Crystal Structures of *catena*-[Diligatocadmium(II) Tetra-μ-cyanocadmate(II)] Host Clathrates: Diamminecadmium(II) Tetracyanocadmate(II)-Benzene(1/2), Diamminecadmium(II) Tetracyanocadmate(II)-Aniline(1/2), Ethylenediaminecadmium(II) Tetracyanocadmate(II)-Aniline(1/2), and a Novel Type Bis(aniline)cadmium(II) Tetracyanocadmate(II)-Aniline(2/1)

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Abstract. The crystal structures of the four title clathrate compounds $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$, **I**, $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$, **II**, $Cd(NH_2CH_2CH_2NH_2)Cd(CN)_4 \cdot 2\,C_6H_5NH_2$, **III**, and $Cd(C_6H_5NH_2)_2Cd(CN)_4 \cdot 0.5C_6H_5NH_2$, **IV**, have been analyzed by single crystal X-ray diffraction methods. Compound **I** crystallizes in the monoclinic space group $C2/c$, $a = 12.063(2)$, $b = 12.174(2)$, $c = 14.621(1)$ Å, $\beta = 90.976(9)°$, $Z = 4$, $R = 0.042$ for 2388 reflections; **II**: monoclinic $C2/c$, $a = 12.1951(9)$, $b = 12.078(1)$, $c = 14.6921(7)$ Å, $\beta = 93.436(5)°$, $Z = 4$, $R = 0.039$ for 2374 reflections; **III**: monoclinic Cc, $a = 11.027(1)$, $b = 12.0767(9)$, $c = 15.837(1)$ Å, $\beta = 92.059(9)°$, $Z = 4$, $R = 0.041$ for 2883 reflections; and **IV**: monoclinic $P2_1/n$, $a = 15.169(2)$, $b = 16.019(2)$, $c = 8.866(1)$ Å, $\beta = 95.73(1)°$, $Z = 4$, $R = 0.052$ for 3612 reflections. The three-dimensional *catena*-[diamminecadmium(II) tetra-μ-cyanocadmate(II)] hosts of **I** and **II** are substantially isostructural to that of the already known Hofmann-Td-type $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$. The three-dimensional en-Td-type *catena*-[*catena*-μ-ethylenediaminecadmium(II) tetra-μ-cyanocadmate(II)] host of **III**, reinforced by the *catena*-μ-en linking between the octahedral Cd atoms, accommodates the aniline as the guest with a monoclinic distortion from the tetragonal symmetry of the previously reported en-Td-type benzene clathrate. In **IV** dual behavior of aniline, one as the unidentate ligand in the three-dimensional host and the other as the guest in the cage-like cavity, has been demonstrated.

Key words. Aniline, benzene, crystal structures, disorder, en-Td-type clathrate, ethylenediamine, Hofmann-Td-type clathrate, tetracyanocadmate.

1. Introduction

A number of aniline-guest clathrates have been reported for the Hofmann-type and Hofmann-Td-type hosts with composition $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_5NH_2$

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(M = Mn, Fe, Co, Ni, Cu, Zn, or Cd and M′ = Ni, Pd, or Pt in Hofmann-type; M = Cd and M′ = Cd or Hg in Hofmann-Td-type) [1–3], although no detailed data of single crystal structures are available. One exception is that of the Hofmann-dabtn-type compound $Cd[NH_2(CH_2)_4NH_2]Ni(CN)_4 \cdot 1.5C_6H_5NH_2$ [4], including those host structures derived from the Hofmann-type. After a vibrational spectroscopic investigation of the Hofmann-type aniline clathrates [5a], Akyüz [5b] reported a series of coordination complexes of aniline, $M(C_6H_5NH_2)_2M′(CN)_4$ (M = Mn, Fe, Co, or Cu and M′ = Ni; M = Ni or Cd and M′ = Pt), the composition being derived by replacing the ammine ligands of the Hofmann-type host $M(NH_3)_2M′(CN)_4$ by the aniline ones. The IR spectroscopic data suggested the structures were similar to that of the Hofmann-type host: according to the assignments a pair of aniline molecules ligate to the octahedral M atom in the two-dimensional $[MM′(CN)_4]$ network in place of the ammine ligands in the Hofmann-type, but the networks are stacked closely without accommodation of guest molecules in the interlayer space.

Our aim in this paper is to obtain single crystal data for Hofmann-type or analogous types of aniline-guest clathrates and to investigate whether or not the aniline-ligated metal-complex host accommodates guest when the square planar $M′(CN)_4$ unit in the Hofmann-type host is replaced by the tetrahedral $Cd(CN)_4$ unit. We report the crystal structures of a Hofmann-Td-type benzene clathrate $Cd(NH_3)_2Cd(CN)_4 \cdot 2 C_6H_6$, **I**, an aniline clathrate $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$, **II**, an en-Td-type aniline clathrate $Cd(NH_2CH_2CH_2NH_2)Cd(CN)_4 \cdot 2C_6H_5NH_2$, **III**, and an aniline clathrate of a novel host $Cd(C_6H_5NH_2)_2Cd(CN)_4 \cdot 0.5C_6H_5NH_2$, **IV**; compound **I** supplements the information on the host structure of the Hofmann-Td-type when the guest is the simplest six-membered aromatic molecule.

As for the Hofmann-Td-type, single crystal structural data are available only for a benzene clathrate $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$, **V** [6]; the base-centered monoclinic host structures of **I** and **II** are substantially isostructural to the triclinic tetracyanomercurate(II) host of **V**. The host of the en-Td-type, in which the three-dimensional *catena*-[cadmium(II) tetra-μ-cyanocadmate(II)] framework is reinforced with the ambidentate en (ethylenediamine = 1,2-diaminoethane) ligand to give *catena*-[*catena*-μ-ethylenediaminecadmium(II) tetra-μ-cyanocadmate(II)] structure, had been assumed to be incapable of accommodating an aniline molecule as the guest owing to the ca. 8.3 Å span length of Cd—en—Cd in $Cd(en)Cd(CN)_4 \cdot 2 C_6H_6$, **VI** [7]. The present en-Td-type compound, **III**, is the first example of an en-bridged host accommodating aniline as the guest molecule. What we have obtained as **IV** had already been described as one of the adducts between cadmium cyanide and organic bases, $4Cd(CN)_2 \cdot 5C_6H_5NH_2$, by Mesnard and Gode [8] without any comments on its inclusion structure. This aniline compound is a clathrate compound of aniline in the three-dimensional metal complex host *catena*-[*cis*-bis(aniline)cadmium(II) tetra-μ-cyanocadmate(II)]; a pair of aniline molecules ligate to the octahedral Cd atom at the *cis* positions. The host framework structure is considerably different from those of the Hofmann-Td-type; a cage-like cavity is provided for the guest aniline molecule. Structural features of these benzene and aniline compounds will be discussed with respect to the distortion of the three-dimensional framework of *catena*-[cadmium tetra-μ-cyanocadmate] induced by the guest molecule and the ligand coordinated to the octahedral cadmium atom.

2. Experimental

2.1. PREPARATION

2.1.1. catena-[trans-*Diamminecadmium(II) tetra-μ-cyanocadmate(II)]-benzene*(1/2), $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$, I

Conc. NH_3 (20 mL) was added to an aqueous solution containing 5 mmol each of $CdCl_2$ and $K_2[Cd(CN)_4]$ in 100 mL; the pH was adjusted to 9 by adding citric acid. The aqueous solution was covered with a layer of neat benzene and kept standing in a refrigerator at ca. 5°C for a few days; colorless crystals were obtained. *Anal. Found*: C, 32.68; H, 3.19; N, 16.74%. *Calcd.* for $C_{16}H_{18}N_6Cd_2$: C, 37.02; H, 3.49; N, 16.19%. The poor results appear to be due to the instability of the crystal under ambient conditions.

2.1.2. catena-[trans-*Diamminecadmium(II) tetra-μ-cyanocadmate(II)]-aniline*(1/2), $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$, II

Using the aqueous solution of pH 9 as above and neat aniline, colorless crystals were obtained. *Anal. Found*: C, 35.78; H, 3.78; N, 20.13%. *Calcd.* for $C_{16}H_{20}N_8Cd_2$: C, 34.99; H, 3.67; N, 20.40%.

