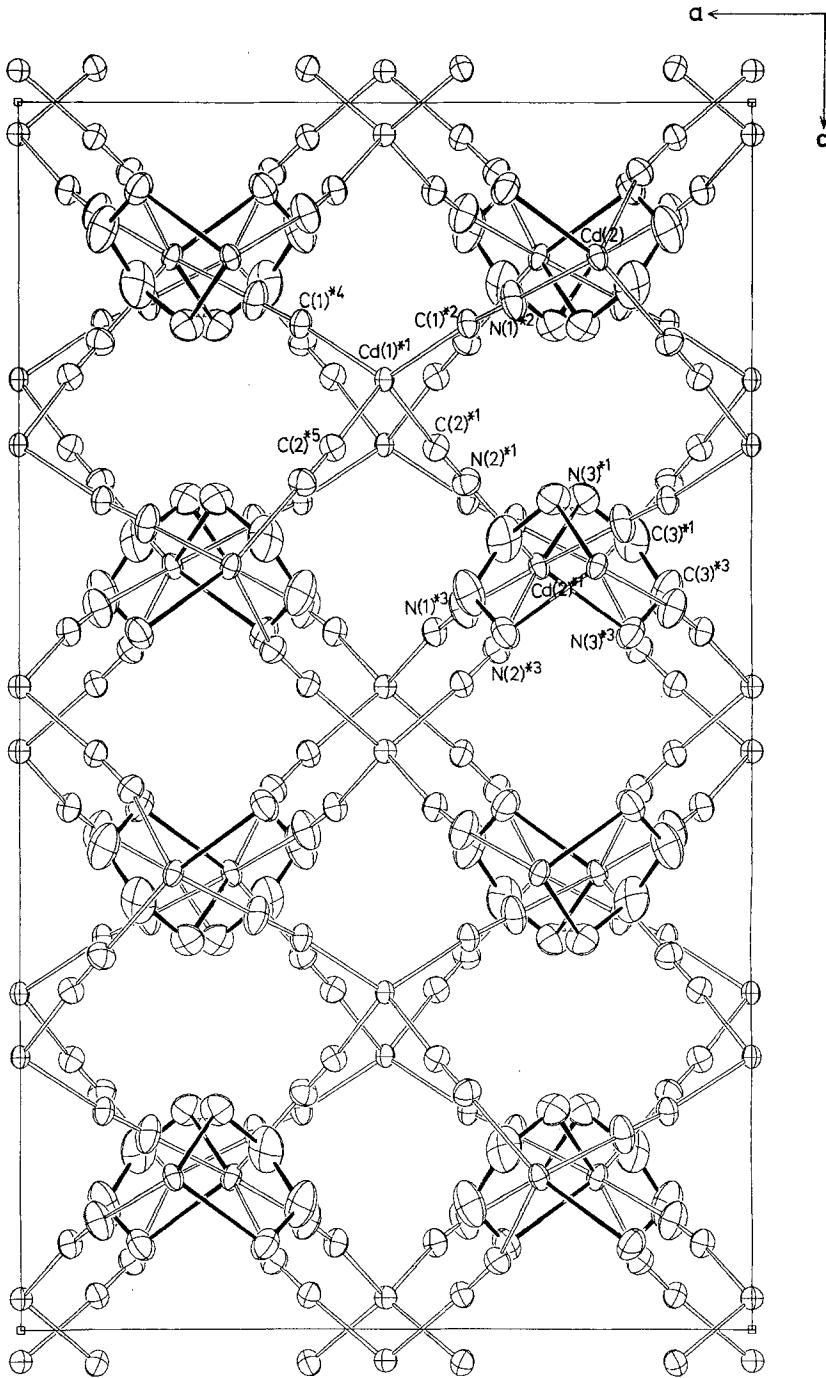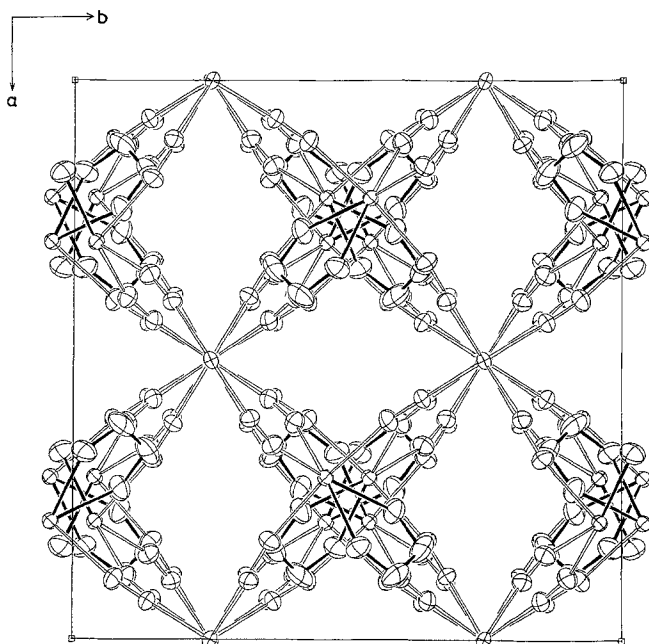
Fig. 2(i).

