Journal of Inclusion Phenomena **6** (1988), 143–156.

The Crystal Structures of α,ω-Diaminoalkanecadmium(II) Tetracyanonickelate(II)-Aromatic Molecule Inclusion Compounds. IV. (1,6-Diaminohexane)cadmium(II) Tetracyanonickelate(II)-*m*-Toluidine(1/1), -*p*-Toluidine(1/1), and -2,4-Xylidine(1/1) Clathrates, and the Coordination Complex Bis(*p*-toluidine) (1,6-diaminohexane)cadmium(II) Tetracyanonickelate(II)

TAI HASEGAWA and TOSCHITAKE IWAMOTO*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

(Received: 1 June 1987)

Abstract. The crystal structures of the four title compounds have been analyzed by single crystal X-ray diffraction methods at room temperature. Three with a general formula $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4{\cdot}G$ ($G =$ *m*-toluidine, **Im**; *p*-toluidine, **Ip**; and 2,4-xylidine, **Ix**) are the inclusion compounds of the respective aromatic molecules in the three-dimensional metal complex host (1,6-diaminohexane)cadmium(II) tetracyanonickelate(II). The remaining one is a coordination complex of *p*-toluidine, bis(*p*-toluidine) (1,6-diaminohexane)cadmium(II) tetracyanonickelate(II), **II**. **Im**, **Ix**, and **II** crystallize under similar experimental conditions; **Ip** is obtained using the *p*-toluidine-mesitylene mixture at higher dilution than that used for **II**. **Im** crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.725(2)$, $b = 7.598(1)$, $c = 7.177(1)$ Å, $\alpha = 90.44(1)$, $\beta = 98.80(1)$, $\gamma = 95.70(1)°$, and $Z = 1$ (the final conventional $R = 0.037$ for 3526 reflections); **Ip**: monoclinic, $P2/m$, $a = 9.540(2)$, $b = 7.611(1)$, $c = 7.120(1)$ Å, $\beta = 100.95(1)°$, and $Z = 1$ ($R = 0.027$ for 1700 reflections); **Ix**: monoclinic, $P2/m$, $a = 9.628(2)$, $b = 7.613(1)$, $c = 7.122(1)$ Å, $\beta = 100.01(1)°$, and $Z = 1$ ($R = 0.049$ for 2704 reflections); **II**: monoclinic, $P2_1/n$, $a = 12.107(3)$, $b = 10.117(2)$, $c = 12.471(3)$ Å, $\beta = 113.67(2)°$, and $Z = 2$ ($R = 0.037$ for 2616 reflections).

The structures of **Im**, **Ip** and **Ix** are similar to that of the *o*-toluidine inclusion compound of the same metal complex host.

In **II** a *trans* pair of the *p*-toluidine molecules ligate to the cadmium atom in the two-dimensional network formed by the *catena*-μ-linkages of $—Cd—NH_2(CH_2)_6NH_2—Cd—$ and —NC—Ni—CN—Cd—NC—Ni—CN— intersecting at each Cd atom; two cyanide groups of the tetracyanonickelate(II) moiety have free N-ends.

Key words. Hofmann-type clathrate, crystal structure analysis, tetracyanonickelate, 1,6-diaminohexane, toluidine, xylidine, toluidine complex.

Supplementary Data relating to this article are deposited with the British Library as supplementary publication No. SUP 82060 (98 pages).

---

* Author for correspondence.

1. Introduction

This paper reports the crystal structures of the four title compounds; three of them are the clathrate compounds of *m*-toluidine, *p*-toluidine, and 2,4-xylidine, respectively, in the three-dimensional metal complex host (1,6-diaminohexane)cadmium(II) tetracyanonickelate(II), the fourth being a metal complex containing *p*-toluidine as a unidentate ligand. As has been reported in the previous papers [1–4], α,ω-diaminoalkanes with long carbon chains give three-dimensional host structures by bridging adjacent two-dimensional metal complex networks of *catena*-[cadmium(II) tetra-μ-cyanonickelate(II)]. The crystal structures of the 2,5-xylidine [2], pyrrole, aniline, and *N*,*N*-dimethylaniline clathrates [4] of Hofmann-dabn-type host (dabn = 1,4-diaminobutane) $Cd[NH_2(CH_2)_4NH_2]Ni(CN)_4$, and the *o*-toluidine clathrate of Hofmann-dahxn-type host (dahxn = 1,6-diaminohexane) $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4$ [3] have demonstrated the three-dimensional metal complex host structures accommodating the respective aromatic molecules as the guest.

As for the Hofmann-dahxn-type toluidine compounds prepared under similar experimental conditions, using the 1 : 10 mixture of each isomer and mesitylene as the organic phase, the *o*- and the *m*-isomers afforded the compounds with the composition $Cd(dahxn)Ni(CN)_4 \cdot CH_3C_6H_4NH_2$, whereas the *p*-isomer was found as $Cd(dahxn)Ni(CN)_4 \cdot 2CH_3C_6H_4NH_2$. Although the difference in the number of guest molecules had suggested the structural isomerism for the Hofmann-dahxn-type host was affected by the geometry of the guest molecule, the *p*-isomer compound was not a clathrate but a coordination complex of *p*-toluidine behaving as a unidentate ligand to the cadmium atom [5]. The clathrate of *p*-toluidine crystallized at the interface between the aqueous solution containing the host moieties and the organic phase of the *p*-toluidine-mesitylene mixture with a far lower content of *p*-toluidine (1 : 200) than that used for the preparation of the *p*-toluidine complex; the preliminary results have already been reported [6]. Although it had been stated in the previous paper [3] that xylidines were incapable of being accommodated in the Hofmann-dahxn-type host, the accommodation was accomplished by careful adjustment of pH in the aqueous phase.

