

The Crystal Structures of α, ω -Diaminoalkane-cadmium(II) Tetracyanonickelate(II) – Aromatic Molecule Inclusion Compounds. VII: Three-Dimensional Host Structures Built of *catena*-[Cadmium(II) Tetra- μ -cyanonickelate(II)] Layers and 1,3-Diaminopropane, 1,5-Diaminopentane or 1,7-Diaminoheptane Pillar

HIDETAKA YUGE, MIKI ASAI, ATSUSHI MAMADA,
SHIN-ICHI NISHIKIORI and TOSCHITAKE IWAMOTO*

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

(Received in final form: 4 May 1995)

Abstract. The crystal structures of four novel Hofmann-diam-type clathrates $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 1.72(o\text{-MeC}_6\text{H}_4\text{NH}_2)$, **3-o**, $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 0.5(m\text{-ClC}_6\text{H}_4\text{NH}_2)$, **3-m**, $[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot 1.5(p\text{-MeC}_6\text{H}_4\text{NH}_2)$, **5-p** and $[\text{Cd}(\text{dahpn})\text{Ni}(\text{CN})_4] \cdot 1.5(2\text{-MeC}_9\text{H}_6\text{N})$, **7-q** have been determined by single crystal X-ray diffraction method [tn: $n = 3$, daptn: $n = 5$, dahpn: $n = 7$ for $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$]. **3-o** crystallizes in the monoclinic space group $P2_1/m$, $a = 7.538(2)$, $b = 9.314(5)$, $c = 7.670(2)$ Å, $\beta = 91.03(2)^\circ$, $Z = 1$, $R = 0.047$ for 1252 reflections; **3-m**: orthorhombic $Pbam$, $a = 12.1714(7)$, $b = 15.798(1)$, $c = 7.737(1)$ Å, $Z = 4$, $R = 0.044$ for 1871; **5-p**: monoclinic $P2_1/a$, $a = 13.736(3)$, $b = 22.014(4)$, $c = 7.762(3)$ Å, $\beta = 91.04(3)^\circ$, $Z = 4$, $R = 0.047$ for 5281; and **7-q**: orthorhombic $Pbam$, $a = 13.599(2)$, $b = 27.938(4)$, $c = 7.619(2)$ Å, $Z = 4$, $R = 0.054$ for 3098. Their host structures are topologically the same to those of the previously reported Hofmann-diam-type clathrates: the two-dimensional $[\text{CdNi}(\text{CN})_4]_\infty$ networks are spanned by $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ at every Cd atom to build up the three-dimensional hosts. The number of cavities available for the guest is regulated by the deformation of the 2D networks and the diamine ligand in the host structure.

Key words: Crystal structure, Hofmann-diam-type, cadmium, tetracyanonickelate, 1,3-diaminopropane, 1,5-diaminopentane, 1,7-diaminoheptane, toluidine, chloroaniline, methylquinoline.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82192 (37 pages).

* Author for correspondence.

1. Introduction

In our previous works [1–3] we reported the series of the Hofmann-diam-type clathrates $[\text{Cd}\{\text{NH}_2(\text{CH}_2)_n\text{NH}_2\}\text{Ni}(\text{CN})_4] \cdot x\text{G}$ ($n = 2, 4, 5, 6, 8, \text{ or } 9$; $x = 0.5\text{--}2$) having as a common structural feature the ambidentate α,ω -diamino-alkane (diam) ligand spanning adjacent layers of the two-dimensional (2D) $[\text{Ni}(\text{CN}\text{---}\text{Cd}_{1/4}\text{---})_4]_\infty$ network at every Cd atom to provide the interlayer cavity for the aromatic guest such as $\text{C}_4\text{H}_5\text{N}$, C_6H_6 , PhNH_2 , *o*-, *m*-, or *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$, 2,4- or 2,5- $\text{Me}_2\text{C}_6\text{H}_3\text{NH}_2$, PhNMe_2 , *o*- $\text{Me}_2\text{C}_6\text{H}_4$, the aliphatic $\text{C}_6\text{H}_{13}\text{OH}$, etc. The three-dimensional (3D) Hofmann-diam-type structure is derived from the Hofmann-type $[\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4] \cdot 2\text{G}$ clathrate [1a] by an apparent replacement of a couple of the NH_3 ligands confronting each other in the interlayer space between the 2D networks by a diam ligand bridging between the networks.