Fig. 2(ii).

Fig. 2(iii).

Fig. 2. Structure of Cd(en)Cd(CN)$_4$, **II**. Hydrogen atoms are omitted; thermal ellipsoids with 30% probability; the bonds in Cd(2)—en chelate ring are shown as solid lines. (i) Projection along a-axis. (ii) Projection along b-axis. (iii) Projection along c-axis.

Table IV. Selected atomic distances and bond angles for Cd(en)Cd(CN)$_4 \cdot 2C_6H_6$

Bond length, $l/\text{Å}$

Cd(1)—C(1):	2.222(4)	C(1)—N(1):	1.140(6)
Cd(2)—N(1):	2.334(4)	Cd(2)—N(2):	2.389(8)
N(2)—C(2):	1.26(1)	C(2)—C(2)*[1]:	1.358(9)
C(3)—C(4):	1.34(1)	C(4)—C(4)*[2]:	1.33(1)
C(5)—C(6):	1.35(2)	C(6)—C(7):	1.38(2)
C(7)—C(5)*[1]:	1.37(2)		

Bond angle, $\delta/^\circ$

C(1)—Cd(1)—C(1)*[1]:	113.1(1)	C(1)—Cd(1)—C(1)*[4]:	113.8(1)
C(1)*[3]—Cd(1)—C(1)*[4]:	101.8(1)	Cd(1)—C(1)—N(1):	168.8(4)
C(1)—N(1)—Cd(2):	167.1(4)	N(1)—Cd(2)—N(3):	81.5(2)
Cd(2)—N(2)—C(2):	140.6(6)	N(2)—C(2)—C(2)*[1]:	154.0(5)
C(3)—C(4)—C(4)*[2]:	121.0(7)	C(4)—C(3)—C(4)*[5]:	118.1(9)
C(7)*[1]—C(5)—C(6):	120(1)	C(5)—C(6)—C(7):	120(1)
C(6)—C(7)—C(5)*[1]:	120(1)		

Key to symmetry operations; normal x, y, z; with *[1], $-x, -y, -z$; with *[2], $-x, 1 - y, z$; with *[3], $y, x, 1/2 - z$; with *[4], $1 - y, 1 - x, 1/2 - z$; with *[5], $x, 1 - y, -z$.

Table V.   Selected atomic distances and bond angles for Cd(en)Cd(CN)$_4$

Bond length, l/Å

Cd(1)^{*1}—C(1)^{*2}:	2.192(5)	Cd(1)^{*1}—C(2)^{*1}:	2.229(6)
Cd(2)—N(1)^{*2}:	2.351(6)	Cd(2)^{*1}—N(2)^{*1}:	2.307(5)
C(1)^{*2}—N(1)^{*2}:	1.143(8)	C(2)^{*1}—N(2)^{*1}:	1.132(8)
Cd(2)^{*1}—N(3)^{*1}:	2.378(6)	C(3)^{*1}—N(3)^{*1}:	1.43(1)
C(3)^{*1}—C(3)^{*3}:	1.42(1)		