2. Experimental

2.1. SYNTHESIS

The *m*-toluidine clathrate, (1,6-diaminohexane)cadmium(II) tetracyanonickelate(II)-*m*-toluidine(1/1), **Im**, the 2,4-xylidine clathrate, (1,6-diaminohexane)cadmium(II) tetracyanonickelate(II)-2,4-xylidine(1/1), **Ix**, and the *p*-toluidine complex, bis(*p*-toluidine) (1,6-diaminohexane)cadmium(II) tetracyanonickelate(II), **II**, were prepared under conditions quite similar to those for the *o*-toluidine clathrate [3] using the respective isomer of toluidine or 2,4-xylidine in place of *o*-toluidine. 1,6-Diaminohexane (Aldrich H1, 169–6) was used without further purification. Into the aqueous solution of cadmium chloride and potassium tetracyanonickelate(II) mixed in a 1 : 1 molar ratio twice the molar amount of the diamine was added. The mixture was stirred vigorously for a few hours by a magnetic stirrer; in the final aqueous solution the concentration of each metal species was adjusted at *ca.* 0.1 mol dm^{-3}. After the aqueous solution was filtered through a membrane filter (Millipore, 0.45 μm pore size), the pH was adjusted to 9.62 by adding citric acid and monoethanolamine. Over the aqueous solution in a stoppered flask the organic phase containing the relevant aromatic species was placed and the flask stored for two months at room temperature. The organic phase used was a 1 : 10 toluidine-mesitylene mixture for the *m*- and the *p*-isomer for **Im** and **II**, respectively, and a 1 : 5 2,4-xylidine-mesitylene mixture for **Ix**; for **Ip** the more dilute 1 : 200 *p*-toluidine-mesitylene mixture was used. *Analysis*: Found for **Im**: C, 40.57; H, 4.86; N, 19.69; Cd, 22.5; Ni, 11.9%. Calcd. for $C_{17}H_{25}N_7CdNi$: C, 40.95; H, 5.05; N, 19.66; Cd, 22.54; Ni, 11.77%. Found for **Ip**: C, 39.13; H, 5.00; N, 19.07; Cd, 22.79; Ni, 12.12%. Calcd. for **Ip** for a 100% occupancy by the guest: the same as those for **Im**; calcd. for $Cd(dahxn)Ni(CN)_4 \cdot \mathit{0.9}CH_3C_6H_4NH_2$: C, 40.13; N, 4.98; N, 19.81; Cd, 23.04; Ni, 12.03%. Found for **Ix**: C, 39.07; H, 5.11; N, 19.67% Calcd. for $C_{18}H_{27}N_7CdNi$: C, 42.18; H, 5.31; N, 19.13%. Calcd. for **Ix** as $Cd(dahxn)Ni(CN)_4 \cdot \mathit{0.75}(CH_3)_2C_6H_3NH_2$: C, 39.84; H, 5.06; N, 19.60%. Found for **II**: C, 47.04; H, 5.19; N, 18.63; Cd. 19.0; Ni, 9.94%. Calcd. for $C_{24}H_{34}N_8CdNi$: C, 47.59; H, 5.66; N, 18.50; Cd, 18.56; Ni, 9.69%. Similarly to the case of the *o*-toluidine compound [3], the chelatometric determination of Cd and Ni contents in **Im** gave poor agreements with the calculated values, because the determination was carried out for the mixture of the products at the interface and the bottom of the aqueous phase collected by filtration. Since the C, H, and N analyses were carried out for the single crystals picked from the interface, the Cd and Ni analyses were reexamined by atomic absorption spectrometry for the single crystal specimens. The results found for **Ip** and **Ix** apparently corresponded to the composition of a 90% and a 75% occupancy by the guest, respectively; as is described later, the results of structure refinement were favorable to the full occupancy by the respective guests in the crystals used.

2.2. STRUCTURE DETERMINATION

The crystal data and experimental conditions for intensity data collections are summarized in Table I for all the title compounds; preliminary Weissenberg photographs were checked before the collection of intensity data and the refinement of lattice parameters. Each crystal was coated with epoxy resin in order to prevent spontaneous decomposition under the ambient atmosphere. The intensity statistics were examined for adoption of the appropriate space groups. The structures were solved by the heavy-atom method with block-diagonal least-squares procedures using the programs in UNICSIII [7] including ORTEP [8] and their local versions on a HITAC computer system M–680H in the computation center of this University. The atomic scattering factors used including those for real and imaginary dispersion corrections were taken from the International Tables [9].

The parameters refined were the positional and anisotropic thermal ones for the non-hydrogen atoms of the host components (host-atoms) and of the guest skeletons (guest-atoms) except those for **Ip** and **II**. The hydrogen atoms of the host components in **Im** and **Ix** were located at the calculated positions assuming the sp^3 configuration with the isotropic thermal parameter fixed at 5.0 Å^2; these positional and thermal parameters were not refined but included in the calculations of the final structure factors [10]. The hydrogen atoms of dahxn in **Ip** were located on the difference Fourier map and their positional and isotropic thermal parameters were refined. The hydrogen atoms of the guest molecules in the clathrates were omitted in the refinements. In the case of **II**, the positional and anisotropic thermal parameters for all the non-hydrogen atoms were refined; the calculated positional and the fixed (at 5.0 Å^2) isotropic thermal parameters for the aliphatic and aromatic hydrogen atoms were not refined but included in the calculations of the final structure factors [10].

Each refinement was stopped at the stage when no improvement from the previous cycle was noted. The parameter shift at the final cycle of the refinement was at the level of

Table I. Crystallographic and experimental data

Compound	**Im**	**Ip**	**Ix**	**II**
Formula	$CdNiC_{17}H_{25}N_7$	$CdNiC_{17}H_{25}N_7$	$CdNiC_{18}H_{27}N_7$	$CdNiC_{24}H_{34}N_8$
Formula weight	498.56	498.56	512.58	605.70
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2/m$	$P2/m$	$P2_1/n$
a (Å)	9.725(2)[1]	9.540(2)	9.628(2)	12.107(3)
b (Å)	7.598(1)	7.611(1)	7.613(1)	10.117(2)
c (Å)	7.177(1)	7.120(1)	7.122(1)	12.471(3)
α (°)	90.44(1)	90	90	90
β (°)	98.80(1)	100.95(1)	100.01(1)	113.67(2)
γ (°)	95.70(1)	90	90	90
U (Å^3)	521.4(1)	507.6(1)	514.1(2)	1399.0(1)
Z	1	1	1	2
Dm (g/cm^3 [2])	1.57(2)	1.56(1)	1.56(1)	1.45(1)
Dx (g/cm^3)	1.59	1.59	1.64[3]	1.44
Systematic absences	no	no	no	$0k0$: $k = 2n + 1$ $h01$: $h + 1 = 2n + 1$
Crystal size (mm)	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.4	0.3 × 0.2 × 0.16	0.3 × 0.3 × 0.3
μ(Mo$K\alpha$) (cm^{-1})	18.85	18.85	18.40	14.59
Scan mode	2θ-ω	2θ-ω	2θ-ω	2θ-ω
Scan range	$2° < 2\theta < 65°$	$2° < 2\theta < 62°$	$2° < 2\theta < 80°$	$2° < \theta < 60°$
Peak scan width	$1.5 + 0.5 \tan\theta$, 0.45	$1.5 + 0.55 \tan\theta$, 0.37	$1.2 + 1.5 \tan\theta$, 0.35	$0.9246 + 0.5 \tan\theta$, 0.45
Scan rate (°/min)	4	4	8	4
p: refs. obsvd.	4198	3460	3577	9358
Refs. used[4]	3526	1700	2704	2616
q: no. of parameters	129	153	80	156
R, R_w, S[5]	0.037, 0.032, 0.37	0.027, 0.030, 0.26	0.049, 0.038, 0.35	0.037, 0.028, 0.61
$\lvert F_o\rvert_1$	150	30	150	100
$\lvert F_o\rvert_2$	75	6	75	50

