The Crystal Structures of α, ω-Diaminoalkanecadmium(II) Tetracyanonickelate(II)–Aromatic Molecule Inclusion Compounds. V. Toluidine Clathrates of the Hosts Built of the Diamines, 1,4-Diaminobutane, 1,5-Diaminopentane, and 1,8-Diaminooctane

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Abstract. The crystal structures have been analyzed for the three *o*-toluidine clathrates, *catena-[catena-µ-*(1,4-diaminobutane)cadmium(II) tetra-µ-cyanonickelate(II)]-*o*-toluidine(2/3), **4-o**, *catena-[catena-µ-*(1,5-diaminopentane)cadmium(II) tetra-µ-cyanonickelate(II)]-*o*-toluidine(3/4), **5-o**, and *catena-[catena-µ-*(1,8-diaminooctane)cadium(II) tetra-µ-cyanonickelate(II)]-*o*-toluidine(1/1), **8-o**, for a *m*-toluidine one *catena-[catena-µ-*(1,5-diaminopentane)cadmium(II) tetra-µ-cyano-nickelate(II)]-*m*-toluidine(1/1), **5-m**, and for a *p*-toluidine one *catena-[catena-µ-*(1,8-diaminooctane)cadium(II) tetra-µ-cyanonickelate(II)]-*p*-toluidine(1/1), **8-p**. **4-o** crystallizes in the triclinic space group $P\bar{1}$, $a/\text{Å} = 9.806(3)$, $b/\text{Å} = 14.388(3)$, $c/\text{Å} = 7.725(2)$, $\alpha/° = 89.71(2)$, $\beta/° = 89.96(2)$, $\gamma/° = 98.12(2)$, $V/\text{Å}^3 = 1078.8(5)$, $Z = 2$, 3750 reflections, $R = 0.056$; **5-o**: tetragonal $P4/mmm$, $(a = b)/\text{Å} = 7.485(7)$, $c/\text{Å} = 10.06(3)$, $V/\text{Å}^3 = 563(2)$, $Z = 1$, 573 reflections, $R = 0.19$; **8-o**: monoclinic $P2/m$, $a/\text{Å} = 11.513(4)$, $b/\text{Å} = 7.626(1)$, $c/\text{Å} = 7.101(1)$, $\beta/° = 109.63(3)$, $V/\text{Å}^3 = 587.2(2)$, $Z = 1$, 1682 reflections, $R = 0.058$; **5-m**: orthorhombic *Pbam*, $a/\text{Å} = 12.254(6)$, $b/\text{Å} = 20.62(1)$, $c/\text{Å} = 7.804(1)$, $V/\text{Å}^3 = 1972(1)$, $Z = 4$, 2240 reflections, $R = 0.059$; and **8-p**: triclinic $P\bar{1}$, $a/\text{Å} = 11.52(1)$, $b/\text{Å} = 7.632(3)$, $c/\text{Å} = 7.039(4)$, $\alpha/° = 88.93(4)$, $\beta/° = 109.71(5)$, $\gamma/° = 82.81(9)$, $V/\text{Å}^3 = 576.9(6)$, $Z = 1$, 2598 reflections, $R = 0.042$. Their structures are substantially similar to the already-known structure of *catena-[catena-µ-*(1,6-diaminohexane)cadmium(II) tetra-µ-cyanonickelate(II)]-*o*-toluidine(1/1): the guest toluidine molecules are accommodated in the cavities formed between *catena-*[cadmium(II) tetra-µ-cyanonickelate(II)] layers bridged by the ambidentate α, ω-diaminoalkane ligands at the cadmium(II) atoms. The carbon chain length of the α, ω-diaminoalkane influences the number of cavities per formula unit and the deformation of the metal complex layers.

Key words. cadium, crystal structure, Hofmann-diam-type, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,8-diaminooctane, tetracyanonickelate, toluidine.

1. Introduction

In the previous papers of this series [1–4], the structures of the *catena-[catena-µ-*(α, ω-diaminoalkane)cadmium(II) tetra-µ-cyanonickelate(II)] –aromatic guest(*h/g*)

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inclusion compounds have been discussed in terms of the view that the host structure with a given α, ω-diaminoalkane is influenced by guest molecules with different geometries. As the series of 'Hofmann-diam-type' inclusion compounds $Cd(diam)Ni(CN)_4 \cdot xG$ have been synthesized for the α, ω-diaminoalkanes $NH_2(CH_2)_n NH_2$ (= diam) of $n = 2$–9 [5–7], an investigation was attempted to clarify the effect of the carbon chain length of diam on the crystal structures of clathrates with common guests. In the present stage, single crystals suitable for X-ray structure analysis have been obtained for the o-toluidine clathrates of the hosts with $n = 4$ (Hofmann-dabtn-type), 5 (Hofmann-daptn-type), and 8 (Hofmann-daotn-type); the structure of the $n = 6$ host clathrate (Hofmann-dahxn-type) is already known [2]. The m-toluidine clathrate of the Hofmann-daptn-type and the p-toluidine clathrate of the Hofmann-daotn-type are also included in this paper in order to demonstrate the variety of the host structures with odd-n and even-n diamines.