2.1.3. catena-[trans-catena-μ-*Ethylenediaminecadmium(II) tetra-μ-cyanocadmate(II)]-aniline*(1/2), $Cd(en)Cd(CN)_4 \cdot 2C_6H_5NH_2$, III

En (10 mmol) was added to an aqueous solution containing 5 mmol each of $CdCl_2$ and $K_2[Cd(CN)_4]$ in 100 mL. After the pH was adjusted to 9 by adding citric acid, aniline was added dropwise under vigorous stirring until the aniline was saturated in the aqueous solution; ca. 5 mL of aniline was required. The resulting solution was filtered and kept standing in a refrigerator at ca. 5°C for a few days; colorless crystals were obtained. *Anal. Found*: C, 37.29; H, 3.87; N, 19.43%. *Calcd.* for $C_{18}H_{22}N_8Cd_2$: C, 37.58; H, 3.85; N, 19.48%.

2.1.4. catena-[cis-*Bis(aniline)cadmium(II) tetra-μ-cyanocadmate(II)]-aniline*(2/1), $Cd(C_6H_5NH_2)_2Cd(CN)_4 \cdot 0.5C_6H_5NH_2$, IV

$CdCl_2$ and $K_2[Cd(CN)_4]$ (5 mmol each), and 3 g of sodium citrate were dissolved in 100 mL of H_2O; 5 mL (ca. 50 mmol) of aniline was added to this solution under stirring. After the resulting white precipitate was filtered off, the filtrate was kept standing at 5°C for a few days; colorless prismatic crystals of the clathrate were obtained. As Mesnard and Gode described [8], recrystallization of the white precipitate from hot water gave the compound $4Cd(CN)_2 \cdot 5C_6H_5NH_2$ ($2[Cd(C_6H_5NH_2)_2Cd(CN)_4 \cdot 0.5C_6H_5NH_2]$), which was ascertained to be crystallographically identical to IV. Among the series of the Hofmann-type and analogous clathrates, this is the first case where the clathrate can be recrystallized from the solution, so far in the work of the present authors' group. *Anal. Found*: C, 40.49; H, 3.19; N, 16.22%. *Calcd.* for $C_{19}H_{17.5}N_{6.5}Cd_2$: C, 40.63; H, 3.14; N, 16.21%.

Table I. Crystallographic and experimental data.[a]

Compound[b]	I	II	III	IV
Formula	$Cd_2C_{16}H_{18}N_6$	$Cd_2C_{16}H_{20}N_8$	$Cd_2C_{18}H_{22}N_8$	$Cd_2C_{19}H_{17.5}N_{6.5}$
Formula mass	519.18	549.21	575.25	561.71
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	Cc	$P2_1/n$
a/Å	12.063(2)	12.1951(9)	11.027(1)	15.169(2)
b/Å	12.174(2)	12.078(1)	12.0767(9)	16.019(2)
c/Å	14.621(1)	14.6921(7)	15.837(1)	8.866(1)
β/°	90.976(9)	93.436(5)	92.059(9)	95.73(1)
U/Å³	2146.8(4)	2160.1(3)	2107.6(3)	2143.5(4)
Z	4	4	4	4
D_m/g cm⁻³ [c]	1.61	1.69	1.80(1)	1.78(1)
D_x/g cm⁻³		1.69	1.81	1.74
$F(000)$	1008	1072	1128	1092
μ(Mo K_α)/cm⁻¹	19.83	19.78	20.31	19.94
Crystal size/mm	0.4 × 0.3 × 0.3	0.4 × 0.2 × 0.15	0.25 × 0.2 × 0.15	0.35 × 0.3 × 0.1
Scan range	5° < 2θ < 60°	5° < 2θ < 60°	4° < 2θ < 60°	5° < 2θ < 60°
	0 ⩽ h ⩽ 16, 0 ⩽ k ⩽ 17	0 ⩽ h ⩽ 17, 0 ⩽ k ⩽ 16	0 ⩽ h ⩽ 15, 0 ⩽ k ⩽ 16	0 ⩽ h ⩽ 21, 0 ⩽ k ⩽ 22
	−20 ⩽ l ⩽ 20	−20 ⩽ l ⩽ 20	−22 ⩽ l ⩽ 22	−12 ⩽ l ⩽ 12
Scan width/°	1.260 + 0.3 tan θ	1.260 + 0.3 tan θ	1.207 + 0.3 tan θ	1.155 + 0.3 tan θ
Reflections obs.	3478	3524	3465	6833
used, N_r	2388	2374	2883	3612
N_p [a]	111	129	251	253
R, R_w [a]	0.0418, 0.0681	0.0387, 0.0752	0.0408, 0.0604	0.0522, 0.0465
G.O.F. [a]	1.245	0.897	0.742	1.252
g [a]	0.001813	0.005183	0.005563	0.000227
R_{int} [a]	0.0121	0.0076	0.0075	0.0055
$\Delta\rho$/e Å⁻³	0.80 ~ −1.02	0.60 ~ −0.83	1.61 ~ −0.93	1.02 ~ −0.78

[a] Conditions: Rigaku AFC-5R diffractometer, rotating Mo anode (Mo K_α, $\lambda = 0.70926$ Å for the calculation of unit cell parameter); graphite monochromator; $2\theta - \omega$ scan; Lp-corrected; $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{1/2}$, G.O.F. $= [\Sigma(||F_o| - |F_c||)^2/(N_r - N_p)]^{1/2}$, $w = 1/[\sigma(F_o)^2 + g(F_o)^2]$ (N_p: number of refined parameters; R_{int}: merging index).

[b] $I = Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$; $II = Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$; $III = Cd(NH_2CH_2CH_2NH_2)Cd(CN)_4 \cdot 2C_6H_5NH_2$; $IV = Cd(C_6H_5NH_2)_2 Cd(CN)_4 \cdot 0.5C_6H_5NH_2$.

[c] The densities were measured by the flotation method in 1,2-dibromoethane–mesitylene for II and III, and in chloroform–bromoform for IV; it was difficult to determine the density precisely for I, probably due to decomposition of the specimen in the organic mixture.

2.2. SINGLE CRYSTAL EXPERIMENTS

The crystallographic and experimental data are summarized in Table I. Each crystal was coated with acrylic resin in order to prevent spontaneous liberation of guest molecules from the specimen under ambient conditions. The unit cell dimensions were refined from 2θ values of 25 reflections in the range of $24° < 2\theta < 35°$. Three standard reflections were measured every 200 reflections for **I** and **III** and every 150 reflections for **II** and **IV**: no remarkable decays were observed. The reflections used with the intensities $|F_0| > 4\sigma(F_0)$ were Lp-corrected; absorption correction based on the psi-scan was applied for **II** and **IV**.

The structures were solved by the heavy-atom method. Positions of cadmium atoms were revealed on the Patterson maps; full-matrix least-squares procedures were successively applied using the program SHELX76 [9] on a HITAC M-680H/682H computer system in the Computation Centre of the University of Tokyo. Programs in UNICSIII [10] including ORTEP [11] were used for the calculations other than the full-matrix least-squares. Atomic scattering factors including real and imaginary dispersion corrections were taken from the International Tables [12] and SHELX76. All the non-hydrogen atoms were refined anisotropically; the hydrogen atoms fixed at calculated positions with the isotropic thermal parameter fixed at 6.0 Å^2 each were included in the final structure factor calculations. Tables of the structure factors, anisotropic thermal parameters, and calculated positions of hydrogen atoms, have been deposited as the supplementary material.

Either space group Cc or $C2/c$ was possible from the systematic absences observed for **I**, **II**, and **III**. The centrosymmetric $C2/c$ space group for **I** and **II**, and the non-centrosymmetric Cc space group for **III** were finally adopted because of the better convergence given by applying the respective space groups. The ratio of the maximum parameter shift to its e.s.d. at the final cycle was 0.011 for **I** and 0.006 for **III**; the value of 0.161 for **II** (U_{13} of C(23)) was larger than the two other values but within an acceptable range. The centrosymmetric space group of **II** predicted the disorder of the guest aniline molecules centered at the special positions with the respective site symmetries of $\bar{1}$ and 2, whereas the aniline molecules in **III** were refined without disorder. The space group $P2_1/n$ was the unique choice for **IV** from the systematic absences; the maximum shift to the e.s.d. ratio was 0.014. The amino group of the aniline guest molecule is disordered similar to the case of **II**.