Bond angles, δ/°

Cd(1)^{*1}—C(1)^{*2}—N(1)^{*2}:	173.3(5)	C(1)^{*2}—N(1)^{*2}—Cd(2):	171.1(5)
Cd(1)^{*1}—C(2)^{*1}—N(2)^{*1}:	174.4(5)	C(2)^{*1}—N(2)^{*1}—Cd(2)^{*1}:	163.6(5)
C(2)^{*1}—Cd(1)^{*1}—C(2)^{*5}:	108.7(2)	C(1)^{*2}—Cd(1)^{*1}—C(1)^{*4}:	121.3(2)
C(1)^{*4}—Cd(1)^{*1}—C(2)^{*1}:	108.9(2)	N(2)^{*1}—Cd(2)^{*1}—N(2)^{*3}:	93.1(2)
N(1)^{*1}—Cd(2)^{*1}—N(2)^{*1}:	87.3(2)	N(1)^{*1}—Cd(2)^{*1}—N(2)^{*3}:	96.6(2)
N(3)^{*1}—Cd(2)^{*1}—N(3)^{*3}:	75.8(2)	N(1)^{*3}—Cd(2)^{*1}—N(3)^{*1}:	91.6(2)
N(2)^{*1}—Cd(2)^{*1}—N(3)^{*1}:	96.2(2)	Cd(2)^{*1}—N(3)^{*1}—C(3)^{*1}:	108.7(5)
N(3)^{*1}—C(3)^{*1}—C(3)^{*3}:	119.1(8)		

Key to symmetry operations; normal, x, y, z; with ^{*1}, $1/4 + y, 1/4 + x, 1/4 + z$; with ^{*2}, $1/4 - y, 1/4 - x, 1/4 - z$; with ^{*3}, $1/2 - x, 1/2 - y, 1/2 - z$; with ^{*4}, $3/4 + y, 1/4 + x, 1/4 - z$; with ^{*5}, $3/4 - y, 1/4 - x, 1/4 + z$.

3. Results and Discussion

3.1. STRUCTURE OF I

The structure of **I** is substantially similar to that previously reported [9] with respect to the three-dimensional lattice of the metal complex host providing two kinds of cavities, α and β, containing the guest benzene molecules. However, the structure does not have centers of inversion according to the non-centrosymmetric space group $P4_2 22$. The previous reflection data, collected for an irregular-shaped crystal sealed in a thin glass capillary with a small amount of benzene, lacked hhl (odd l) reflections of significant intensities: the feigned systematic absences misled us to the centrosymmetric $P4_2/mmc$ space group. In the present structure refinement, the reliability index has been improved remarkably from the previous one, although disorder remains in the orientation of the benzene molecule in the β-cavity and of the en ligand.

Both the benzene rings of G1 in the α-cavity and G2 in the β-cavity are slightly contracted, with the C—C bond-lengths shorter by 0.03 to 0.05 Å than the ordinary values of 1.395 Å. The degree of contraction is larger in G1 than G2, and the thermal parameters of the respective C atoms are also larger in G1 than G2. The apparent contraction and large thermal parameters may be caused by the artificial fixation of positional parameters for the C atoms at general positions in order to keep the planarity of the benzene molecules.

The en molecule makes a bridge between two Cd(2) atoms to give an infinite chain of —Cd—en—Cd—en— linkage. The en molecule itself appears to be in a *gauche* form with a dihedral angle of 125° between two C—N bonds in the Newman projection, assuming that a pair of the *gauche* forms are distributed statistically about the a-axis to satisfy the 222 site group at the center of the C(2)—C(2)* bond.

The three-dimensional host structure is built of the infinite —Cd—en—Cd—en— chains extending along the a- and b-axes alternately, and of the tetrahedral Cd(CN)$_4$ moieties

arranged between the crossing —Cd—en—Cd—en— chains with the connections of the N-ends at the Cd atoms in the chains. The bond distances in the metal complex structure are reasonable, except the apparently short C—C and C—N ones in the en ligand. These unusually short distances are due to the disorder mentioned above, and are apparently compensated for by the large thermal parameters of C(2). The bond angles at the tetrahedral Cd(1) and the six-coordinate Cd(2) show considerable deviations from the regular tetrahedral and octahedral angles. Furthermore, the Cd(1)—C(1)—N(1)—Cd(2) linkage bends at C(1) by 168.8(4)° and at N(1) by 140.6(6)°, respectively. Thus, the host moieties, which can be divided into the six-coordinate Cd, tetrahedral Cd, bridging CN, and bridging en, are connected with flexible joints to each other so as to keep the guest molecule tightly compact within the wall of the cavity.