[1] The crystal axes have been set for the sake of comparison of the structures among **Im**, **Ip**, and **Ix**. The angles for **Im** have been revised from those stated in the previous communication [5].

[2] Flotation method in mesitylene-bromoform mixture.

[3] The value for 75% occupancy by the guest is 1.56.

[4] $|F_o| > 3\sigma(F_o)$; L_p corrected.

[5] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, $S = [\Sigma w(|F_o| - |F_c|)^2/(p - q)]^{1/2}$. $w = (|F_o|_1/|F_o|)^2$ for $|F_o| \geqslant |F_o|_1$, $w = 1$ for $|F_o|_1 > |F_o| \geqslant |F_o|_2$, and $w = 0.25$ for $|F_o| < |F_o|_2$.

less than 0.3 times its e.s.d. for almost all of the host-atoms, but those of some guest-atoms were comparable with or exceeded their e.s.d.s owing to the structural disorder of the guest molecules to be mentioned in Section 3.2. Attempts to use a rigid structure of the benzene ring did not give any improvements.

2.2.1. *Clathrates* **Im, Ip,** *and* **Ix**

Since abnormal divergence was observed for some parameters in the intermediate stage of structure refinement with the space group $P1$, the space group $P\bar{1}$ was finally chosen for **Im**. The space group $P2/m$ was chosen for **Ip** and **Ix** from the observations of the Harker's sections on the Patterson maps.

Although the results of elemental analyses for **Ip** and **Ix** suggested, respectively, a 90% and a 75% occupancy rate of the guests, the refinements were carried out assuming a full occupancy rate. No improvements were attained in the refinements with less than 100% occupancy rates for the reliability indices in R; those in R_w were larger (0.032 for **Ip** and 0.042 for **Ix**) than those listed in Table I.

2.2.2. *p-Toluidine Complex,* **II**

The structure was solved without any problems. The space group $P2_1/n$ was uniquely determined from the systematic absences. The ratio of parameter shift to the e.s.d. was less than 10% at the final cycle except the value of 33% for a very small thermal parameter, $U_{13} = -0.0011$, of Cd.

3. Structure Description

3.1. GENERAL

The atomic parameters determined are listed in Table II for all the three clathrates, **Im, Ip,** and **Ix**, and the complex, **II**; the selected bond distances and angles in the host structures of the three clathrates are in Table III. Table IV shows the selected bond distances and angles for **II**.

3.2. CLATHRATES **Im, Ip,** AND **Ix**

The structures determined are shown along with the atomic notations in Figure 1 for **Im**, **Ip**, and **Ix**.

The host structures are substantially similar to one another and to that of the Hofmann-dahxn-type *o*-toluidine compound, $\underline{Cd}[NH_2(CH_2)_6NH_2]Ni(CN)_4 \cdot o\text{-}CH_3C_6H_4NH_2$, **Io**, reported previously [3], although the $P\bar{1}$ space group of **Im** differs from the $P2/m$ of the three others including **Io**. The triclinic distortion in **Im** from the monoclinic system is with the angles $\alpha = 90.44(1)°$ and $\gamma = 95.70(1)°$, the angle $\beta = 98.80(1)°$ deviating little from those in **Io** (100.3(1)°), **Ip** (100.95(1)°), and **Ix** (100.01(1)°); the unusual settings of the crystal axes have been applied for the sake of comparison among these structures.

In each host structure, the dahxn ligand spans adjacent two-dimensional wavy cyanometal complex networks in an all-*trans* conformation of the aliphatic chain, whose bond distances and angles are similar to each other for the mutually corresponding parts

Table II. Atomic parameters with e.s.d.s in parentheses for **Im**, **Ip**, **Ix**, and **II**