3. Results and Discussion

3.1. GENERAL

The refined atomic parameters are listed in Tables II–V for **I**, **II**, **III**, and **IV**, respectively; the selected bond distances and angles are listed in Table VI for **I** and **II**, and Tables in VII and VIII for **III** and **IV**, respectively. The structures of **I**, **II**, **III**, and **IV** are illustrated in Figures 1–4 with the atomic notations, respectively.

The common structural feature observed for these four hosts is that the three-dimensional host framework is built of the alternate linkage between the tetrahedral Cd(t) atom of the tetracyanocadmate and the octahedral Cd(o) atom through the cyanide bridges. In this respect, the host structures of **I**, **II**, and **III** are isostructural with one

Table II. Final atomic coordinates and equivalent thermal parameters B_{eq} for $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$, **I**

atom	G^a	x/a	y/b	z/c	$B_{eq}/Å^{2b}$
Cd(t)	0.5	0	0.49348(3)	1/4	3.128(8)
Cd(o)	0.5	1/4	1/4	0	3.585(9)
N(1)	1.0	0.1525(4)	0.3360(4)	0.1161(3)	5.29(9)
N(2)	1.0	0.1551(4)	0.6453(4)	0.3915(3)	5.5(1)
N(3)	1.0	0.3897(5)	0.3848(5)	0.0143(5)	6.9(1)
C(1)	1.0	0.1035(4)	0.3894(4)	0.1636(3)	4.07(8)
C(2)	1.0	0.1037(4)	0.5953(4)	0.3414(4)	4.19(8)
C(11)	1.0	0.2600(14)	0.1819(12)	0.4234(10)	13.0(4)
C(12)	1.0	0.3339(11)	0.1665(11)	0.5045(11)	10.8(4)
C(13)	1.0	0.3213(12)	0.2394(14)	0.5724(9)	12.1(4)
C(21)	1.0	0.6090(10)	0.4725(12)	0.2206(8)	10.7(3)
C(22)	1.0	0.5531(8)	0.3814(9)	0.2342(8)	10.4(3)
C(23)	1.0	0.5585(19)	0.5700(10)	0.2341(9)	17.7(9)

^{a} Multiplicity.
^{b} $B_{eq} = 8\pi^2[\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j]/3$.

Table III. Final atomic coordinates and equivalent thermal parameters B_{eq} for $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$, **II**

atom^a	G^b	x/a	y/b	z/c	$B_{eq}/Å^{2c}$
Cd(t)	0.5	0	0.47577(3)	1/4	3.158(8)
Cd(o)	0.5	1/4	1/4	0	3.63(1)
N(1)	1.0	0.1566(5)	0.3185(5)	0.1228(4)	5.4(1)
N(2)	1.0	0.1476(5)	0.6322(4)	0.3998(3)	4.82(9)
N(3)	1.0	0.3841(5)	0.3848(5)	0.0236(4)	6.0(1)
C(1)	1.0	0.1069(5)	0.3706(5)	0.1703(4)	4.10(9)
C(2)	1.0	0.0980(4)	0.5795(5)	0.3481(4)	4.09(8)
N(11)*	0.5	0.2603(28)	0.1008(25)	0.3979(18)	13.7(8)
C(11)	1.0	0.2575(20)	0.1715(16)	0.4390(15)	13.5(6)
C(12)	1.0	0.3488(16)	0.1831(18)	0.5135(16)	12.7(5)
C(13)	1.0	0.3349(16)	0.2613(20)	0.5659(16)	13.1(6)
N(21)*	0.5	0.6457(27)	0.4618(53)	0.1519(16)	23(2)
C(21)	1.0	0.6027(19)	0.4431(12)	0.1976(9)	14.7(6)
C(22)	1.0	0.5461(12)	0.3498(9)	0.2282(6)	10.4(4)
C(23)	1.0	0.5441(33)	0.5436(13)	0.2269(12)	20(1)

^{a} Atom in disorder has been asterisked.
^{b} Multiplicity.
^{c} $B_{eq} = 8\pi^2[\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j]/3$.

another and to that of the Hofmann-Td-type compound $Cd(NH_3)_2Hg(CN)_4 \cdot 2$ C_6H_6, **V** [6]. The en-reinforced three-dimensional host of **III** is isostructural to that of the previously reported en-Td-type compound $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$, **VI** [7]. In **IV**, the remarkable difference from the three others is the ligation of the aniline ligands to Cd(o) at the *cis* positions in contrast with the *trans*-bis-ligation of the ammine ligands in **I** and **II**, and of the two N-ends of the catena-μ-en ligands in **III**.

Table IV. Final atomic coordinates and equivalent thermal parameters B_{eq} for Cd(en)Cd(CN)$_4$ · 2C$_6$H$_5$NH$_2$, **III**

atom	G^a	x/a	y/b	z/c	$B_{eq}/\text{Å}^{2b}$
Cd(t)	1.0	−0.0034(1)	0.48929(3)	0.25044(7)	2.067(7)
Cd(o)	1.0	0.25	0.25367(8)	0.0	1.893(7)
N(1)	1.0	0.1543(9)	0.3387(8)	0.1093(6)	3.2(2)
N(2)	1.0	−0.1453(9)	0.3333(8)	0.3889(7)	3.5(2)
N(3)	1.0	0.1587(9)	0.6303(7)	0.3988(6)	2.9(2)
N(4)	1.0	−0.1653(9)	0.6309(8)	0.1036(6)	3.3(2)
N(5)	1.0	0.4164(9)	0.3697(8)	0.0372(6)	3.6(2)
N(6)	1.0	0.5838(11)	0.6299(8)	−0.0282(9)	5.3(2)
C(1)	1.0	0.1050(9)	0.3917(9)	0.1618(8)	2.6(2)
C(2)	1.0	−0.1046(10)	0.3752(9)	0.3358(7)	2.8(2)
C(3)	1.0	0.1057(8)	0.5868(7)	0.3469(7)	2.3(1)
C(4)	1.0	−0.1147(11)	0.5841(7)	0.1570(7)	2.9(2)
C(5)	1.0	0.4483(9)	0.4645(9)	−0.0125(7)	3.3(2)
C(6)	1.0	0.5502(12)	0.5373(10)	0.0183(9)	4.2(2)
N(11)	1.0	0.2699(14)	0.1156(10)	0.4011(8)	6.2(3)
C(11)	1.0	0.2590(9)	0.1910(6)	0.4651(6)	3.8(2)
C(12)	1.0	0.3272(10)	0.1827(10)	0.5403(9)	4.2(2)
C(13)	1.0	0.3112(16)	0.2564(9)	0.6026(9)	5.5(3)
C(14)	1.0	0.2280(14)	0.3406(10)	0.5964(9)	5.0(3)
C(15)	1.0	0.1634(11)	0.3560(11)	0.5187(9)	5.2(2)
C(16)	1.0	0.1794(13)	0.2803(12)	0.4562(8)	4.7(2)
N(21)	1.0	0.5975(11)	0.6431(8)	0.2424(7)	5.5(2)
C(21)	1.0	0.5379(9)	0.5374(7)	0.2469(6)	2.8(1)
C(22)	1.0	0.6030(12)	0.4444(10)	0.2321(6)	4.1(2)
C(23)	1.0	0.5507(13)	0.3406(9)	0.2487(7)	4.1(2)
C(24)	1.0	0.4345(13)	0.3320(9)	0.2732(8)	4.0(2)
C(25)	1.0	0.3690(10)	0.4318(10)	0.2882(6)	3.9(2)
C(26)	1.0	0.4169(9)	0.5310(9)	0.2736(7)	3.7(2)

^{a} Multiplicity.
^{b} $B_{eq} = 8\pi^2[\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\boldsymbol{a}_j]/3$.

The coordination spheres about Cd(t) and Cd(o) are little distorted in the host frameworks of **I** and **II**. Including the recent result of 2.225(3) Å in K$_2$[Cd(CN)$_4$] [13], the Cd—C distances range from 2.19 to 2.23 Å for little distorted tetrahedral Cd(CN)$_4$ moieties involved in three-dimensional framework structures. About Cd(o) the Cd—N distances range from 2.32 to 2.36 Å with N—Cd—N angles of 90 ± 1° for **I** and **II**. In the benzene clathrate, **I**, Cd(o) takes an elongated octahedral configuration with the longest distance of 2.359(5) Å for Cd—N(NH$_3$) and the shorter ones of 2.322(5) and 2.330(4) Å for Cd—N(CN). In contrast, in the aniline clathrate, **II**, the octahedron is compressed with the shortest value, 2.319(6) Å, for Cd—N(NH$_3$) and the longest value, 2.342(5) and 2.352(5) Å, for Cd—N(CN).