3.2. STRUCTURE OF II AND REARRANGEMENT OF THE METAL COMPLEX IN I TO II

As shown in Table VI, the powder X-ray diffraction pattern of II' agrees well with that of II; the Raman and infrared spectra also showed the agreement between II' and II. The similarities of diffraction patterns between II and IV, and between IV' and IV, support the

Table VI. Comparison of powder X-ray diffraction patterns[#]

II'		II				IV'		IV			
2θ	I	2θ	I	hkl	$2\theta_{cal*}$	2θ	I	2θ	I	hkl	$2\theta_{cal*}$
11.61	6	11.47	5	112	11.43	11.55	10	11.50	9	112	11.51
14.41	11	14.29	14	211	14.28	12.63	9	12.44	9	200	12.47
15.04	6	14.92	4	004	14.91	14.48	9	14.40	7	211	14.23
17.60	81	17.47	100	220	17.46	17.72	76	17.61	71	220	17.67
17.86	11	17.74	13	213	17.77	19.48	100	19.39	100	204	19.42
19.53	100	19.42	100	204	19.39	21.19	26	21.10	26	312	21.14
21.08	25	20.95	31	312	20.93	22.90	5	22.80	2	321	22.89
22.79	6	22.64	7	321	22.63	23.13	6	23.14	6	224	23.14
24.27	17	24.14	14	116	24.11	24.08	25	24.01	20	116	24.03
26.02	5	25.89	9	411	25.84	25.14	15	25.04	21	400	25.08
27.55	4	27.83	10	420	27.77	26.18	3	26.12	2	411	26.14
28.15	9	28.02	10	413	27.97	28.15	14	28.05	13	420	28.10
29.42	22	29.31	24	325	29.24		sh	29.21	12	404	29.26
30.07	18	29.95	15	316	29.93	29.40	14	29.35	19	325	29.38
31.56	12	31.40	17	431	31.36	29.93	26	29.95	28	008	29.91
31.82	34	31.70	43	424	31.66	31.98	41	31.88	40	424	31.92
33.31	3	33.24	4	433	33.17	35.05	20	34.98	23	228	34.95
35.02	15	34.90	18	336	34.85	35.82	12	35.70	9	440	35.77
35.11	15	35.00	14	228	34.99	36.87	4	36.75	4	219	36.68
35.52	10	35.37	25	440	35.34	37.13	4	37.05	4	417	37.08
36.81	6	36.61	7	435	36.54	37.75	11	37.62	9	532	37.70
37.16	7	37.00	9	417	36.96	38.05	4	37.95	3	600	38.02
37.44	12	37.32	19	532	37.27	38.75	8	38.72	9	110	38.73
38.44	6	38.34	6	611	38.30	38.65	8			602	38.79
39.39	18	39.29	19	516	39.24	39.50	23	39.44	23	408	39.42
39.47	18	39.39	14	408	39.36	40.18	8	40.10	7	620	40.16

Cu$K\alpha$ (λ = 1.54184 Å), nickel-filtered, GM-counter.
* The 2θ values are calculated for II from its unit cell parameters; those for IV are from the estimated parameters a = 14.20 and c = 23.90 Å.

idea that the four metal complexes, II', II, IV', and IV are isostructural to each other; the isostructural powder X-ray diffraction patterns have already been observed for I and II [8]. Therefore, it is concluded that the host structure of I turns into the structure of II with the liberation of the guest benzene molecules; a similar process may occur in the change from III to IV'. The difference in partial volume of the unit cell per formula unit of $Cd(en)Cd(CN)_4$ between I and II, 224.3 $Å^3$, is reasonable for the volume of two cavities enclathrating the benzene molecules in I.

In the structure of II the en is no longer a bridging ligand but a bidentate one chelating to a Cd atom in its three-dimensional network linked only by CN ligands. The bond lengths about the coordination spheres of tetrahedral Cd(1) and six-coordinate Cd(2) are slightly contracted from those in I, and the tetrahedral structure about the $Cd(CN)_4$ moiety shows considerable recovery from the distorted geometry in I to a regular tetrahedron. From the viewpoint of coordination chemistry, the metal complex structure in II appears to be stabler than that in I.