Atom	G^a	x/a	y/b	z/c	$B_{eq}/Å^{2}$ ^{b}
Im					
host-atoms					
Cd	0.50	0.0	0.0	0.0	2.327(8)
Ni	0.50	0.0	0.5	0.5	2.36(1)
N(1)	1.00	0.0526(3)	0.7868(3)	0.2288(3)	4.0(1)
N(2)	1.00	0.0635(3)	0.2297(3)	0.2282(3)	3.9(1)
C(1)	1.00	0.0354(3)	0.6783(3)	0.3336(3)	2.93(9)
C(2)	1.00	0.0426(3)	0.3325(3)	0.3334(3)	2.93(9)
N(3)	1.00	0.2288(3)	0.0178(4)	−0.0603(3)	4.1(1)
C(3)	1.00	0.2537(3)	0.0222(5)	−0.2585(4)	4.3(1)
C(4)	1.00	0.4062(3)	0.0132(5)	−0.2782(4)	4.3(1)
C(5)	1.00	0.4228(3)	0.0074(5)	−0.4898(5)	5.1(1)
guest-atoms					
N(4)	0.50	0.7564(8)	0.435(1)	0.037(2)	12.6(6)
C(6)	1.00	0.6361(8)	0.4733(8)	0.036(2)	18.7(6)
C(7)	1.00	0.549(2)	0.500(1)	0.861(4)	51(2)
C(8)	1.00	0.595(2)	0.476(1)	0.241(3)	34(1)
C(9)	0.50	0.398(2)	0.519(2)	0.201(4)	23(2)
Ip					
host-atoms					
Cd	0.25	0.0	0.0	0.0	2.09(1)
Ni	0.25	0.0	0.5	0.5	2.38(2)
N(1)	1.00	0.0622(3)	0.2209(4)	0.2302(4)	3.8(1)
C(1)	1.00	0.0405(3)	0.3273(4)	0.3340(4)	2.9(1)
N(2)	0.50	0.2297(4)	0.0	−0.0598(5)	3.8(2)
C(2)	0.50	0.2522(5)	0.0	−0.2581(7)	3.9(2)
C(3)	0.50	0.4066(5)	0.0	−0.2790(7)	3.8(2)
C(4)	0.50	0.4227(5)	0.0	−0.4888(7)	3.9(2)
H(1)	1.00	0.287(4)	0.080(5)	0.022(6)	9(1)
H(2)	1.00	0.200(3)	0.101(5)	−0.323(4)	5.3(8)
H(3)	1.00	0.474(4)	0.106(5)	−0.192(5)	7(1)
H(4)	1.00	0.363(4)	0.106(5)	−0.569(5)	6.1(9)
guest-atoms					
N(3)	0.25	0.253(3)	0.5	0.006(4)	19(2)
C(5)	0.25	0.381(2)	0.5	−0.086(3)	10(1)
C(6)	0.25	0.425(2)	0.5	0.282(3)	11(1)
C(7)	0.25	0.376(2)	0.5	0.126(3)	9(1)
C(8)	0.25	0.436(2)	0.5	0.014(4)	11(1)
C(9)	0.25	0.579(4)	0.5	0.359(5)	17(2)
C(10)	0.25	0.368(3)	0.5	−0.236(4)	15(2)
C(11)	0.25	0.408(3)	0.5	0.455(4)	14(2)
Ix					
host-atoms					
Cd	0.25	0.0	0.0	0.0	1.952(7)
Ni	0.25	0.0	0.5	0.5	2.18(1)
N(1)	1.00	0.0616(3)	0.2210(3)	0.2287(3)	3.72(8)
C(1)	1.00	0.0412(2)	0.3281(3)	0.3345(3)	2.66(6)
N(2)	0.50	0.2293(3)	0.0	−0.0575(4)	3.6(1)
C(2)	0.50	0.2519(3)	0.0	−0.2587(5)	3.5(1)

Atom	G[a]	x/a	y/b	z/c	$B_{eq}/\text{Å}^2$ [b]
Ix					
host-atoms					
C(3)	0.50	0.4060(3)	0.0	−0.2789(5)	3.3(1)
C(4)	0.50	0.4237(3)	0.0	−0.4866(5)	3.3(1)
guest-atoms					
N(3)	0.25	0.645(2)	0.5	0.327(5)	19(2)
C(5)	0.50	0.351(4)	0.5	0.044(3)	39(1)
C(6)	0.50	0.631(3)	0.5	0.156(4)	30(1)
C(7)	0.50	0.417(2)	0.5	0.181(4)	29.9(8)
C(8)	0.25	0.436(3)	0.5	0.440(8)	30(2)
II					
Cd	0.50	0.5	0.5	0.5	2.323(7)
Ni	0.50	0.5	0.0	0.5	2.51(1)
N(1)	1.00	0.5290(3)	0.2838(3)	0.5733(3)	3.6(1)
C(1)	1.00	0.5218(3)	0.1742(3)	0.5506(3)	2.9(1)
N(2)	1.00	0.3244(3)	0.1039(4)	0.2706(3)	4.9(1)
C(2)	1.00	0.3890(3)	0.0615(3)	0.3564(3)	3.4(1)
N(3)	1.00	0.3052(2)	0.5176(4)	0.4860(2)	2.8(1)
C(3)	1.00	0.2402(3)	0.3913(4)	0.4835(4)	4.4(2)
C(4)	1.00	0.1056(3)	0.4070(5)	0.4464(5)	5.4(2)
C(5)	1.00	0.0691(3)	0.4992(7)	0.5194(4)	4.9(1)
N(4)	1.00	0.4116(2)	0.4192(3)	0.2956(3)	3.1(1)
C(6)	1.00	0.4928(3)	0.4326(4)	0.2415(3)	3.1(1)
C(7)	1.00	0.5676(4)	0.3295(4)	0.2417(4)	4.3(1)
C(8)	1.00	0.6544(4)	0.3483(5)	0.1960(4)	5.1(2)
C(9)	1.00	0.6684(4)	0.4657(4)	0.1499(4)	4.8(2)
C(10)	1.00	0.5918(4)	0.5694(5)	0.1482(4)	5.0(2)
C(11)	1.00	0.5058(4)	0.5526(4)	0.1961(4)	4.0(1)
C(12)	1.00	0.7649(5)	0.4833(9)	0.1022(5)	8.1(3)

[a] G: multiplicity.

[b] $B_{eq} = 4[\Sigma_i \Sigma_j B_{ij}\mathbf{a}_i\mathbf{a}_j]/3$. Value of the isotropic thermal parameter is listed for the hydrogen atoms of **Ip**.

(see Table III). The coordination structures about the Cd and Ni atoms are also similar to one other: the structure of the $Ni(CN)_4$ moiety is little distorted from the D_{4h} symmetry, and the Cd atom is in a compressed octahedral coordination by six nitrogen atoms. The $Ni(CN)_4$ square plane and the CdN_6 octahedron share the edge with the dihedral angle of *ca.* 35° between the former plane and the equatorial plane of the latter.

The guest molecule in each clathrate is accommodated in the cavity formed between the networks of cyanometal complex and surrounded by four dahxn columns similar to the *o*-toluidine molecule in **Io**. However, it was impossible to picture an acceptable shape of the guest molecule from the structure refinement. The peaks of electron density were tentatively assigned to the skeleton of a tetra-substituted benzene molecule like 1,2,4,5-tetramethylbenzene or 1,4-diamino-2,5-dimethylbenzene, but with 50% each occupancy for each of the substituents, for the statistically distributed *m*-toluidine and 2,4-xylidine in **Im** and **Ix**. In **Ip** the electron densities were so scattered in the cavity as to give apparent distributions of a pair of *p*-toluidine molecules, each of which should have a 50%

Table III. Selected atomic distances and bond angles fo **Im**, **Ix**, and **Ix**