The distortion about the coordination sphere is greater in **III** for both Cd(o) and Cd(t). The Cd(o)—N distances range from 2.30 to 2.39 Å with the angles from 85

Table V. Final atomic coordinates and equivalent thermal parameters B_{eq} for $Cd(C_6H_5NH_2)_2Cd(CN)_4 \cdot 0.5C_6H_5NH_2$, **IV**

atom[a]	G[b]	x/a	y/b	z/c	$B_{eq}/Å^{2c}$
Cd(t)	1.0	0.62969(4)	0.32092(3)	0.04285(6)	2.59(1)
Cd(o)	1.0	0.26645(3)	0.35213(3)	0.06772(6)	2.52(1)
N(1)	1.0	0.4106(4)	0.3075(8)	0.0647(8)	3.6(1)
N(2)	1.0	0.7183(4)	0.2200(4)	0.3539(8)	3.7(1)
N(3)	1.0	0.7108(4)	0.2382(4)	−0.2626(8)	3.2(1)
N(4)	1.0	0.6922(5)	0.5210(4)	0.0407(8)	4.1(2)
C(1)	1.0	0.4845(5)	0.3077(5)	0.0537(9)	3.1(2)
C(2)	1.0	0.6916(5)	0.2558(5)	0.2480(9)	3.1(2)
C(3)	1.0	0.6799(5)	0.2672(5)	−0.1650(9)	2.8(1)
C(4)	1.0	0.6712(5)	0.4539(5)	0.0479(9)	3.3(2)
N(11)	1.0	0.1283(4)	0.4345(4)	0.0513(9)	4.5(2)
C(11)	1.0	0.0472(4)	0.3892(5)	0.0532(10)	3.3(2)
C(12)	1.0	0.0034(6)	0.3590(6)	−0.0823(11)	4.7(2)
C(13)	1.0	−0.0751(6)	0.3129(6)	−0.0786(12)	5.4(2)
C(14)	1.0	−0.1072(6)	0.2951(6)	0.0567(13)	5.1(2)
C(15)	1.0	−0.0628(7)	0.3241(7)	0.1914(12)	5.3(2)
C(16)	1.0	0.0154(6)	0.3710(6)	0.1897(11)	4.5(2)
N(21)	1.0	0.3274(5)	0.4258(5)	0.2997(8)	4.3(2)
C(21)	1.0	0.2616(6)	0.4635(5)	0.3832(9)	3.4(2)
C(22)	1.0	0.2304(7)	0.4187(6)	0.5016(10)	4.4(2)
C(23)	1.0	0.1625(9)	0.4525(8)	0.5759(13)	7.1(3)
C(24)	1.0	0.1286(9)	0.5319(9)	0.5345(18)	8.4(4)
C(25)	1.0	0.1633(11)	0.5776(8)	0.4207(16)	8.1(4)
C(26)	1.0	0.2319(8)	0.5428(6)	0.3438(11)	5.2(2)
N(31)*	0.5	0.5212(19)	0.5949(17)	0.2908(28)	10.3(8)
C(31)	1.0	0.5173(13)	0.5485(16)	0.3839(19)	9.0(5)
C(32)	1.0	0.5535(9)	0.4690(15)	0.3989(22)	7.9(4)
C(33)	1.0	0.5378(11)	0.4159(13)	0.5088(28)	10.7(5)

[a] Atom in disorder has been asterisked.
[b] Multiplicity.
[c] $B_{eq} = 8\pi^2[\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \boldsymbol{a}_i\boldsymbol{a}_j]/3$.

to 97°; the Cd(t)—C distances range from 2.21 to 2.25 Å and the angles range from 99 to 117°. The bond lengths and angles related to en are not unusual.

The coordination sphere about Cd(t) in **IV** is slightly distorted from a regular tetrahedron with the average distance of 2.22(1) Å and the C—Cd—C angles ranging between 105.0(3) to 114.8(3)°. The distortion from a regular octahedron is greater for Cd(o) with the average Cd—N distance of 2.36(8) Å and the N—Cd—N angles between 77.0(2) to 96.7(2)°. The Cd—N(aniline) distances of 2.468(7) and 2.469(7) Å are considerably greater than those of Cd—N(CN) ranging from 2.278(7) to 2.351(7) Å.

3.2. THE STRUCTURES OF **I**, **II**, AND **III**

Two kinds of cavities, α and β, are formed in the Hofmann-Td-type and en-Td-type host frameworks; the former is approximated to a rectangular box, the latter to a

Table VI.   Selected bond and atomic distances and bond angles for **I** and **II**

distance/Å	**I**	**II**	distance/Å	**I**	**II**
Cd(t)—C(1)	2.194(5)	2.207(5)	Cd(t)—C(2)	2.198(5)	2.206(5)
Cd(o)—N(1)	2.330(4)	2.342(5)	Cd(o)—N(2)*1	2.322(5)	2.352(5)
Cd(o)—N(3)	2.359(5)	2.319(6)			
C(1)—N(1)	1.126(6)	1.140(7)	C(2)—N(2)	1.130(7)	1.137(7)
C(11)—C(12)	1.48(2)	1.52(3)	C(12)—C(13)	1.34(2)	1.24(3)
C(13)—C(11)*2	1.37(3)	1.39(3)	C(21)—C(22)	1.31(1)	1.41(2)
C(21)—C(23)	1.35(2)	1.49(4)	C(22)—C(22)*3	1.37(2)	1.33(3)
C(23)—C(23)*3	1.49(4)	1.31(8)			
N(11)—C(11)		1.05(3)	N(21)—C(21)		0.91(4)
N(3)···N(11)*5		3.39(3)	N(3)···N(21)*6		3.18(4)

angle/°	**I**	**II**
C(1)—Cd(t)—C(2)	110.6(2)	111.1(2)
C(1)—Cd(t)—C(1)*4	109.5(2)	109.7(2)
C(1)—Cd(t)—C(2)*4	107.4(2)	107.1(2)
C(2)—Cd(t)—C(2)*4	111.3(3)	110.8(2)
N(1)—Cd(o)—N(2)*1	90.1(2)	90.2(2)
N(1)—Cd(o)—N(3)	89.5(2)	90.4(2)
N(3)—Cd(o)—N(2)*1	91.2(2)	90.7(2)
Cd(t)—C(1)—N(1)	176.5(5)	174.2(5)
Cd(t)—C(2)—N(2)	177.0(5)	178.8(5)
Cd(o)—N(1)—C(1)	170.2(5)	165.3(5)
Cd(o)—N(2)*1—C(2)*1	176.1(5)	176.4(5)
C(11)—C(12)—C(13)	116(1)	113(2)
C(12)—C(11)—C(13)*2	118(1)	123(2)
C(12)—C(13)—C(11)*2	126(1)	124(2)
C(22)—C(21)—C(23)	119(1)	108(2)
C(21)—C(22)—C(22)*3	122(1)	127(1)
C(21)—C(23)—C(23)*3	119(1)	125(2)
N(11)—C(11)—C(12)		116(3)
N(11)—C(11)—C(13)*2		120(3)
N(21)—C(21)—C(22)		139(5)
N(21)—C(21)—C(23)		109(4)

Key to symmetry operations.
*1: $x, -y+1, z-1/2$; *2: $-x+1/2, -y+1/2, -z+1$; *3: $-x+1, y, -z+1/2$; *4: $-x, y,$ $-z+1/2$; *5: $-x+1/2, y+1/2, -z+1/2$; *6: $-x+1, -y+1, -z$

biprismatic cage, in the pseudotetragonal and tetragonal unit cells of **V** and **VI** [6, 7]. The guest molecules in both cavities are shown in Figure 5. In the base-centered monoclinic unit cells of **I** and **II**, the site symmetry of the center of the cavity is $\bar{1}$ for α and 2 for β, respectively. The atomic coordinates of the benzene molecules in **I** show the unique orientations in both cavities; the bond lengths and the angles, though somewhat distorted, are acceptable. However, the aniline molecules in **II** show disorder related to the inversion center in α and to the twofold axis in β, respectively. The unusually short C—N distances of 1.05(3) Å for N(11)—C(11) in α and 0.91(4) Å for N(21)—C(21) in β are due to the disorder related by the