2. Preparation

Crystals of catena-[catena-μ-(1,4-diaminobutane)cadium(II) tetra-μ-cyanonickelate(II)]-o-toluidine(2/3), **4-o**, catena-[catena-μ-(1,5-diaminopentane)cadium(II) tetra-μ-cyanonickelate(II)]-o-toluidine(3/4), **5-o**, catena-[catena-μ-(1,5-diaminopentane)cadium(II) tetra-μ-cyanonickelate(II)]-m-toluidine(1/1), **5-m**, catena-[catena-μ-(1,8-diaminooctane)cadmium(II) tetra-μ-cyanonickelate(II)]-o-toluidine(1/1), **8-o**, and catena-[catena-μ-(1,8-diaminooctane)cadmium(II) tetra-μ-cyanonickelate(II)]-p-toluidine(1/1), **8-p**, were prepared by the methods already reported [1–6]. Anal. Found for **4-o**: C, 42.4; H, 4.88; N, 20.0; Cd, 21.4; Ni, 11.2%. Calcd. for $C_{37}H_{51}N_{15}Cd_2Ni_2$: C, 42.40, H, 4.90; N, 20.04; Cd, 21.45; Ni 11.19%. Found for **5-o**: C, 42.1; H, 5.16; N, 19.6; Cd, 20.6; Ni, 11.0%. Calcd. for $C_{55}H_{78}N_{22}Cd_3Ni_3$: C, 39.66; H, 4.78; N, 20.23; Cd, 23.20; Ni, 12.11%. Found for **8-o**; C, 43.0; H, 4.74; N, 17.6; Cd, 21.6; Ni, 11.3%; Found for **8-p**: C, 43.0; H, 5.20; N, 18.5; Cd, 21.2; Ni, 11.3%. Calcd. for $C_{19}H_{29}N_7CdNi$: C, 43.33; H, 5.55; N, 18.61; Cd, 21.34; Ni, 11.14%. These results support the formulated host/guest ratios [6a], although some values, in particular the H and N values for **8-o**, deviated considerably from the calculated ones. However, the values for Cd and Ni, determined immediately after preparation, lie in a range which is acceptable enough to support the stoichiometry. From our experience in the analytical procedures for these clathrate compounds, the deviation is usually caused by the imperfect crystallization of the bulk specimens.

3. Structure Determination and Description

3.1. GENERAL

The crystal data and experimental conditions are summarized in Table 1 along with the crystal data already reported for catena-[catena-μ-(1,6-diaminohexane)cadmium(II) tetra-μ-cyanonickelate(II)]-o-toluidine(1/1), **6-o** [2]. The X-ray

data collections and the structure analyses were carried out in a similar way to those described in our previous papers [1–4]. The structures were solved by the heavy-atom method using the programs in UNICSIII [8] including ORTEP [9] and their local versions on a HITAC computer system M-680H in the computer center of this university; Patterson, Fourier, difference Fourier syntheses and block-diagonal least-squares procedures were applied. The atomic scattering factors including the real and imaginary dispersion corrections were taken from the International Tables [10]. The occupancy factor of the guest molecule was fixed at unity from the results of elemental analyses. The Tables of structure factors, anisotropic thermal parameters, calculated positions of hydrogen atoms, selected bond distances and angles, and least-squares planes have been deposited with the British Library (77 pages).

The atomic coordinates and equivalent isotropic thermal parameters are listed in Tables II–VI for **4-o**, **5-o**, **5-m**, **8-o**, and **8-p**, respectively; their structures are illustrated in Figures 1–5, respectively.

3.2.1. *catena-[catena-μ-(1,4-Diaminobutane)cadmium(II) tetra-μ-cyano-nickelate(II)]-o-toluidine(2/3)*, **4-o**

The centrosymmetric space group $P\bar{1}$ was applied. All the non-hydrogen atoms of the host moieties could be located on the Fourier map. Two kinds of cavities were found. The guest in one cavity centered at 1/2,1/4,0 showed the benzene ring and the amino nitrogen uniquely but the methyl carbon was distributed on both sides of the amino group; their occupancy factors were included in the refined parameters. Since the guest in the other cavity at 1/2,0,1/2 showed a vague ring-like distribution of the electron densities about the inversion center, a rigid model of the *o*-toluidine molecule whose ring center coincided with the cavity center was rotated to find the atomic positions making the R value minimum. Then the atomic parameters were refined with release from the rigid conditions. At the final stage all the non-hydrogen atoms were refined anisotropically; the largest Δ/σ was 0.80 for C(20), the methyl carbon of the guest in the latter cavity.

The structure in Figure 1 is similar to that of the Hofmann-dabtn-type aniline clathrate, **4-a** [3]: the 1,4-diaminobutane (dabtn) ligand takes a *(trans)₃-cis-trans* conformation of the aliphatic skeleton to bridge adjacent layers of the cyanometal network *catena*-[cadmium(II) tetra-μ-cyanonickelate(II)] at the cadmium atoms. A pair of the 'cis protrusion' of the *(trans)₃-cis-trans* skeletons invade one of the four cavity units [3] in the unit cell so that the stoichiometric ratio of the host to the guest, h/g, is 2/3, the same as that of **4-a**. Two of the three guests are accommodated in the cavities at 1/2,1/4,0 and the equivalent position, the remaining one being in the cavity centered at 1/2,0,1/2, similarly to the case of **4-a**. Although the atomic parameters of the aniline molecule in the latter cavity could not be determined in **4-a** [3], those of the *o*-toluidine in **4-o** were determined with acceptable precision. In Figure 1, one of the methyl carbons, C(15), with the occupancy factor of 0.59(4) is shown for the former guest, and the apparently tetrasubstituted structure, enforced from the centrosymmetric space group, for the latter one.

Table I. Crystallographic and experimental data

General formula Cd[NH$_2$(CH$_2$)$_n$NH$_2$]Ni(CN)$_4 \cdot x$[y-CH$_3$C$_6$H$_4$NH$_2$]

No.	4-o	5-o	5-m	6-o[b]	8-o	8-p
n	4	5	5	6	8	8
x	3/2	4/3	1	1	1	1
y	ortho	ortho	meta	ortho	ortho	para
FW	524.06	520.23	484.51	498.55	526.59	526.59
crystal system	triclinic	tetragonal	orthorhombic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P4/mmm$	$Pbam$	$P2/m$	$P2/m$	$P\bar{1}$
a/Å	9.806(3)	7.485(7)	12.254(6)	9.541(2)	11.513(4)	11.52(1)
b/Å	14.388(3)	$= a$/Å	20.62(1)	7.569(2)	7.626(1)	7.632(3)
c/Å	7.725(2)	10.06(3)	7.804(1)	7.199(1)	7.101(1)	7.039(4)
α/°	89.71(2)	90	90	90	90	88.93(4)
β/°	89.96(2)	90	90	100.3(1)	109.63(3)	109.71(5)
γ/°	98.12(2)	90	90	90	90	82.81(9)
V/Å^3	1078.8(5)	563(2)	1972(1)	511.5(2)	587.2(2)	576.9(6)
Z	2	1	4	1	1	1
Dx/g cm^{-3}	1.61	1.52	1.63	1.62	1.49	1.51
Dm/g cm^{-3}	1.60(1)	1.50(2)	1.62(1)	1.61(1)	1.49(1)	1.50(1)