Distance (Å)	**Im**	**Ip**	**Ix**
Ni—C	1.854(2), 1.858(2)	1.857(3)	1.850(2)
C—N(CN)	1.138(3), 1.136(3)	1.141(4)	1.150(3)
Cd—N(CN)	2.352(2), 2.354(2)	2.344(3)	2.345(2)
Cd—N(am)*	2.322(3)	2.310(4)	2.314(3)
N—C(am)	1.479(4)	1.468(6)	1.486(5)
C—C(am1)	1.519(4)	1.508(7)	1.515(4)
C—C(am2)	1.552(5)	1.530(7)	1.518(5)
C—C(am3)	1.546(6)	1.51(1)	1.510(6)
Angle (°)			
Ni—C—N	177.7(3), 177.4(3)	178.5(3)	177.5(3)
C—Ni—C	90.4(2)	90.1(2)	90.2(1)
Cd—N—C(CN)	159.3(2), 154.9(2)	155.3(2)	155.8(9)
N(CN)—Cd—N(CN)	91.0(1)	91.6(2)	91.7(1)
N(am)—Cd—N(CN)	89.7(2), 90.1(2)	89.7(2)	89.4(2)
Cd—N(am)—C(am)	118.7(2)	119.6(4)	118.3(3)
N—C—C(am)	113.1(3)	114.8(6)	113.6(2)
C—C—C(am1)	110.1(4)	112.2(6)	111.7(4)
C—C—C(am2)	110.2(5)	112.5(9)	112.9(6)

* The (am) denotes the value related to the dahxn atoms; the numbering is in the order from the N atom side.

Table IV. Selected atomic distances and bond angles for **II***

Distance (Å)

Ni—C(1):	1.855(3);	C(1)—N(1):	1.139(4);	Cd—N(1):	2.342(3)
Ni—C(2):	1.862(3);	C(2)—N(2):	1.126(4);		
Cd—N(3):	2.301(4);	N(3)—C(3):	1.494(5);	C(3)—C(4):	1.513(5)
C(4)—C(5):	1.489(8);	C(5)—C(5′):	1.544(5);		
Cd—N(4):	2.474(3);	N(4)—C(6):	1.405(6);	C(6)-C(7):	1.381(6)
C(7)—C(8)	1.395(8);	C(8)—C(9):	1.360(7);	C(9)—C(10):	1.395(7)
C(10)—C(11):	1.403(8);	C(11)—C(6):	1.375(6);	C(9)—C(12):	1.519(9)

Angle (°)

C(1)—Ni—C(2):	87.6(2);	Ni—C(1)—N(1):	174.7(3)
Ni—C(2)—N(2):	177.0(4);	C(1)—N(1)—Cd:	145.8(3)
N(1)—Cd—N(3):	95.2(2);	Cd—N(3)—C(3):	116.8(3)
N(3)—C(3)—C(4):	114.2(4);	C(3)—C(4)—C(5):	115.2(6)
C(4)—C(5)—C(5′):	111.4(6);	N(1)—Cd—N(4):	91.6(2)
N(3)—Cd—N(4):	86.6(2);	Cd—N(4)—C(6):	111.5(3)
N(4)—C(6)—C(7):	120.8(6);	C(6)—C(7)—C(8):	119.8(6)
C(7)—C(8)—C(9):	122.3(7);	C(8)—C(9)—C(10):	117.9(6)
C(9)—C(10)—C(11):	120.3(7);	C(10)—C(11)—C(6):	120.6(7)
C(8)—C(9)—C(12):	120.9(8);	C(11)—C(6)—C(7):	119.0(5)
C(10)—C(9)—C(12):	121.1(8)		

* Atom C(5′) is generated by the inversion at 0.5, 0.5, 0.5.