Among the Hofmann-diam-type series, it appears to be rather more difficult to obtain single crystals suitable for X-ray structure determination for the host with odd-*n* diamine than even-*n* ones, although the three examples are known for $[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot o\text{-MeC}_6\text{H}_4\text{NH}_2$, **5-o** [3g], $[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot m\text{-MeC}_6\text{H}_4\text{NH}_2$, **5-m** [3g], and $[\text{Cd}(\text{danon})\text{Ni}(\text{CN})_4] \cdot 0.5(o\text{-Me}_2\text{C}_6\text{H}_4)$, **9-o** [3h] (daptn: $n = 5$; danon: $n = 9$). The host structure of **9-o**, the Hofmann-danon-type *o*- $\text{Me}_2\text{C}_6\text{H}_4$ clathrate, is a rather rare case for the danon; generally the other series of the clathrates $[\text{Cd}(\text{danon})_2\text{Ni}(\text{CN})_4] \cdot 2\text{G}$ are obtained with the composition and structures different from the present Hofmann-diam-type series under similar preparation conditions [4].

This paper reports the four newly prepared Hofmann-diam-type clathrates of the odd-*n* hosts, Hofmann-tn-type ($n = 3$), Hofmann-daptn-type ($n = 5$) and Hofmann-dahpn-type ($n = 7$): $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 1.72(o\text{-MeC}_6\text{H}_4\text{NH}_2)$, **3-o**, $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 0.5(m\text{-ClC}_6\text{H}_4\text{NH}_2)$, **3-m**, $[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot 1.5(p\text{-MeC}_6\text{H}_4\text{NH}_2)$, **5-p** and $[\text{Cd}(\text{dahpn})\text{Ni}(\text{CN})_4] \cdot 1.5(2\text{-MeC}_9\text{H}_6\text{N})$, **7-q**. The structural features of **3-m**, **5-p** and **7-q** are similar to that of **5-m** already reported [3g]; that of **3-o** is rather similar to that of $[\text{Cd}(\text{en})\text{Ni}(\text{CN})_4] \cdot 2\text{C}_6\text{H}_6$, **2** [2]. The number of methylene carbons has been given to each of the numberings for the respective compounds. Their structural details are described on the basis of the concept that the number of the cavities available for the guest depends on the deformation of the host lattice with respect to the 2D network and the diam skeleton.

2. Experimental

2.1. PREPARATION

2.1.1. $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 1.72(o\text{-MeC}_6\text{H}_4\text{NH}_2)$, **3-o** and $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 0.5(m\text{-ClC}_6\text{H}_4\text{NH}_2)$, **3-m**

Single crystals were prepared by a procedure similar to those already reported [3], but with a 10 times molar amount of tn to $\text{CdNi}(\text{CN})_4$ dissolved in their mother

aqueous solutions. At room temperature **3-o** crystallizes as yellow flakes and **3-m** as yellow plates. *Anal. Found* for **3-o**: C, 40.3; H, 4.64; N, 20.3; Cd, 22.8; Ni, 12.1%. *Calcd.* for $C_{19.04}H_{25.48}CdN_{7.72}Ni$ ($x = 1.72$: crystallographically refined occupancy): C, 42.9; H, 4.81; N, 20.3; Cd, 21.1; Ni, 11.0%, and for $C_{17.5}H_{23.5}CdN_{7.5}Ni$ ($x = 1.5$): C, 41.2; H, 4.64; N, 20.6; Cd, 22.0; Ni, 11.5%. *Found* for **3-m**: C, 28.8; H, 3.21; N, 21.8; Cl, 4.28; Cd, 27.0; Ni, 14.0%. *Calcd.* for $C_{10}H_{13}CdCl_{0.5}N_{6.5}Ni$: C, 29.1; H, 3.17; N, 22.0; Cl, 4.29; Cd, 27.2; Ni, 14.2%.

$PhNH_2$, *o*- $ClC_6H_4NH_2$, and 2,6- $Me_2C_6H_3NH_2$ also gave crystalline products, but these were too poor in quality for a single-crystal X-ray experiment.

2.1.2. $[Cd(daptn)Ni(CN)_4] \cdot 1.5(p-MeC_6H_4NH_2)$, **5-p** and $[Cd(dahpn)Ni(CN)_4] \cdot 1.5(2-MeC_9H_6N)$, **7-q**

Single crystals were prepared by procedures similar to those already reported [3]. Both **5-p** and **7-q** crystallize as yellow plates in a refrigerator at *ca* 5 °C. *Anal. Found* for **5-p**: C, 42.6; H, 5.14; N, 19.5; Cd, 20.8; Ni, 11.0%. *Calcd.* for $C_{19.5}H_{27.5}CdN_{7.5}Ni$: C, 43.5; H, 5.15; N, 19.5; Cd, 20.9; Ni, 10.9%. *Found* for **7-q**: C, 50.8; H, 5.12; N, 16.5; Cd, 17.8; Ni, 9.18%. *Calcd.* for $C_{26}H_{31.5}CdN_{7.5}Ni$: C, 50.4; H, 5.12; N, 16.9; Cd, 18.1; Ni, 9.46%.