$F(000)$	530	263.33	976	252	268	268
crystal size (mm)	$0.25 \times 0.2 \times 0.2$	$0.2 \times 0.2 \times 0.25$	$0.15 \times 0.15 \times 0.13$	$0.15 \times 0.15 \times 0.08$	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.2 \times 0.13$
$\mu(MoK_\alpha)/cm^{-1}$	18.65	17.90	20.3	19.23	17.17	17.47
scan mode	$2\theta - \omega$	$2\theta - \omega$	ω	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
2θ scan range	$3° < 2\theta < 55°$	$3° < 2\theta < 70°$	$2° < 2\theta < 65°$	$2° < 2\theta < 70°$	$2° < 2\theta < 70°$	$2° < 2\theta < 60°$
peak scan width/°	$1.3 + 0.5 \tan\theta$	$1.8 + 0.5 \tan\theta$	$0.97 + 0.5 \tan\theta$		$1.3 + 0.5 \tan\theta$	$1.3 + 0.5 \tan\theta$
systematic absences	no	no	h0l: odd h / 0k1: odd k	no	no	no
collection range	$-12 \leq h \leq 12$ $0 \leq k \leq 18$ $-9 \leq l \leq 10$	$0 \leq h \leq 12$ $0 \leq k \leq 12$ $0 \leq l \leq 16$	$0 \leq h \leq 18$ $0 \leq k \leq 31$ $0 \leq l \leq 11$		$-18 \leq h \leq 17$ $0 \leq k \leq 12$ $0 \leq l \leq 11$	$-14 \leq h \leq 16$ $-10 \leq k \leq 10$ $-9 \leq l \leq 10$
no. of reflcns. total	5350	1520	4053	2545	2942	3749
used ($>3\sigma(F_0)$), N_0	3750	573[c]	2240	1973	1682	2598
refined params., N_P	308	14	176	113	155	137
R,[d] R_w[d]	0.056, 0.055	0.192, 0.180	0.059, 0.044	0.035, 0.031	0.058, 0.053	0.042, 0.047
GOF[e]	1.570	2.058	1.306		0.782	0.694
F_{max}	50	20	50	150	25	45.5
F_{min}	25	10	25	75	12.5	22.7

[a]Diffractometer: Rigaku AFC-6A; radiation: $MoK_\alpha (\lambda = 0.70926 \text{ Å})$; monochromator: graphite; temperature: ambient; scan rate: 4°/min; correction: Lp.

[b]Cited from Ref. 2.

[c]$|F_0| > \sigma(F_0)$.

[d]$R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $R_w = \Sigma[w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}$. Weighting schemes are: $w = (F_{max}/F_0)^2$ for $|F_0| > F_{max}$, $w = 1$ for $F_{max} \geq |F_0| \geq F_{min}$, $w = 0.25$ of $|F_0| < F_{min}$.

[e]$GOF = [\Sigma w(|F_0| - |F_c|)^2/(N_0 - N_P)]^{1/2}$.

Table II. Atomic parameters for **4-o**

atom[a]	G[b]	x	y	z	$B_{eq}/\text{Å}^2$ [c]
Cd	1.0	0.6446(6)	0.26574(4)	0.49982(7)	1.91(2)
Ni(1)	0.5	0.0	0.0	0.0	2.19(5)
Nl(2)	0.5	0.0	0.5	0.0	2.11(5)
N(1)	1.0	0.0315(8)	0.1455(5)	0.2808(9)	4.0(3)
N(2)	1.0	0.1044(7)	0.3798(5)	0.2753(8)	3.3(3)
N(3)	1.0	0.0959(7)	0.3806(5)	0.7194(8)	3.4(3)
N(4)	1.0	0.0208(8)	0.1486(5)	0.7249(9)	3.8(3)
N(5)	1.0	0.2912(7)	0.2492(6)	0.509(1)	4.7(4)
N(6)	1.0	0.8369(8)	0.2839(6)	0.471(1)	5.4(4)
N(7)	1.0	0.335(2)	0.274(2)	−0.010(2)	15(1)
N(8)*	0.5	0.759(3)	−0.016(2)	0.406(3)	9(1)
C(1)	1.0	0.0187(8)	0.0902(5)	0.1750(9)	2.7(3)
C(2)	1.0	0.0688(8)	0.4256(5)	0.1683(9)	2.5(3)
C(3)	1.0	0.0617(7)	0.4262(5)	0.8266(9)	2.4(3)
C(4)	1.0	0.0132(8)	0.0933(5)	0.8300(9)	2.7(3)
C(5)	1.0	0.3956(9)	0.3301(6)	0.482(1)	4.0(4)
C(6)	1.0	0.5428(9)	0.3066(7)	0.500(1)	4.4(4)
C(7)	1.0	0.6511(9)	0.3744(8)	0.466(1)	4.9(5)
C(8)	1.0	0.795(1)	0.3744(8)	0.507(2)	5.5(5)
C(9)	1.0	0.457(2)	0.255(1)	0.015(2)	10(1)
C(10)	1.0	0.554(2)	0.336(2)	−0.028(2)	11(1)
C(11)	1.0	0.674(2)	0.332(1)	−0.021(2)	9.3(9)
C(12)	1.0	0.744(2)	0.247(2)	0.027(2)	13(1)
C(13)	1.0	0.646(2)	0.168(1)	0.078(2)	11(1)
C(14)	1.0	0.497(2)	0.177(1)	0.066(2)	10(1)
C(15)*	0.59(4)	0.387(2)	0.131(2)	0.102(3)	7(1)
C(16)*	0.41(4)	0.442(3)	0.383(3)	−0.046(4)	7(2)
C(17)	1.0	0.642(4)	−0.011(2)	0.444(5)	12(2)
C(18)	1.0	0.611(4)	0.054(2)	0.597(4)	11(2)
C(19)	1.0	0.476(4)	0.054(2)	0.631(4)	9(2)
C(20)*	0.5	0.720(3)	0.101(2)	0.631(4)	9(2)

[a]Atom in disorder has been asterisked.
[b]Multiplicity.
[c]$B_{eq} = 4[\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j]/3$.