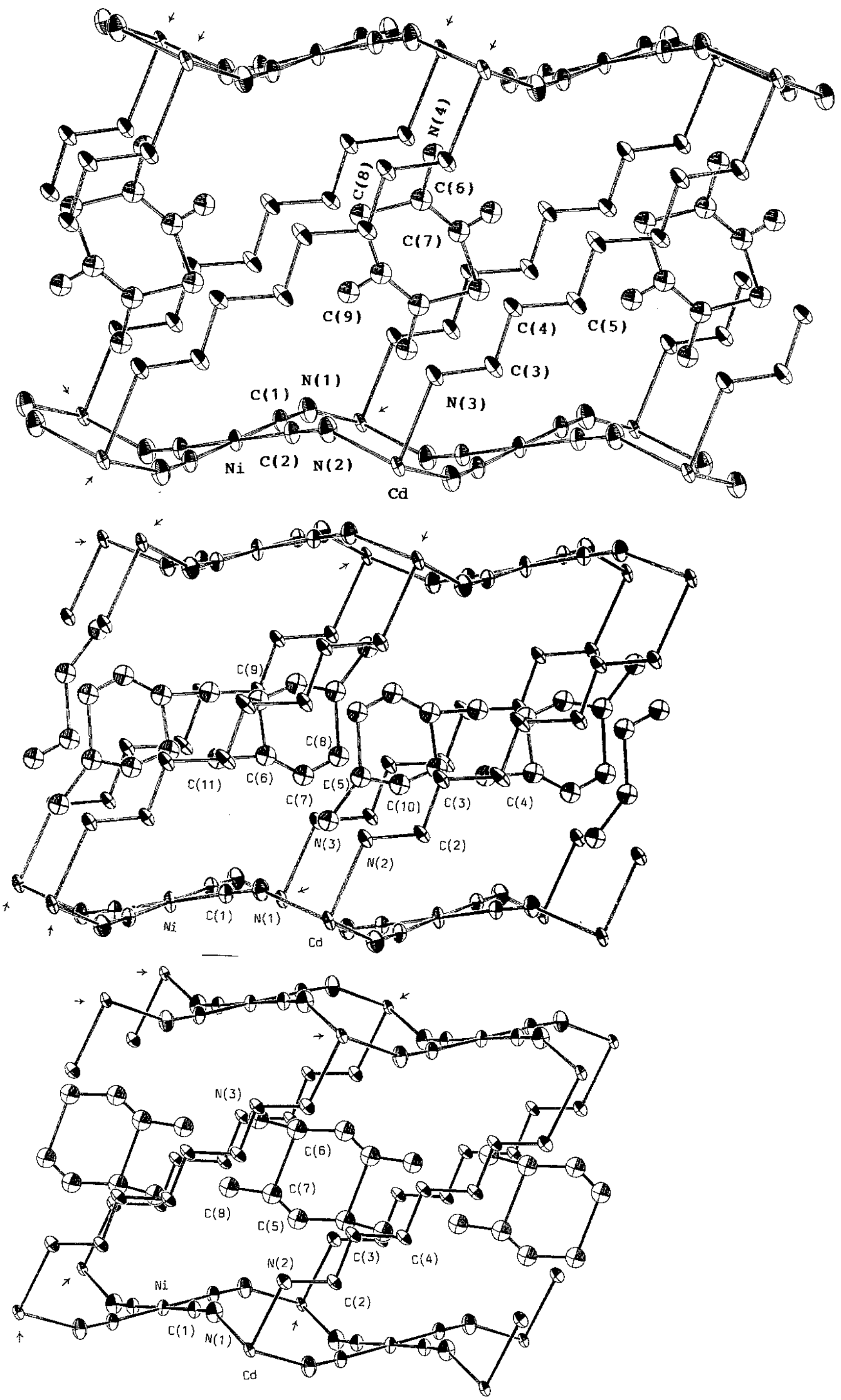

Fig. 1. ORTEP views of **Im** (top), **Ip** (middle) and **Ix** (bottom). 30% thermal ellipsoids are shown for the host atoms and isotropic spheres of 5.0 Å^2 for the guest atoms; hydrogen atoms are omitted. Each of the unit cells is cornered by the Cd atom at the origin and other seven Cd atoms indicated by arrows. The guest molecules should be seen as tentative images.

occupancy, related by the center of inversion; the shape of the molecule is not reasonable when the repulsions from the cavity wall are taken into account.

All the benzene rings are more or less distorted from a regular hexagon, and the thermal parameters are extremely large, as listed in Table II. Each guest shown in Figure 1 is only of a tentative image: the distances and angles for the guest-atoms have little significance and are not listed in Table III.

3.3. *p*-TOLUIDINE COMPLEX, **II**

Figure 2 shows a perspective view of the complex, and the projection along the *b*-axis is illustrated in Figure 3. As Figures 2 and 3 show, the *p*-toluidine behaves as a unidentate ligand coordinating at the amino-nitrogen to the Cd atom in a two-dimensional network extending along the *bc*-plane, the network being built of the *catena-μ*-linkages of —Ni—CN—Cd—NC—Ni— along the *b*-axis and of —Cd—dahxn—Cd— along the *c*-axis with the intersection at each Cd atom. The ambidentate dahxn ligand involved in the *catena-μ*-linkage is in a *cis–trans–cis* skeletal conformation with the Cd-dahxn-Cd length of 12.47 Å which is shorter by *ca.* 0.5 Å than the corresponding distance in **Ip**. A *trans* pair of cyano groups in the tetracyanonickelate(II) moiety are released from coordination to a Cd atom. The Cd atom takes an all-*trans* N_6-octahedral structure with a slight distortion from the regular octahedron. The longest Cd—N distance, 2.474(3) Å for the Cd—*p*-toluidine linkage, is longer by 0.13–0.17 Å than those for the Cd—NC and Cd—dahxn linkages.

4. Discussion

4.1. HOST STRUCTURES AND ORIENTATION OF GUEST MOLECULES IN **Im**, **Ip**, AND **Ix**

Although the structure of **Im** is distorted to triclinic symmetry from the monoclinic ones of **Io**, **Ip** and **Ix**, the degree of distortion is so small that the hosts can be seen to comprise a substantially isostructural series. All the skeletal atoms of dahxn and the guest molecules in **Ip** and **Ix**, as well as **Io**, are located on the mirror planes at $y/b = 0$ and 0.5, respectively, although those in the triclinic **Im** deviate by *ca.* 0.2 Å for the dahxn atoms and *ca.* 0.5 Å for the guest-atoms at maximum from the calculated planes.

The cavities formed in these host structures are similar in nature and shape to those observed for the Hofmann–dabn-type previously reported [2, 4]. Each cavity is roofed and floored by the networks of cyanometal complex, and columned and walled by the dahxn ligands; the openings of the cavity at both sides along the *c*-axis are small enough to hinder the guest from traveling to the next one except for **Ip** as illustrated in Figure 4. Comparison of the present host structure should be done with the Hofmann-dabn-type 2,5-xylidine and *N*,*N*-dimethylaniline clathrates because of the geometric similarity in the guest molecules. The all-*trans* conformation of the dahxn ligand is in contrast with the *cis-trans* one of the dabn in these Hofmann-dabn-type clathrates, although an all-*trans* dabn was demonstrated in the crystal structure of the pyrrole clathrate, the guest being considerably smaller than the toluidine and xylidine molecules. The *cis-trans* dabn behaves as the column and wall of the cavity in these Hofmann-dabn-type, similar to the dahxn in the present ones. However, a gap is left between neighboring pairs of dabn ligands along the crystal *c*-axis, whereas the dahxn ligands with all-*trans* skeletal conformation are arranged without a gap. The gap in the Hofmann-dabn-type is filled by the substituent groups of the guest which