Table VII.　Selected bond and atomic distances and bond angles for **III**

distance/Å

Cd(t)—C(1)	2.22(1)	Cd(t)—C(2)	2.25(1)
Cd(t)—C(3)	2.244(9)	Cd(t)—C(4)	2.21(1)
Cd(o)—N(1)	2.30(1)	Cd(o)—N(2)*¹	2.38(1)
Cd(o)—N(3)*²	2.330(9)	Cd(o)—N(4)*³	2.38(1)
Cd(o)—N(5)	2.366(9)	Cd(o)—N(6)*⁴	2.39(1)
N(1)—C(1)	1.20(1)	N(2)—C(2)	1.09(1)
N(3)—C(3)	1.12(1)	N(4)—C(4)	1.15(1)
N(5)—C(5)	1.44(1)	C(5)—C(6)	1.49(1)
C(6)—N(6)	1.40(1)		
N(11)—C(11)	1.37(2)	N(21)—C(21)	1.43(1)
C(11)—C(12)	1.39(2)	C(21)—C(22)	1.36(2)
C(12)—C(13)	1.35(2)	C(22)—C(23)	1.41(2)
C(13)—C(14)	1.37(2)	C(23)—C(24)	1.36(2)
C(14)—C(15)	1.41(2)	C(24)—C(25)	1.43(2)
C(15)—C(16)	1.36(2)	C(25)—C(26)	1.33(2)
C(16)—C(11)	1.39(2)	C(26)—C(21)	1.42(2)
N(11)···N(21)*⁴	3.12(2)		

angle/°

C(1)—Cd(t)—C(2)	110.2(3)	C(1)—Cd(t)—C(3)	115.0(4)
C(1)—Cd(t)—C(4)	98.6(4)	C(2)—Cd(t)—C(3)	100.2(4)
C(2)—Cd(t)—C(4)	116.4(4)	C(3)—Cd(t)—C(4)	117.1(2)
N(1)—Cd(o)—N(2)*¹	178.3(4)	N(1)—Cd(o)—N(3)*²	92.9(3)
N(1)—Cd(o)—N(4)*³	86.5(3)	N(1)—Cd(o)—N(5)	85.5(4)
N(1)—Cd(o)—N(6)*⁴	92.9(4)	N(2)*¹—Cd(o)—N(3)*²	88.1(3)
N(2)*¹—Cd(o)—N(4)*³	92.6(4)	N(2)*¹—Cd(o)—N(5)	93.0(3)
N(2)*¹—Cd(o)—N(6)*⁴	88.6(4)	N(3)*²—Cd(o)—N(4)*³	177.4(3)
N(3)*²—Cd(o)—N(5)	97.3(3)	N(3)*²—Cd(o)—N(6)*⁴	86.5(4)
N(4)*³—Cd(o)—N(5)	85.2(3)	N(4)*³—Cd(o)—N(6)*⁴	91.0(4)
N(5)—Cd(o)—N(6)*⁴	176.0(4)		
Cd(t)—C(1)—N(1)	174.1(9)	Cd(t)—C(2)—N(2)	166(1)
Cd(t)—C(3)—N(3)	175.5(8)	Cd(t)—C(4)—N(4)	174(1)
Cd(o)—N(1)—C(1)	173.9(9)	Cd(o)—N(2)*¹—C(2)*¹	175(1)
Cd(o)—N(3)*²—C(3)*²	170.6(8)	Cd(o)—N(4)*³—C(4)*³	170.4(9)
Cd(o)—N(5)—C(5)	122.5(6)	Cd(o)—N(6)*⁴—C(6)*⁴	128.2(9)
N(5)—C(5)—C(6)	119(1)	C(5)—C(6)—N(6)	121(1)
C(12)—C(11)—N(11)	122(1)	C(22)—C(21)—N(21)	119(1)
C(16)—C(11)—N(11)	121(1)	C(26)—C(21)—N(21)	120(1)
C(16)—C(11)—C(12)	118(1)	C(26)—C(21)—C(22)	121(1)
C(13)—C(12)—C(11)	120(1)	C(23)—C(22)—C(21)	119(1)
C(14)—C(13)—C(12)	123(1)	C(24)—C(23)—C(22)	121(1)
C(15)—C(14)—C(13)	119(1)	C(25)—C(24)—C(23)	118(1)
C(16)—C(15)—C(14)	118(1)	C(26)—C(25)—C(24)	122(1)
C(15)—C(16)—C(11)	123(1)	C(25)—C(26)—C(21)	119(1)

Key to symmetry operations.
*¹: $x + 1/2$, $-y + 1/2$, $z - 1/2$; *²: x, $-y + 1$, $z - 1/2$; *³: $x + 1/2$, $y - 1/2$, z; *⁴: $x - 1/2$, $y - 1/2$, z.

Table VIII.   Selected bond distances and angles for **IV**

distance/Å

Cd(t)—C(1)	2.224(8)	Cd(t)—C(2)	2.222(8)
Cd(t)—C(3)	2.236(8)	Cd(t)—C(4)	2.221(9)
Cd(o)—N(1)	2.303(7)	Cd(o)—N(2)*1	2.278(7)
Cd(o)—N(3)*2	2.307(7)	Cd(o)—N(4)*3	2.359(7)
Cd(o)—N(11)	2.468(7)	Cd(o)—N(21)	2.469(7)
N(1)—C(1)	1.135(9)	N(2)—C(2)	1.140(9)
N(3)—C(3)	1.125(9)	N(4)—C(4)	1.124(9)
N(11)—C(11)	1.43(1)	N(21)—C(21)	1.44(1)
C(11)—C(12)	1.40(1)	C(21)—C(22)	1.39(1)
C(12)—C(13)	1.41(1)	C(22)—C(23)	1.39(1)
C(13)—C(14)	1.37(1)	C(23)—C(24)	1.41(2)
C(14)—C(15)	1.39(1)	C(24)—C(25)	1.39(2)
C(15)—C(16)	1.41(1)	C(25)—C(26)	1.42(2)
C(16)—C(11)	1.38(1)	C(26)—C(21)	1.38(1)
N(31)—C(31)	1.12(2)	C(31)—C(32)	1.39(2)
C(32)—C(33)	1.33(2)	C(33)—C(31)*4	1.44(3)

angle/°

C(1)—Cd(t)—C(2)	105.0(3)	C(1)—Cd(t)—C(3)	114.8(3)
C(1)—Cd(t)—C(4)	117.7(3)	C(2)—Cd(t)—C(3)	110.1(3)
C(2)—Cd(t)—C(4)	109.8(3)	C(3)—Cd(t)—C(4)	105.5(3)
N(1)—Cd(o)—N(2)*1	93.4(2)	N(1)—Cd(o)—N(3)*2	102.9(2)
N(1)—Cd(o)—N(4)*3	88.4(2)	N(1)—Cd(o)—N(11)	165.2(2)
N(1)—Cd(o)—N(21)	83.2(2)	N(2)*1—Cd(o)—N(3)*2	96.7(2)
N(2)*1—Cd(o)—N(4)*3	100.0(3)	N(2)*1—Cd(o)—N(11)	91.3(3)
N(2)*1—Cd(o)—N(21)	176.5(2)	N(3)*2—Cd(o)—N(4)*3	159.3(2)
N(3)*2—Cd(o)—N(11)	90.6(2)	N(3)*2—Cd(o)—N(21)	83.5(2)
N(4)*3—Cd(o)—N(11)	77.0(2)	N(4)*3—Cd(o)—N(21)	80.5(3)
N(11)—Cd(o)—N(21)	92.2(2)		
Cd(t)—C(1)—N(1)	174.2(7)	Cd(t)—C(2)—N(2)	175.7(7)
Cd(t)—C(3)—N(3)	174.6(7)	Cd(t)—C(4)—N(4)	175.6(8)
Cd(o)—N(1)—C(1)	161.3(7)	Cd(o)—N(2)*1—C(2)*1	177.9(7)
Cd(o)—N(3)*2—C(3)*2	165.5(6)	Cd(o)—N(4)*3—C(4)*3	159.2(7)
Cd(o)—N(11)—C(11)	117.0(5)	Cd(o)—N(21)—C(21)	114.2(5)
C(12)—C(11)—N(11)	120.0(8)	C(22)—C(21)—N(21)	118.6(8)
C(16)—C(11)—N(11)	119.6(8)	C(26)—C(21)—N(21)	118.8(8)
C(16)—C(11)—C(12)	120.2(8)	C(26)—C(21)—C(22)	122.6(9)
C(13)—C(12)—C(11)	119.5(9)	C(23)—C(22)—C(21)	119(1)
C(14)—C(13)—C(12)	120.4(9)	C(24)—C(23)—C(22)	120(1)
C(15)—C(14)—C(13)	119.9(9)	C(25)—C(24)—C(23)	121(1)
C(16)—C(15)—C(14)	120.4(9)	C(26)—C(25)—C(24)	120(1)
C(15)—C(16)—C(11)	119.5(8)	C(25)—C(26)—C(21)	118(1)
C(32)—C(31)—N(31)	129(3)	C(33)—C(32)—C(31)	124(2)
N(31)—C(31)—C(33)*4	107(2)	C(32)—C(31)—C(33)*4	123(2)
C(32)—C(33)—C(31)*4	113(2)		