Although the three-dimensional structure with —Cd(1)—CN—Cd(2)— linkages is still conserved in II, it is difficult to interpret the process of change from I to II in terms of a simple mechanism. As illustrated in Figure 3, a tetrahedral $Cd(CN)_4$ moiety in I is assumed to be

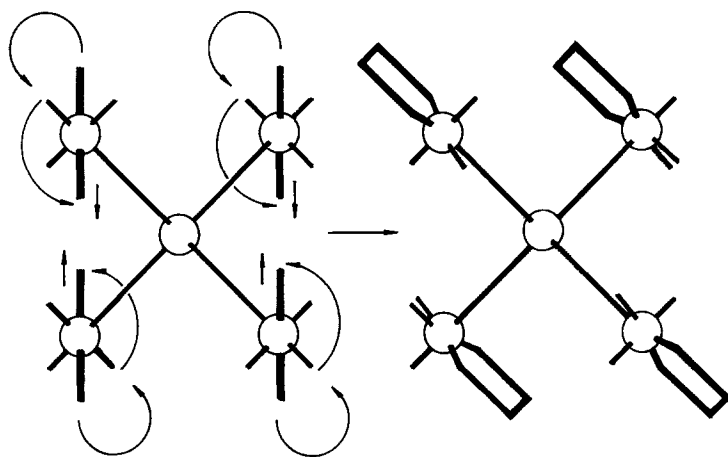

Fig. 3.   Model for rearrangement of the coordination sphere about a tetrahedral $Cd(CN)_4$ moiety in the change from I (left) to II (right). Circle: Cd; thick line: en; thin line: CN.

unmoved in the change from I to II. In order to give the structure of II, the dissociation of en—N at one side of the six-coordinate Cd, the recombination of the en—N dissociated from another side of six-coordinate Cd, and the replacement of another $Cd(CN)_4$ moiety to fill the coordination site left after the dissociation of an en—N end should occur at each six-coordinate Cd linked with the N-end of the central $Cd(CN)_4$ moiety. This means that dissociation-recombination of en and replacement of other $Cd(CN)_4$ moieties should occur to a great extent if a $Cd(CNCd)_4$ unit is kept rigid. Therefore, it is reasonable to suppose that complex dissociation-recombination processes occur at every coordination sphere about the six-coordinate Cd atom accompanied by replacement of a $Cd(CN)_4$ moiety.

Acknowledgement

References and Notes

1. H. M. Powell and J. H. Rayner, *Nature (London)* **163**, 566 (1949).
2. J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 319 (1952).
3. R. Baur and G. Schwarzenbach, *Helv. Chim. Acta* **43**, 842 (1960).
4. T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki, and S. Fujiwara, *Bull. Chem. Soc. Jpn.* **40**, 1174 (1967).
5. T. Iwamoto, *Isr. J. Chem.* **18**, 240 (1979).
6. T. Iwamoto, *J. Mol. Struct.* **75**, 51 (1981).
7. T. Iwamoto: 'The Hofmann-type and Related Inclusion Compounds' (*Inclusion Compounds* v. 1, Eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), pp. 29–57. Academic Press, London (1984).
8. T. Iwamoto and D. F. Shriver, *Inorg. Chem.* **11**, 2570 (1972).
9. T. Iwamoto, *Chem. Lett.*, 723 (1973).
10. T. Iwamoto, M. Kiyoki, Y. Ohtsu, and Y. Takeshige–Kato, *Bull. Chem. Soc. Jpn.* **51**, 240 (1978).
11. S. Nishikiori, T. Iwamoto, and Y. Yoshino, *Chem. Lett.*, 1509 (1979).
12. T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. & Chem. Res.* **55**, 69 (1979); for ORTEP 80 in UNICSIII, C. K. Johnson: ORTEP Report ORNL–3794, Oak Ridge National Laboratory, Tennessee, U.S.A. (1965).
13. International Tables for X-Ray Crystallography, v. IV, pp. 71–98. Kynoch Press (1974) (Distr. D. Reidel Publ. Co., Dordrecht).
14. Tables of anisotropic thermal parameters and structure factors for **I** and **II** have been deposited with the British Library Lending Division under SUP. 82018 (30 pages).