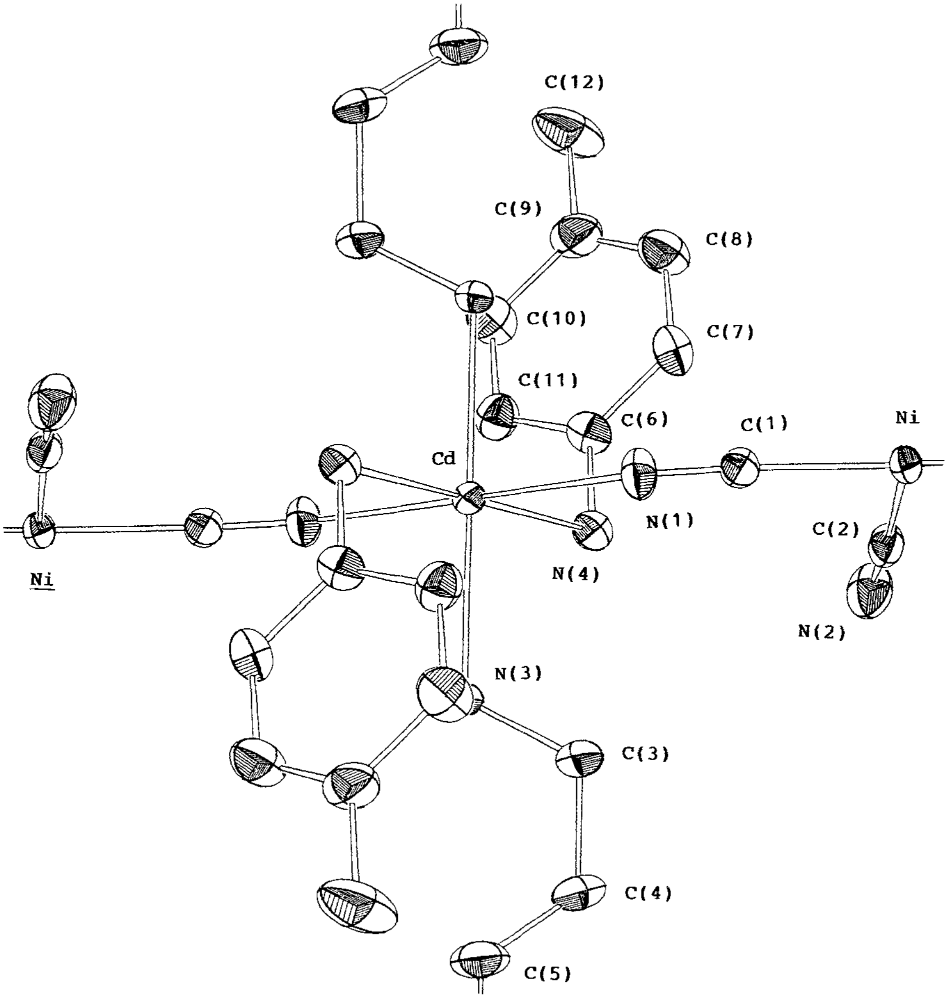

Fig. 2. ORTEP view of the coordination structure about the Cd atom (at 0.5, 0.5, 0.5) in **II** (Ni at 0.5, 1.0, 0.5); hydrogen atoms are omitted.

is accommodated in the cavity obliquely against the crystal *ac*-plane; this arrangement of guest molecules makes the *b*-dimension double, with the 2_1 symmetry (15.010 Å for the 2,5-xylidine compound and 15.267 Å for the *N*,*N*-dimethylaniline one). In other words, the filled arrangement of the all-*trans* dahxn is favorable to the *P*2/*m* space group of **Io**, **Ip**, and **Ix**, and the slightly distorted structure of **Im**.

The geometry of the guest molecule, so far among the three toluidine isomers and 2,4-xylidine, appears not to have any significant correlations with the volume of the unit cell, the values in Å^3 being 511.5(2) for **Io**, 521.4(1) for **Im**, 507.6(1) for **Ip**, and 514.1(2) for **Ix**. Since no significant expansion is observed for **Ix** in spite of the guest molecule being more voluminous by a methyl group than toluidine isomers, the effective volume of the cavity should be almost equal in these four clathrates. It means that the cavity does not fit the guest molecule tightly. As described in Section 3.2, the images of the respective guest molecules are disordered and/or distorted with the extremely large thermal amplitudes and

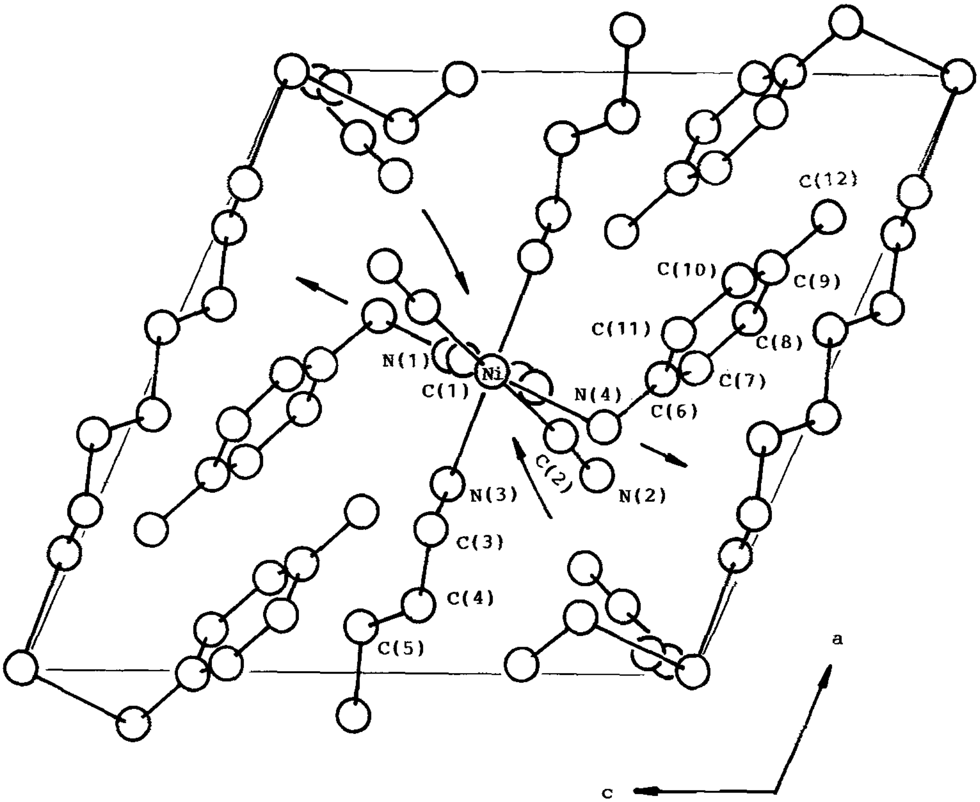

Fig. 3. Projection of **II** structure along the *b*-axis; arrows show the directions of releasing the *p*-toluidines from coordination and making the three-dimensional linkage of **Ip** host structure in the thermal conversion of **II** to **Ip**.