2.2. CRYSTALLOGRAPHY

The crystallographic and experimental data are summarized in Table I. Each crystal was coated with epoxy resin to prevent spontaneous liberation of the guest molecules from the specimen during data collection. The cell dimensions were refined, each using 25 reflections ($30 < 2\theta < 40^\circ$). Three standard reflections were monitored after every 150: no significant decay was observed. Corrections were made for L_p and empirical absorption [5], but not for extinction. Positions of Cd and Ni were located from Patterson syntheses. All non-H atoms found in the subsequent Fourier and Fourier-difference syntheses were refined anisotropically through the block-diagonal least-squares procedures. Hydrogen atoms in the host moieties located at calculated positions were included in the final structure factor calculations. All calculations were performed using the programs in UNICSIII [6] on a HITAC M-680H computer in the Computer Center of the Institute for Molecular Science, Okazaki. Atomic scattering factors were taken from Ref. [7]. Tables of the structure factors, anisotropic thermal parameters, calculated positions of H atoms, and interatomic distances and angles have been deposited with the British Library (37 pages).

The atomic coordinates with the equivalent isotropic thermal parameters, B_{eq} , are listed in Tables II to V for **3-o**, **3-m**, **5-p** and **7-q**, respectively; the ORTEP [8] views of the structures are illustrated in Figures 1–4, respectively.

TABLE I. Crystallographic and experimental data^a.

Compound	3-o	3-m	5-p	7-q
<i>n</i>	3	3	5	7
<i>x</i>	1.72 [1.5] ^b	1/2	3/2	3/2
Guest	<i>o</i> -MeC ₆ H ₄ NH ₂	<i>m</i> -ClC ₆ H ₄ NH ₂	<i>p</i> -MeC ₆ H ₄ NH ₂	2-MeC ₉ H ₆ N
Formula mass	533.61 [510.03]	413.09	538.09	620.19
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	<i>P</i> 2/ <i>m</i>	<i>Pbam</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>Pbam</i>
<i>a</i> /Å	7.538(2)	12.1714(7)	13.736(3)	13.599(2)
<i>b</i> /Å	9.314(5)	15.798(1)	22.014(4)	27.938(4)
<i>c</i> /Å	7.670(2)	7.737(1)	7.762(3)	7.610(2)
β /°	91.03(2)	90	91.04(3)	90
<i>V</i> /Å ³	538.4(3)	1487.7(2)	2346.7(10)	2894.4(10)
<i>Z</i>	1	4	4	4
<i>D_m</i> ^c /g cm ⁻³	1.57(2)	1.86(1)	1.54(1)	1.44(1)
<i>D_x</i> /g cm ⁻³	1.65 [1.57]	1.84	1.52	1.42
<i>F</i> (000)	269.76 [257]	812	1092	1264
Crystal size/mm	0.25 × 0.22 × 0.10	0.50 × 0.25 × 0.25	0.35 × 0.27 × 0.25	0.30 × 0.25 × 0.10
μ (MoK α)/cm ⁻¹	18.83 [18.79]	27.84	17.29	14.12
Scan mode	2 θ - ω	2 θ - ω	2 θ - ω	ω
<i>hkl</i> ranges	0-10, 0-13	0-17, 0-22,	-19 to 19, 0-30,	0-19, 0-39,
(4 < 2 θ < 60°)	-10 to 10	0-10	-10 to 0	0-10
Scan width/°	1.418 + 0.3 tan θ	1.155 + 0.3 tan θ	0.945 + 0.3 tan θ	1.008 + 0.3 tan θ
Transmission factors	0.90-0.99	0.89-0.99	0.90-1.00	0.80-1.00
Reflections measured	1814	2541	7616	4873
used (> 3 σ (<i>F</i> ₀)), <i>N_r</i>	1252	1871	5281	3098
No. of parameters, <i>N_p</i>	173	155	263	272
<i>R</i> , <i>R_w</i>	0.0468, 0.0578	0.0444, 0.0532	0.0472, 0.0631	0.0535, 0.0574
GOF	0.729	0.962	1.178	1.578
<i>F</i> _{max}	24	40	40	70
<i>F</i> _{min}	12	20	20	35
(Δ / σ) _{max} : host	0.01	0.01	0.12	0.11
: guest	0.03	0.04	0.24	0.52
$\Delta\rho$ _{max} /e Å ⁻³	0.90	0.65	0.79	0.80

^aGeneral formula: [Cd{NH₂(CH₂)_{*n*}NH₂}Ni(CN)₄] \cdot *x*Guest; diffractometer: Rigaku AFC-5S; radiation: MoK α (λ = 0.71069 Å); monochromator: graphite; temperature: ambient; correction: Lp and absorption.

^bThe relevant values for *x* = 1.5 are shown in brackets.

^cThe densities were measured by the flotation method in a bromoform-mesitylene mixture.