3.2.2. catena-[catena-μ-(1,5-Diaminopentane)cadmium(II) tetra-μ-cyano-nickelate(II)]-o-toluidine(3/4), 5-o

The apparently high symmetry of the space group *P4/mmm* predicted disorder in the orientations of the 1,5-diaminopentane (daptn) ligand and the guest molecule. Only the atoms comprising the two-dimensional cyano-metal network could be detected clearly on the Fourier map; they were refined anisotropically. However, the electron densities were distributed so vaguely in the interlayer space between the networks that it was impossible to find any discrete atomic positions for the daptn and the guest.

The host structure of **5-o** in Figure 2 is isostructural to those of the Hofmann-type, Hofmann-en-type, and Hofmann-pn-type, when the comparison is limited to the arrangement and stacking of the cyanometal complex layers, the 7.485(7) Å
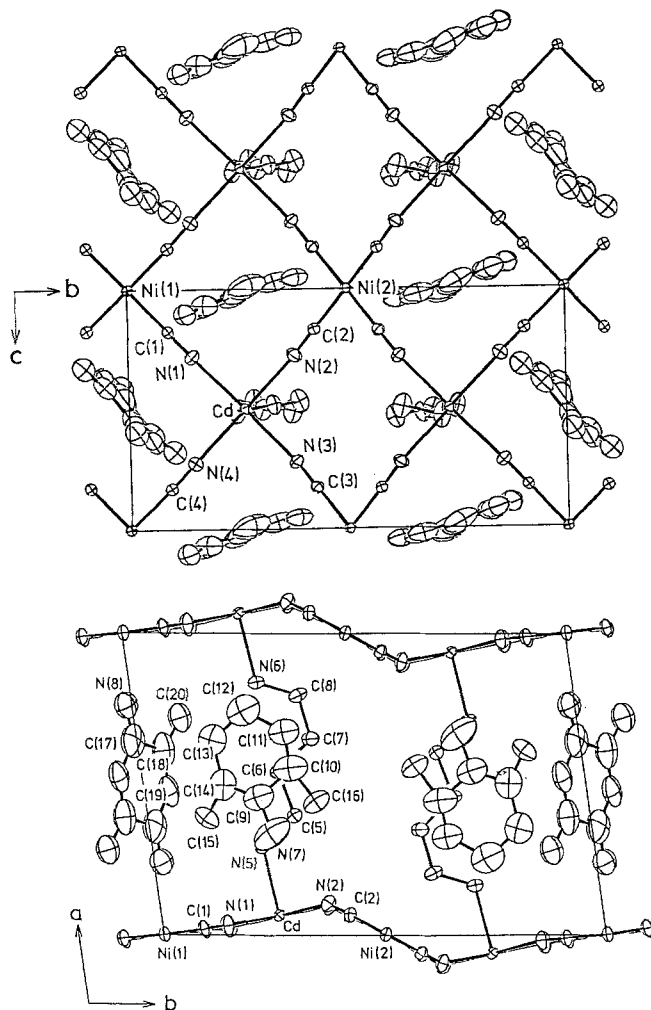
Fig. 1. Structure of **4-o**. *Top*: view along the *a*-axis; *bottom*: view along the *c*-axis. The substituents in the guest *o*-toluidine molecules are disordered.

Table III. Atomic parameters for **5-o**

atom	G^a	x	y	z	$B_{eq}/\text{Å}^{2\ b}$
Cd	0.0625	0.0	0.0	0.0	3.1(1)
Ni	0.0625	0.5	0.5	0.0	7.2(4)
C	0.25	0.215(5)	0.215	0.0	10(2)
N	0.25	0.325(5)	0.325	0.0	9(2)

[a]Multiplicity.

[b]$B_{eq} = 4[\Sigma_i \Sigma_j \beta_{ij}\, \mathbf{a}_i \mathbf{a}_j]/3$.
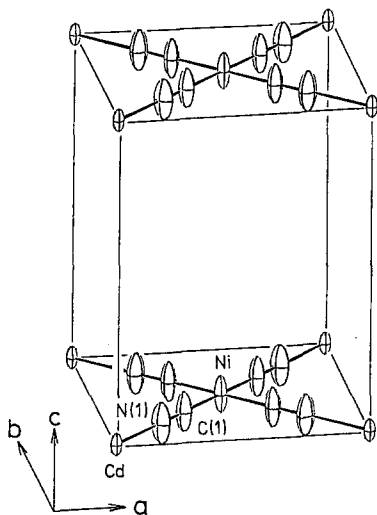
Fig. 2. Tetragonal array of the *catena*-[cadmium tetra-μ-cyano-nickelate(II)] network in **5-o**.

a-dimension of the tetragonal unit cell is similar to those of the Hofmann-type (7.542 Å) and the Hofmann-en-type (7.657 Å) benzene clathrates [11], and of the Hofmann-pn-type (7.570 Å) pyrrole clathrate [12].

The 10.06(3) Å *c*-dimension, i.e. the interlayer distance, is too short for the daptn to span the layers by taking an all-*trans* conformation as for the en in the Hofmann-en-type: it needs a distance of ca. 13.4 Å. It is unreasonable in the tetragonal unit cell to take a tilting bridge like the dabtn in the Hofmann-dabtn-type pyrrole clathrate, **4-pyr** [3]. However, the distance is large enough to accommodate the guest in the interlayer space. The *h*/*g* ratio of 3/4 in **5-o** determined by chemical analyses means that two-thirds of the total cavity units are occupied by guests and one-third by daptn ligands at random. Such a random occupation of cavity units has been observed for the Hofmann-pn-type pyrrole clathrate [12], although the ratio is 2/3 and the guest occupancy rate is three-quarters in the Hofmann-pn-type. The vague distribution of electron densities may be due to an extremely high degree of disorder in the location and orientation of the daptn and the guest.