Key to symmetry operations.
*1: $x - 1/2$, $-y + 1/2$, $z - 1/2$;   *2: $x - 1/2$, $-y + 1/2$, $z + 1/2$;   *3: $-x + 1$, $-y + 1$, $-z$;
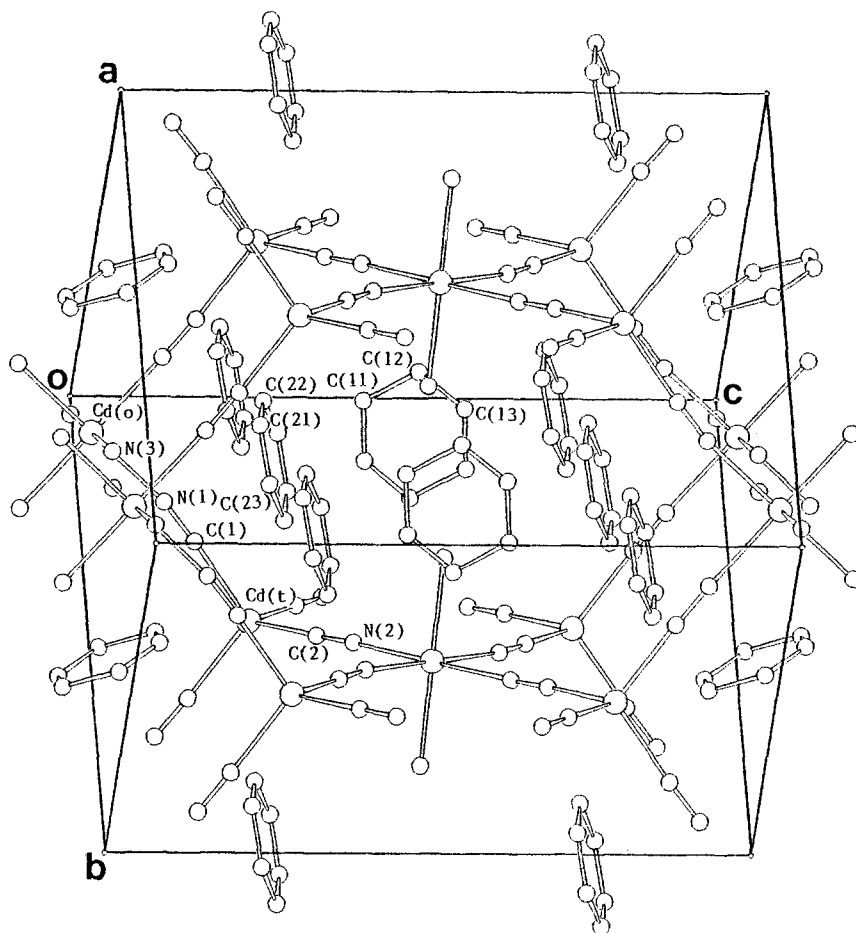*4: $-x + 1$, $-y + 1$, $-z + 1$.

Fig. 1.   A perspective view of the unit cell of I; a ball-and-stick drawing.

respective symmetry elements unable to correlate with the molecular symmetry of aniline in the cavities. The rigid model treatment for the aniline molecules, assuming that a pair of rigid aniline molecules were distributed under the restraint from the symmetry in each of the cavities, did not converge.

   In contrast with the tetragonal $P4_2 22$ unit cell of **VI**, the monoclinic Cc space group of **III** makes it possible to determine the unique orientations of the en skeleton in the host and of the guest aniline molecules in the cavities; the en, and the benzene molecule in the β-cavity, were distributed statistically about the twofold axis in **VI** [7]. The structure of **III** is rather a rare case solved without disorder for the Hofmann-type and analogous clathrates.

3.3. THE NOVEL ANILINE CLATHRATE OF THE ANILINE-LIGATED HOST, **IV**

As shown in Figure 4, the host is comprised of the three-dimensional framework of *catena*-[cadmium(II) tetra-μ-cyanocadmate(II)]. Although the naming of the
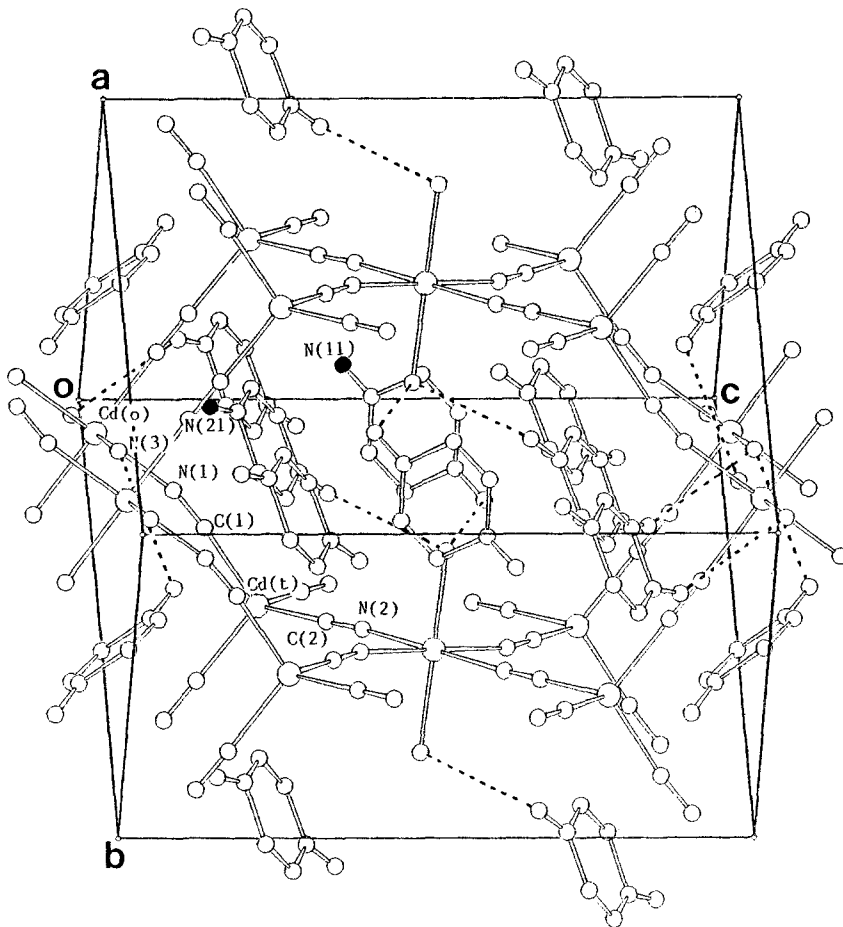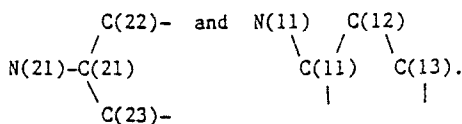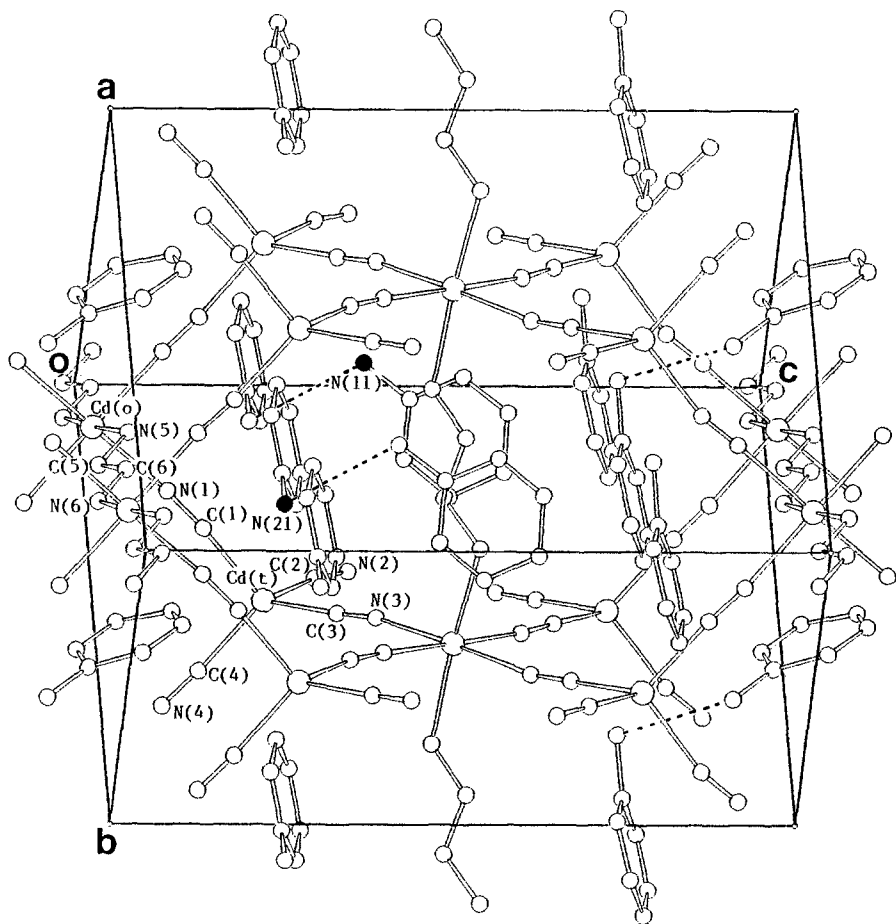
Fig. 2. A perspective view of the unit cell of **II**; a ball-and-stick drawing; the hydrogen bonds are shown with dotted lines; the NH₂ group of the aniline is statistically distributed about the symmetry element at the center of the cavity, $\bar{1}$ for G1 in α and 2 for G2 in β; for the atomic numbering of the guest atoms N(11) and N(21) are shown with solid circles in the sequence:

$$
\begin{array}{cc}
\begin{array}{c}
\quad\quad C(22)- \\
\quad / \\
N(21)-C(21) \\
\quad \backslash \\
\quad\quad C(23)-
\end{array}
&
\begin{array}{c}
\text{and} \quad N(11) \quad C(12) \\
\quad\quad\quad \backslash \quad / \quad \backslash \\
\quad\quad\quad C(11) \quad C(13). \\
\quad\quad\quad | \quad\quad | \\
\end{array}
\end{array}
$$

framework is apparently the same as those of the three former compounds, the ligating configuration of the nitrogen bases about Cd(o) is different being *cis* compared with *trans* in the former compounds.

The aniline guest molecule is accommodated in the cage-like cavity framed by the cyanide linkage between the Cd(t) and Cd(o) atoms. The 12-membered top of the cage, including all the participating atoms, is approximated to a tetragon cornered
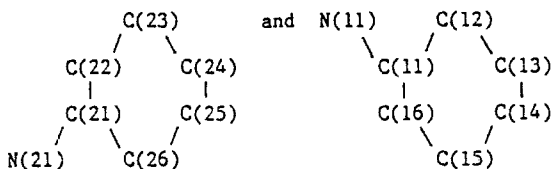
Fig. 3. A perspective view of the unit cell of **III**; a ball-and-stick drawing; the hydrogen bonds are shown with dotted lines; for the atomic numbering of the guest atoms N(11) and N(21) are shown with solid circles in the sequence:

```
              C(23)         and   N(11)        C(12)
            /      \                  \        /      \
       C(22)        C(24)             C(11)          C(13)
         |            |                 |              |
       C(21)        C(25)             C(16)          C(14)
       /      \      /                    \        /
   N(21)        C(26)                       C(15)
```

by the four Cd atoms. Cd(t) on the top is spanned by Cd(o) through the cyanide bridges to Cd(t) on the bottom and Cd(o) on the top by Cd(t) to Cd(o) on the bottom, respectively; the pillars of —NC—Cd(t)—CN— and —CN—Cd(o)—NC— are bent outside of the cage. Thus, twelve Cd atoms, six Cd(t) and six Cd(o), participate in the cage framework. The cage can be approximated to a decahedron, although there are no direct chemical bonds connecting the expanded corners
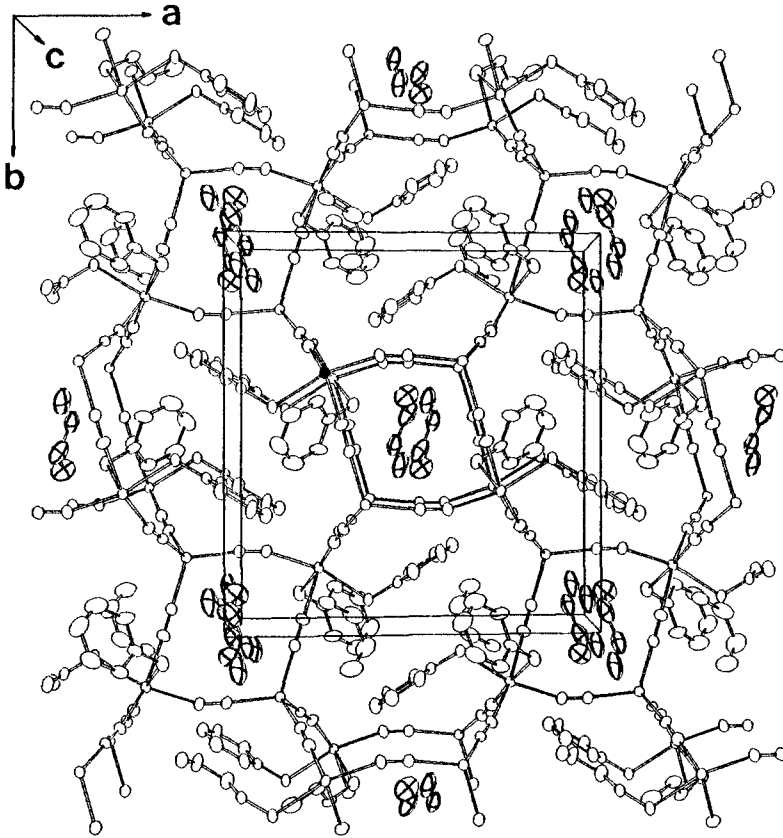
Fig. 4. A perspective view of the unit cell of **IV**; 30% probability for the thermal ellipsoids; the NH_2 of the guest aniline is statistically distributed about the symmetry element $\bar{1}$ at the center of the cavity; the anisotropic peripheries are shown for those ellipsoids of the guest atoms. For the atomic numbering Cd(o) is shown with a solid ellipsoid; N(3), C(3), C(12), C(13), and all the atoms of the L2 aniline at the coordinates given in Table V are out of the range in this view with the sequence:
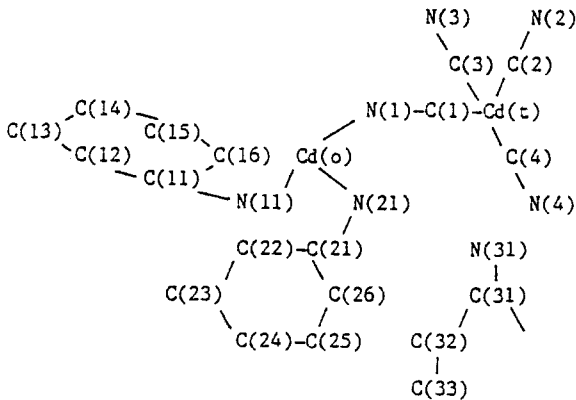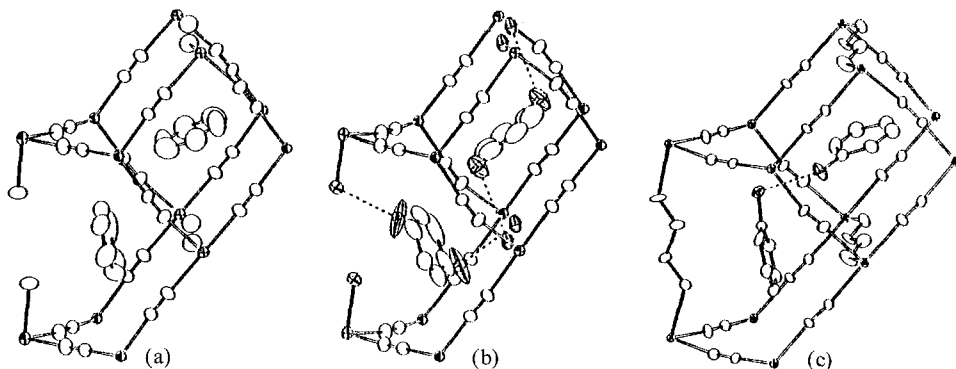
Fig. 5. ORTEP views of the guest molecules G1 in α- and G2 in β-cavities for I (a), II (b), and III (c); thermal ellipsoids are shown with 30% probability; the anisotropic sections are shown for the Cd atoms; the anisotropic peripheries are shown for the amino-N-atoms involved with the hydrogen bonds; in (b) each of the statistically-distributed amino groups is depicted for the guest aniline molecules.