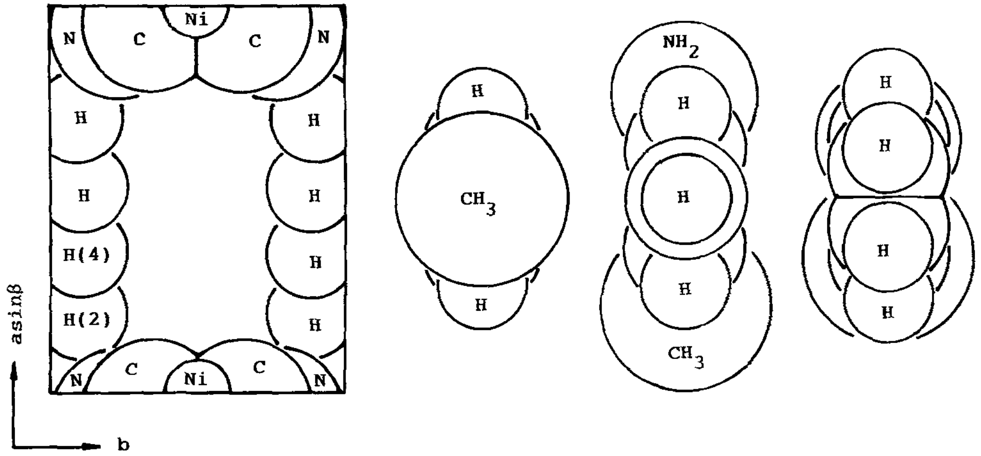

Fig. 4. View of the opening of the cavity in **Ip**, and the projections of *p*-, *m*-, and *o*-toludine molecule pictured with van der Waals radii: C and N of CN group, 1.7 Å; C, 1.5 Å; H, 1.1 Å; CH$_3$, 2.0 Å; and NH$_2$, 1.8 Å.

the low precision positional parameters. The reason such disordered and distorted structures have been observed is not only due to the centrosymmetric space groups but also due to the freedom of motion allowed for the guest molecules in the cavities with loose packing. The crystal structure analyses at low temperatures are desirable to allow discussion of the motional behavior of the guests; the results for **Io** and **Ix** will be reported elsewhere [11].

4.2. COORDINATION OF *p*-TOLUIDINE IN **II** AND THERMAL CONVERSION OF **II** TO **Ip**

Low values of stability constants in solution have been reputed for a 1 : 1 cadmium(II)-*o*-toluidine complex ($\log K_1 = -0.10$) and for a 1 : 1 and a 1 : 2 cadmium(II)-*p*-toluidine complex ($\log K_1 = 0.26$, $\log \beta_2 = -0.01$); log K values for the protonated species are 4.44 for *o*-toluidine and 4.79 for *p*-toluidine [12]. As for *m*-toluidine no data have been reported except for the silver(I) complexes of stability constants comparable with those of the other two isomers. From these data, we cannot conclude that *p*-toluidine is preferable to the *o*- and *m*-isomers in ligating to the cadmium(II), even in the presence of 1,6-diaminohexane or other possible ligands such as citric acid and monoethanolamine. The preference of complex formation to clathration may be due to solubility or kinetic effects, because the more dilute guest-organic solvent mixture is favorable for formation of the clathrate.

As has been previously reported [6], **II** is thermally converted to **Ip** upon heating under ambient atmosphere accompanied by the liberation of one mole of the *p*-toluidine ligands from a formula unit at the first stage of the thermal decomposition: then another one mole of *p*-toluidine is converted from ligand to guest in a solid state reaction. After the thermal formation of **Ip**, the guest *p*-toluidine molecule is liberated at the second stage of the whole thermal decomposition processes. The infrared and Raman spectra, and the powder X-ray diffraction pattern of the thermally produced **Ip** coincide with those observed for **Ip** prepared by the present wet method.

Part of the three-dimensional host structure in **Ip** is preserved in the two-dimensional networks in **II**. Upon heating, the *p*-toluidine ligands are released from coordination to the Cd atom, the opened sites of which are filled with the nearest (4.156(3) Å from the Cd atom) free N-ends of the CN groups to form the three-dimensional linkage of the host structure. Concurrently, the skeleton of the dahxn turns from the *cis–trans–cis* in **II** to the all-*trans* conformation in **Ip**. The process appears to proceed without any large-scale transformation and/or transfer of the host moieties. On the other hand, one of the released *p*-toluidine molecules should be liberated from the solid phase of the clathrate, whereas the other should be retained as the guest. As can be seen in Figure 4, the opening of the cavity along the *c*-axis of the crystal has little steric hindrance for a *p*-toluidine molecule passing through to the next cavity if the molecule takes the orientation of the smallest projection against the opening; the projections for *o*- and *m*-toluidine are considerably larger than that for *p*-toluidine.

The thermal conversion of **II** to **Ip** gives the first example of a Lewis base, generally thought to be more stable as a ligand than as a guest, being converted thermally from a ligand to a guest in metal complex systems.

Acknowledgement

This work was supported by the Grants-in-Aid for the Special Project Research on the Properties of Molecular Assemblies (Nos. 58118007, 59112006, and 60104003) from the Ministry of Education, Science and Culture, Japan.

References

1. T. Hasegawa, S. Nishikiori, and T. Iwamoto: *J. Incl. Phenom.* **1**, 365 (1984).
2. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **2**, 341 (1985).
3. T. Hasegawa, S. Nishikiori, and T. Iwmaoto: *J. Incl. Phenom.* **2**, 351 (1985).
4. S. Nisikiori and T. Iwamoto: *Inorg. Chem.* **25**, 788 (1986).
5. T. Hasegawa, S. Nishikiori, and T. Iwamoto: *Chem. Lett.* 1659 (1985).
6. T. Hasegawa, S. Nishikiori, and T. Iwamoto: *Chem. Lett.* 793 (1986).
7. T. Sakurai and K. Kobayashi: *Rep. Inst. Phys. & Chem. Res.* **55**, 69 (1979).
8. C. K. Johnson: *ORTEP Report ORNL-3794*, Oak Ridge National Laboratory, Tennessee, U.S.A. (1965).
9. *International Tables for X-Ray Crystallography*, v. IV, pp. 71–98. Kynoch Press (1974) (Distr. D. Reidel Publ. Co., Dordrecht).
10. Tables of anisotropic thermal parameters, calculated positions of hydrogen atoms, and structure factors for **Im**, **Ip**, **Ix**, and **II** have been deposited with the British Library Lending Division under SUP. 82060 (98 pages).
11. T. Hasegawa, S. Nishikiori, and T. Iwamoto, to be submitted to *J. Incl. Phenom.* (Presented at Tenth European Crystallographic Meeting, 2B-08, Wroclaw, August (1986).)
12. *Stability Constants, Supplement No. 1* Special Publication 25, The Chemical Society, London (1971), pp. 491–492, p. 542.