3.2.3. *catena*-[*catena*-μ-(1,5-Diaminopentane)cadmium(II) tetra-μ-cyano-nickelate(II)]-*m*-toluidine(1/1), **5-m**

The space group *Pbam* gave a more reasonable result than *Pba*² which was also possible from the systematic absences. Two images of daptn, L1 and L2, were found to bridge the same pair of Cd atoms in the adjacent networks, although a methylene group was missing in L2. A methylene group in L1, C(4), was distributed statistically about the mirror plane at *c* = 0 on which all the other skeletal atoms of daptn were located. All the non-hydrogen atoms of the guest molecule were found on the Fourier map, but significant discrimination between the methyl and the amino groups was impossible. The guest molecule was distributed statistically about the mirror plane at *c* = 0.5 on which two phenyl carbons and one substituent were located. All the

Table IV. Atomic parameters for **5-m**

atom[a]	G[b]	x	y	z	$B_{eq}/Å^{2}$ [c]
Cd	0.5	0.16768(5)	0.17723(3)	0.0	2.61(2)
Ni	0.5	0.40868(8)	0.27655(5)	0.5	2.83(4)
N(1)	1.0	0.2884(4)	0.2077(2)	0.2174(6)	4.4(2)
N(2)	1.0	0.5371(4)	0.3452(2)	0.2260(5)	4.4(2)
N(3)	0.5	0.0733(7)	0.2744(4)	0.0	7.2(5)
N(4)	0.5	0.2843(5)	0.5723(3)	0.0	3.7(3)
C(1)	1.0	0.3335(5)	0.2326(2)	0.3279(6)	3.6(2)
C(2)	1.0	0.4873(4)	0.3198(3)	0.3335(6)	3.4(2)
C(3)	0.5	0.1192(9)	0.3344(4)	0.0	7.2(7)
C(4)*	0.25	0.231(2)	0.3562(9)	0.036(2)	3.1(9)
C(5)*	0.25	0.255(2)	0.426(1)	0.0	10(2)
C(6)*	0.25	0.355(2)	0.4561(9)	0.0	6(1)
C(7)*	0.25	0.374(1)	0.5256(8)	0.0	4.8(9)
C(8)*	0.25	0.040(2)	0.3940(8)	0.0	6(1)
C(9)*	0.25	0.145(2)	0.472(1)	0.0	7(1)
C(10)*	0.25	0.169(2)	0.561(1)	0.0	9(1)
C(11)	0.5	0.1600(8)	0.4256(7)	0.5	6.8(6)
C(12)*	0.5	0.261(1)	0.4293(7)	0.574(2)	5.3(6)
C(13)*	0.5	0.316(1)	0.4882(6)	0.582(2)	5.2(6)
C(14)	0.5	0.271(1)	0.5446(6)	0.5	7.1(6)
C(15)*	0.5	0.170(1)	0.5380(8)	0.0418(2)	7.6(8)
C(16)*	0.5	0.114(1)	0.4783(9)	0.404(2)	7.6(9)
C(17)*	0.5	0.097(1)	0.3619(7)	0.5	9.5(9)
C(18)*	0.5	0.408(1)	0.4953(6)	0.687(2)	6.6(8)

[a] Atom in disorder has been asterisked. C(17) and C(18) have a 0.5 probability of being either a methyl carbon or an amino nitrogen.
[b] Multiplicity.
[c] $B_{eq} = 4[\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j]/3$.

non-hydrogen atoms were refined anisotropically; hydrogen atoms of the daptn and the guest, fixed at calculated positions with the isotropic thermal parameter of 5.0 Å^2 each, were included in the final structure factor calculation. The largest Δ/σ value of 1.38 was observed for one of the phenyl carbons C(15); except for this and another phenyl carbon C(14), shifts of less than 1 were obtained.

The structure of **5-m** is substantially analogous to those of other members of the Hofman-diam-type series: the daptn spans adjacent layers of the cyanometal network bending considerably at the nitrogen atoms connecting the octahedral Cd and the square-planar $[Ni(CN)_4]^{2-}$. However ambiguities have remained in the structure with regard to the L1-L2 disorder in the daptn bridge, and to the orientation of the guest molecule.

L1 takes a *cis-(trans)*₃*-cis-trans* conformation but the conformation of L2 cannot be determined due to the absence of a methylene carbon from the skeleton. Assuming that all the daptn bridges take one of the two orientations, L1 or L2, in an interlayer space along the *a*-axis, it requires too short a contact between adjacent bridges: 2.73(3) Å between C(8) and C(10*⁷) for L2 and 3.34(3) Å between C(6) and C(7*⁸) for L1 (symmetry operation for *7: $-x, 1-y, z$; for *8:
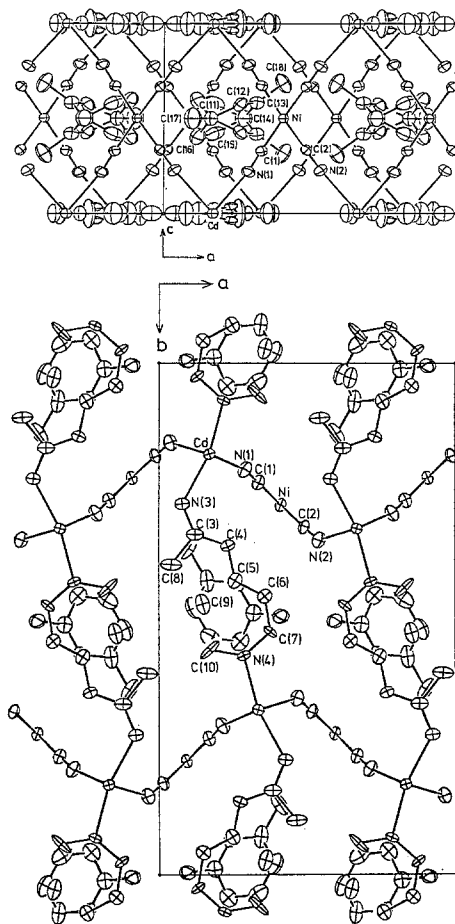
Fig. 3. Structure of **5-m**. *Top*: projection along the *b*-axis; *bottom*: projection along the *c*-axis. 1,5-Diaminopentane bridging the cyanometal networks is disordered.

$1 - x$, $1 - y$, z). When L1 and L2 are arranged alternatively along the *a*-axis, no contacts shorter than 4 Å between L1 and L2 occur for any methylene carbons.