around the equatorial plane. The wide opening at each side is covered by the phenyl rings of the anilines ligating to Cd(o) so as to entrap the guest aniline molecule inside. One aniline ligand, L1, covers the cavity with a dihedral angle of 10.4° between the aromatic planes of the ligand and the guest. The other ligand, L2, protruding outside the cavity, covers the opening of the neighboring cavity.

Since the center of the cavity coincides with the inversion center, e.g. (1/2, 1/2, 1/2), of the $P2_1/n$ unit cell, the aniline guest molecule should be distributed about the inversion center. A molecular image similar to that of p-phenylenediamine has been adopted: the best convergence has been given from among several models including the rigid model distributing about the inversion center. The apparently short (1.12(2) Å) C(31)—N(31) distance of the aniline guest is due to the disorder, similar to that observed for II.

When we view the three-dimensional extension of the cadmium cyanide framework alone in Figure 4, a honeycomb-like structure is seen. Besides the cage-like cavity, a channel-like cavity with an octagonal, but apparently hexagonal, cross-section is given in the framework. The channel is occupied by the phenyl rings of the L1 and L2 anilines protruding from Cd(o) to shield the cage-like cavities.

The coordination sphere about Cd(t) is slightly distorted from a regular tetrahedron with the average Cd–C distance of 2.22(1) Å and the C—Cd—C angles ranging between 105.0 and 119.8°. The distortion is greater for Cd(o) from a regular octahedron with the average Cd—N distance of 2.36(8) Å and the N—Cd—N angles between 77.0(2) and 96.7(2)°. The Cd—N(aniline) distances, 2.468(7) and 2.469(7) Å, are considerably greater than those of Cd—N(CN) ranging from 2.278(7) to 2.351(7) Å.

3.4. COMPARISON OF THE STRUCTURES

Assuming that a tetragonal 4_2 or $\bar{4}$ Hofmann-Td-type host was derived from the tetragonal $4/m$ Hofmann-type host just by the replacement of the square planar $M'(CN)_4$ unit in the latter by the tetrahedral $M'(CN)_4$ unit, the cavities formed in

Table IX.   Dihedral angles (°) between the aromatic plane of the guest and the diagonal plane of the cavity

Compound	α-cavity	β-cavity
$Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$	23.9	18.3
$Cd(en)Cd(CN)_4 \cdot 2C_6H_6$	0.0	0.0
$Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$	37.7	35.1
$Cd(en)Cd(CN)_4 \cdot 2C_6H_5NH_2$	22.0	17.3

the Td-type host, α and β, have the same volume and the diagonal plane of the same dimensions as each other. This is the case for Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ [13] and the en-Td-type $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$, **VI** [7]; the tetragonal symmetry of **VI** results in the disorders in the molecular orientation of the en ligand and of the benzene molecule in the β-cavity, and in the arrangement of the benzene molecules in both α- and β-cavities on the respective diagonal planes. However, the Hofmann-Td-type hosts of **I** and **II** are monoclinically distorted, and that of **V** triclinically.

The degree of distortion to the monoclinic system in **I**, $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$, and **II**, $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$, is so small that the lattice parameters can be converted into the pseudotetragonal triclinic systems, respectively, similar to those parameters observed for **V**, $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$ [6]. The parameters of **V** can be converted to those of the pseudo-base-centered monoclinic ones: $a = 11.997$, $b = 12.145$, and $c = 14.619$ Å, $\alpha = 90.2$, $\beta = 90.9$, and $\gamma = 90.0°$, the values being very similar to those for **I**. However, the cavities are considerably distorted so as to arrange the aromatic plane of the guest obliquely against the diagonal plane. As listed in Table IX, the dihedral angle between the aromatic plane and the diagonal plane is at most 37.7° for the aniline in the β-cavity of **II**; the angle is 0° in the tetragonal host of **VI**. The Cd(o)–N(NH₃) bonds confronting each other between Cd(o) atoms turn aside from the line between the Cd(o) atoms to accept the obliquely arranged guest molecules.

The monoclinic β angle of **II**, larger by ca. 2.4° than those of **I** and **V**, gives the slight elongation of the cavities in order to accommodate the larger aniline molecule accompanied with the compression of the coordination sphere about Cd(o); the interatomic distances of 3.39(3) Å for N(3)···N(11) and 3.18(4) Å for N(3)···N(21) suggest the formation of a weak hydrogen bond between the ammine ligand and the amino group of the aniline guest in each cavity. The benzene and the aniline guests in the respective α cavities show rather isotropic thermal oscillations, whereas those in the β cavities have the greater freedom of motion along the molecular planes. The dihedral angles between the aromatic planes of the guests in the α- and β-cavities are 79.4, 78.0 and 82.7° for **I**, **II**, and **III**, respectively.

The reason why the aniline molecule is accommodated in the en-spanned three-dimensional host of **III** should be noted. The Cd—en—Cd span length of ca. 8.3 Å in the tetragonal structure of **VI** had been assumed to be too short to accommodate aniline molecules in the host isostructural to **VI**. A distance of at least 8.6 Å had been assumed necessary to accommodate an aniline molecule along

its longest dimension, because the shortest c dimension observed for the Hofmann-type aniline clathrate is 8.65 Å in $Cd(NH_3)_2Pd(CN)_4 \cdot 2C_6H_5NH_2$ [2c]. The monoclinic distortion of the host framework in **III** is favorable for accommodation of the aniline molecule as the guest. However, the *catena-μ*-en linkage between Cd(o) atoms in **III** makes the Cd(o)—(en)—Cd(o) distance of 8.18 Å shorter than the Cd(o)—$(NH_3 \cdots NH_3)$—Cd(o) distances in **I**, 8.57 Å, and **II**, 8.58 Å, and additionally, the β-angle of 92.059(9)° is smaller than 93.436(5)° in **II**. These observations mean that the crystal packing is more compact in **III** than in **II**. In fact, the thermal parameters of the guest atoms are much smaller in **III** than in **II**. This is due to the hydrogen-bond formation between the guest aniline molecules in the α- and β-cavities with the $N(11) \cdots N(21)$ interatomic distance of 3.12(2) Å, as shown in Figure 5. The opening between the α and β cavities is large enough to allow the interaction between the two hydrogen-bonded aniline molecules. The hydrogen-bond formation makes the effective volume of the guest molecules decrease so much that the en-spanned host of **III** can accommodate the aniline molecules as the guests accompanied with the monoclinic distortion.

Unlike the layered structure of the Hofmann-type host involved with a square planar $M'(CN)_4$ unit, the tetrahedral $M'(CN)_4$ unit gives a three-dimensional structure along with Cd(o) coordinated by two unidentate ligands, as has been seen for the Hofmann-Td-type. Bulky unidentate ligands like pyridine, aniline, isoquinoline, etc., do not essentially forbid the accommodation of guests between the interlayer space in the Hofmann-type-analogous hosts derived by their coordination at the octahedral site, even though no inclusion structures are yet known. However, because of its bulkiness, trans-*bis*-coordination of aniline ligands is impossible for the Td-type hosts to keep the three-dimensional host structures like the Hofmann-Td-type. Instead, the aniline ligands coordinate at the *cis*-positions to Cd(o) in **IV** to give the present host structure. This fact prompts us to develop novel host structures using bulky ligands to supplement the three-dimensional cyanide-linked framework. Attempts using pyridine and isoquinoline are in progress.

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