Similar problems have also been observed for the contact between the daptn bridge and the guest molecule distributed statistically about the mirror plane at $c = 1/2$, and between the neighboring guest molecules along the *a*-axis. The guest is clipped by a pair of daptn bridges on the mirror planes at $c = 0$ and 1, respectively; a substituent group of the guest, C(18), is only 2.55(2) Å apart from C(7) of L1 at $c = 1$. Hence the orientation of the daptn bridges should be L2 at $c = 1$ and L1 at $c = 0$, respectively, for the guest molecule taking the orientation to hold the position of C(18). As for the interguest distance, C(18*[8]) of the neighboring guest along the *a*-axis has too short a contact of 2.26(2) Å with C(18): the neighboring guest should take the orientation related with the symmetry operation $1 - x$, $1 - y$, $1 - z$, which makes the distance 3.69(2) Å acceptable for the van der Waals contact. At least these conditions should be satisfied in every interlayer space, which should lead to an ordered structure. However, the steric conditions in

one interlayer space are independent of those in other spaces: the observed disorder in the crystal structure should be due to random distribution of the ordered interlayer structures.

3.2.4. *catena-[catena-μ-(1,8-Diaminooctane)cadmium(II) tetra-μ-cyano-nickelate(II)]-o-toluidine(1/1)*, **8-o**

All the host atoms were found on the Fourier map reasonably by applying the space group $P2/m$. The guest atoms were vaguely distributed in the cavity centered at 1/2, 1/2, 0. After a rigid model of the guest skeleton was translated and rotated on the mirror plane at $b = 1/2$ to find the minimum R, the rigid conditions were relaxed in the final refinement; the hydrogen atoms of 1,8-diaminooctane (daotn) fixed at calculated positions, with Biso fixed at 6.0 Å^2, were included in the structure factor calculation; the maximum Δ/σ was 0.32.

The structure in Figure 4 is similar to that of **6-o** [2]: the even-numbered, α, ω-daiminoalkane skeleton takes the all-*trans* conformation, and the cavity for the guest is surrounded by the four all-*trans* bridges. The increment of two methylene units in the skeleton of daotn from that in 1,6-diaminohexane (dahxn) causes the ca. 2 Å elongation in the *a*-dimension and the ca. 9° enlargement in the β-angle of **8-o** from **6-o**. The guest *o*-toluidine molecule distributes statistically as a pair of the images related to the inversion center which is required from the centrosymmetric space group $P2/m$. Although a similar distribution has been observed for **6-o**, the degree of overlap, i.e. the separation of the coupled images, is clearer in **8-o** than **6-o** owing to the greater volume of the cavity in **8-o**.

Table V. Atomic parameters for **8-o**.

atom[a]	G[b]	x	y	z	$B_{eq}/Å^{2}$ [c]
Cd	0.25	1.0	0.0	0.0	2.32(2)
Ni	0.25	1.0	0.5	0.5	2.77(4)
N(1)	1.0	1.0573(5)	0.2230(6)	0.2455(6)	4.3(2)
N(2)	0.5	0.8051(6)	0.0	0.0172(9)	4.6(3)
N(3)*	0.25	0.254(4)	0.5	0.035(6)	16(2)
C(1)	1.0	1.0380(5)	0.3287(6)	0.3449(6)	3.1(2)
C(2)	0.5	0.7879(7)	0.0	0.212(1)	4.4(3)
C(3)	0.5	0.6548(7)	0.0	0.202(1)	4.3(3)
C(4)	0.5	0.6424(7)	0.0	0.409(1)	4.9(4)
C(5)	0.5	0.5065(8)	0.0	0.396(1)	5.1(4)
C(6)*	0.25	0.368(3)	0.5	0.064(5)	10(2)
C(7)*	0.25	0.426(3)	0.5	−0.0113(5)	10(2)
C(8)*	0.25	0.526(2)	0.5	−0.097(4)	8(1)
C(9)*	0.25	0.650(4)	0.5	0.105(6)	12(1)
C(10)*	0.25	0.581(4)	0.5	0.270(6)	12(2)
C(11)*	0.25	0.467(4)	0.5	0.255(6)	13(2)
C(12)*	0.25	0.321(3)	0.5	−0.292(6)	12(2)

[a]Atom in disorder has been asterisked.
[b]Multiplicity.
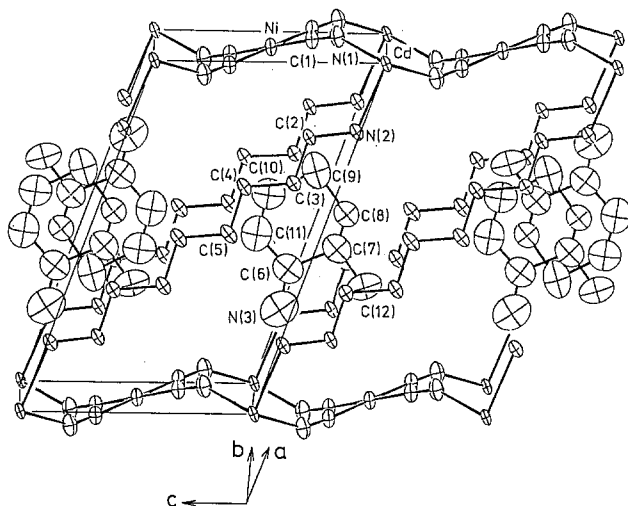[c]$B_{eq} = 4[\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j]/3$.

Fig. 4. Structure of **8-o** as a perspective view along the *a*-axis. The guest *o*-toluidine molecule is distributed about the center of inversion at 1/2, 1/2, 0.

3.2.5. catena-[catena-μ-(1,8-Diaminooctane)cadmium(II) tetra-μ-cyano-nickelate(II)]-p-toluidine(1/1), **8-p**

The structure was refined through the processes similar to **8-o**. The amino and the methyl groups of the guest could not be discriminated from each other: both were seen as a methyl group. At the final cycle of the refinement the largest Δ/σ was 0.36.

Table VI. Atomic parameters for **8-p**.

atom[a]	G[b]	x	y	z	$B_{eq}/Å^2$ [c]
Cd	0.5	1.0	0.0	0.0	2.12(1)
Ni	0.5	1.0	0.5	0.5	2.33(3)
N(1)	1.0	1.0466(4)	0.2174(5)	0.2357(6)	3.7(2)
N(2)	1.0	0.9277(5)	0.2327(5)	0.7415(6)	4.0(2)
N(3)	1.0	0.8040(4)	0.0144(6)	0.0151(6)	3.9(2)
C(1)	1.0	1.0309(4)	0.3234(5)	0.3379(6)	2.8(1)
C(2)	1.0	0.9514(4)	0.3358(5)	0.6458(6)	2.9(2)
C(3)	1.0	0.7869(4)	0.0250(8)	0.2138(7)	3.9(2)
C(4)	1.0	0.6546(4)	0.0185(8)	0.2011(8)	3.9(2)
C(5)	1.0	0.6420(4)	0.0171(9)	0.4119(8)	4.4(2)
C(6)	1.0	0.5984(4)	0.0029(8)	0.3974(7)	3.9(2)
C(7)	1.0	0.617(1)	0.522(1)	−0.015(2)	11.7(7)
C(8)	1.0	0.600(2)	0.523(1)	0.171(2)	12.3(7)
C(9)	1.0	0.482(2)	0.502(1)	0.179(2)	11.2(7)
C(10)*	1.0	0.739(1)	0.552(2)	−0.044(2)	12.4(9)

[a]Atom in disorder has been asterisked; C(10) has a 0.5 probability of being either a methyl carbon or an amino nitrogen.
[b]Multiplicity.
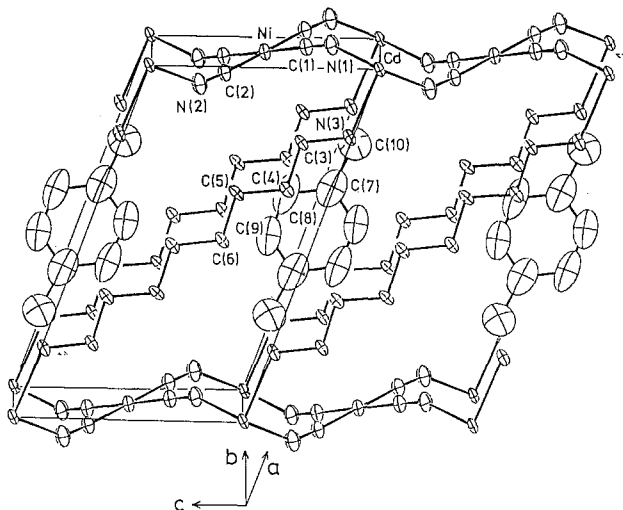[c]$B_{eq} = 4[\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j]/3$.

Fig. 5. Structure of **8-p** as a perspective view along the a-axis. The amino and the methyl groups of the guest p-toluidine molecule have not been distinguished from one another.

The structure in Figure 5 is essentially similar to that of **8-o** except for the distortion of the unit cell from the monoclinic $P2/m$ for **8-o** to the triclinic $P\bar{1}$. The a and b dimensions, and the α and β angles are similar to each other, but the c dimension and the γ angle contract by ca. 0.6 Å and 7.2° in **8-p** from **8-o**. The ca. 10 Å^3 decrease in the unit cell volume is due to the decrease in the effective volume occupied by the guest molecule: the statistical distribution of the orientations makes the effective volume larger for the o-toluidine than for the p-toluidine molecule.

4. Comparison of the Structures

4.1. GENERAL FEATURES

A rectangular box can be imagined for the cavity in the Hofmann-, Hofmann-en-, and Hofmann-pn-type clathrates whose tetragonal hosts are built of layers of the $catena$-[metal(II) tetra-μ-cyanonickelate(II)] network [3]. The box has the top and bottom framed with the mesh of the network; the side edges are alternatively supported by a pair of the ammine ligands in the Hofmann-type or by the bridge of en or pn in the other two. The box can be defined as the cavity unit.

The shape of the unit is distorted obliquely when the carbon number of the diam skeleton is greater than 3 except for **5-o**. The distortion is accompanied by the bending of the two-dimensional cyanometal network to give a monoclinic or triclinic unit cell structure; in the orthorhombic structure of **5-m**, the cavity itself is distorted to a monoclinic box. Some of the units are occupied by the diam moieties in place of guests: the rate of the occupation determines the h/g ratio in the composition formula. The ambidentate diam ligand appears to be a column supporting the ceiling on the floor, both being comprised of the cyanometal

network. So far, among the observed structures [1–4, 13] including the present ones, the columns are arrayed on the planes which are parallel to one another for some structures or approximately parallel for the others. In general, the guests are accommodated between the column planes.

The features to be compared for the toluidine clathrates are the conformation of the diam skeletons with different carbon numbers, the bending in the metal complex network, and the arrangement of the guest molecule, although they are correlated with one another.

4.2. CONFORMATION OF THE DIAM SKELETON

When the carbon number of diam is greater than 5, the conformation is always all-*trans* so far in the known structures of **6-o** [2] and the Hofmann-dahxn-type *m*-toluidine, *p*-toluidine, and 2,4-xylidine clathrates [4], and **8-o, 8-p** and the Hofmann-daotn-type 1-hexanol [13] clathrates, the last being an exceptional case of an aliphatic guest in the Hofmann-diam-type series. In these structures little space is left between the diam columns on the column plane. Hence, a channel-like cavity structure can be seen: the channel is walled by the diam columns with the cyanometal networks forming the ceiling and floor. However, the channel is compartmentalized for every guest by the electron clouds of the diam ligands and the cyanide groups in the bending network. The cavity is surrounded by four diam columns and capped by the crosses of the tetracyanonickelate(II) moieties; the aromatic plane of the guest is parallel to the column planes.

The all-*trans* conformation of dabtn in 4-pyr [3] is favorable for making the interlayer distance short enough to accommodate the pyrrole molecule, which is the smallest guest in the Hofmann-diam-type series. However, the dabtn in **4-o** and the daptn in **5-m** take the *cis-trans* mixed conformation. Hence the step from 4 to 6 appears to be critical for the carbon number of diam to take the all-*trans* conformation of the skeleton whether for the smallest guest or for the substituted benzene guests: it is difficult for the odd-numbered skeleton to take an all-*trans* conformation in the bridge between almost parallel cyanometal networks.

A considerably wide gap is formed between adjacent columns on the column plane in the host of the diam with the *cis-trans* mixed conformation. The guest is clipped between a couple of diam columns on adjacent column planes, as exemplified by **4-o, 4-a, 5-m**, and the Hofmann-dabtn-type, 2,5-xylidine [1] and *N,N*-dimethylaniline clathrates [3]. In these cases, the aromatic plane of the guest is not parallel to the column plane but arranged slantwise so as to fill the gap with its substituent groups. In **4-o** and **4-a**, the gap is great enough to provide another cavity, centered at 1/2, 0, 1/2, for the guest molecule.

4.3. BENDING IN THE CYANOMETAL NETWORK

The tetracyanonickelate(II) moiety in each structure holds almost the square-planar configuration within a maximum 2° deviation from the rectangle in the bonding angles and a 0.07 Å deviation from the best-fit plane. The coordination geometry about the cadmium is distorted from a regular octahedron to a certain extent. The Cd—N(CN) distance, ranging from 2.337(5) to 2.426(5) Å, is always longer by ca.

Table VII. Dihedral angle δ between [CdN$_4$] and [NiC$_4$] planes.

[CdN$_4$] plane	[NiC$_4$] plane	$\delta/°$
	4-o	
Cd,N(1),N(2),N(3),N(4)	Ni(1),C(1),C(1)*^{5},C(4)*^{2},C(4)*^{7}	6.4
Cd,N(1),N(2),N(3),N(4)	Ni(2),C(2),C(2)*^{8},C(3)*^{3},C(3)*^{5}	40.9
	5-m	
Cd,N(1),N(1)*^{3},N(2)*^{2},N(2)*^{4}	Ni,C(1),C(1)*^{5},C(2),C(2)*^{5}	24.2
Cd*^{9},N(2),N(2)*^{3},N(1)*^{9},N(1)*^{10}	Ni,C(1),C(1)*^{5},C(2),C(2)*^{5}	63.1
	8-o	
Cd,N(1),N(1)*^{2},N(1)*^{3},N(1)*^{6}	Ni,C(1),C(1)*^{4},C(1)*^{5},C(1)*^{7}	40.5
	8-p	
Cd,N(1)*^{1},N(2),N(1)*^{4},N(2)*^{5}	Ni,C(1),C(2),C(1)*^{6},C(2)*^{6}	42.9

Symmetry operations. For **4-o** *2: $-x, -y, 1-z$; *3: $-x, -1-y, 1-z$; *5: $x,y, z-1$, *7: $-x, -y, -z$; *8: $x, -y, -z$. For **5-m** *2: $x-1/2, 1/2-y,z$; *3: $x, y, -z$; *4: $x-1/2, 1/2-y, -z$; *5: $x, y, 1-z$; *9: $1/2+x, 1/2-y,z$; *10: $1/2+x, 1/2-y, -z$. For **8-o** *2: $x, -y, z$; *3: $2-x, y, -z$; *4: $2-x, y, 1-z$; *5: $x, 1-y, z$; *6: $2-x, -y, -z$; *7: $2-x, 1-y, 1-z$. For **8-p** *1: $x, y, z-1$; *4: $2-x, -y, -z$; *5: $2-x, -y, 1-z$; *6: $2-x, 1-y, 1-z$. These notations coincide with those used in the tables of selected bond distances and angles and of least-squares planes deposited.

0.07-0.1 Å than the Cd—N(amine) distance, from 2.242(6) to 2.294(8) Å; the maximum deviation from the rectangle, 5.4°, has been observed for **5-m**.

The two-dimensional cyanometal network is comprised of the square planes of [Ni(CN)$_4$]$^{2-}$ and the equatorial planes of the CdN$_6$ octahedra; a square plane shares the nitrogen corners with four octahedra; the Ni—C—N—Cd linkage bends mostly at the nitrogen atom. The degree of bending can be compared by considering the dihedral angle between the square plane of the tetracyanonickelate(II) and the equatorial plane of the octahedron, since the two triclinic unit cells of **4-o** and **8-p** are not greatly distorted from a monoclinic system. Table VII lists the dihedral angles.

The dihedral angles in **8-o** and **8-p** are 40.5° and 42.9° respectively; values about 40° appear to be typical in the hosts of the all-*trans* diam skeletons. This angle is convenient to arrange the all-*trans* diams on the column plane with little gap and to provide the cavity unit surrounded by four diam columns with the tetracyanonickelate(II) crosses forming the ceiling and floor.

In the hosts of the *trans-cis* mixed skeletons, two angles have been observed: 6.4° and 40.9° for **4-o**, and 24.2° and 63.1° for **5-m**. When the skeletal carbon number is even, as is the case of **4-o**, the smaller angle of 6.4° makes a cavity able to accommodate a guest molecule with a shape analogous to those in the Hofmann-type and Hofmann-en-type. The greater angle of 40.9°, comparable with those in **8-o** and **8-p**, makes the *cis-trans* mixed dabtn columns array with little gap on the column plane. The odd-numbered skeleton of dabtn in **5-m** gives a more distorted structure: even the smaller angle of 24.2° is great enough to array the dabtn columns with little gap. The greater angle of 63.1° may be the limit of the

two-dimensional cyanometal network comprised of the square-planar moieties like $[Ni(CN)_4]^{2-}$, $[Pd(CN)_4]^{2-}$, and $[Pt(CN)_4]^{2-}$ and of the equatorial planes of octahedral moieties. The distortion in **5-m** has, of course, been deduced from the bridging of odd-numbered skeletons between two-dimensional networks substantially arranged in parallel.

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6a. The host/guest ratio of 1/2.5 was assumed for **8-o** in Ref. 6, but for the present **8-o** the crystal structure is consistent with the 1/1 ratio. The previous compound might have a different structure from the present one. We have recently obtained a number of $Cd(diam)_2Ni(CN)_4 \cdot 2G$ inclusion compounds for 1,9-diaminonane or 1,10-diaminodecane as diam, which are doubled in the composition. The analytical data for the 1/2.5 ratio suggest the formation of $Cd(daotn)_2Ni(CN)_4 \cdot 2(o\text{-toluidine})$, although no single crystals of the assumed composition have yet been obtained.
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