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

TABLE II. Atomic parameters for [Cd(tn)Ni(CN)₄] \cdot 1.72(*o*-MeC₆H₄NH₂), **3-o**.

Atom ^a	G ^b	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} /Å ^{2c}
Cd	0.25	0	0	0	1.836(8)
Ni	0.25	1/2	0	1/2	2.53(2)
N(1)	0.50	0.2164(13)	0	0.2209(12)	10.7(6)
N(2)	0.50	0.2194(12)	0	0.7811(11)	5.2(2)
N(3)	0.50	0.0707(18)	0.2339 (10)	0.0575(15)	5.5(3)
C(1)	0.50	0.3262(10)	0	0.3286(10)	5.1(2)
C(2)	0.50	0.3281(10)	0	0.6727(10)	3.5(2)
C(3)	0.50	0	0.3629(9)	0	5.0(2)
C(4)	0.25	0.077(3)	1/2	0.039(4)	6.8(6)
C(11)	0.50	0	0.2788(18)	1/2	11.1(6)
C(12)*	0.50	0.162(5)	0.369(3)	0.561(4)	12.9(8)
C(13)	0.50	0.127(3)	1/2	0.545(3)	13.3(7)
C(14)*	0.25	0	0.597(3)	1/2	13.4(13)
C(15)*	0.25	0.343(5)	0.621(5)	0.636(5)	8.2(9)
C(21)	0.36	1/2	0.267(3)	0	10.2(7)
C(22)*	0.36	0.476(5)	0.357(4)	0.175(6)	10.3(9)
C(23)	0.36	0.477(4)	1/2	0.146(4)	13.0(9)
C(24)*	0.18	1/2	0.594(5)	0	9.0(11)
C(25)*	0.18	0.544(11)	0.576(19)	0.297(5)	23(9)

^a Atom in disorder has been asterisked.

^b Multiplicity.

^c $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$.

3. Results and Discussion

3.1. STRUCTURE DESCRIPTION

3.1.1. [Cd(tn)Ni(CN)₄] \cdot 1.72(*o*-MeC₆H₄NH₂), **3-o**

The centrosymmetric space group $P2/m$ was applied. As shown in Figure 1, the flat 2D network of [Ni(CN—Cd_{1/4}—)₄]_∞ on the mirror plane of the unit cell is similar to those observed for the Hofmann-type compounds [M(NH₃)₂Ni(CN)₄] \cdot 2C₆H₆ (M = Mn [9a], Ni [9b], Cu [9c] and Cd [3f, 9d]), **2** [2] and **5-o** [3g]. The tn bridge and the guest *o*-MeC₆H₄NH₂ are in disorder due to the symmetry requirements from the space group. The skeletal atoms of the tn are arrayed along the *b* axis with a slight inclination to the (10 $\bar{1}$) plane, on which the Cd—N(1)—C(1)—Ni linkage in the network is extended. There are two crystallographically independent cavities in the unit cell centered at 0, 1/2, 1/2 and 1/2, 1/2, 0, respectively. The respective guests, with considerably deformed molecular shapes, gave the refined occupancy factor of 1.00(2) in the former cavity and 0.72(2) in the latter. The latter guest is observed with the bent arrangement of the substituents from the aromatic plane,

TABLE III. Atomic parameters for $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 0.5(m\text{-ClC}_6\text{H}_4\text{NH}_2)$, **3-m**.

Atom ^a	G ^b	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^{2c}$
Cd	0.50	0.12877(3)	0.15417(2)	0	2.153(5)
Ni	0.50	0.36711(5)	0.29037(4)	1/2	2.368(10)
N(1)	1.00	0.2493(3)	0.1955(3)	0.2176(5)	3.88(7)
N(2)	1.00	0.4937(3)	0.3784(3)	0.2197(5)	3.98(7)
N(3)	0.50	0.0417(5)	0.2851(4)	0	9.4(3)
N(4)	0.50	0.3237(4)	0.5144(3)	0	3.41(9)
C(1)	1.00	0.2935(3)	0.2313(3)	0.3264(5)	2.85(6)
C(2)	1.00	0.4444(3)	0.3481(3)	0.3290(5)	2.87(6)
C(3)	0.50	0.0738(7)	0.3707(5)	0	7.2(3)
C(4)	0.50	0.1885(5)	0.3941(4)	0	3.9(1)
C(5)	0.50	0.2104(5)	0.4882(4)	0	5.1(2)
C(11)*	0.25	0.1716(11)	0.4952(10)	1/2	4.6(3)
C(12)	0.50	0.0701(8)	0.5543(6)	1/2	5.9(2)
C(13)*	0.25	-0.0253(10)	0.5276(10)	1/2	4.2(3)
C(15)*	0.25	0.0384(12)	0.3879(12)	1/2	7.2(5)
N(11)*	0.25	0.2752(15)	0.5210(9)	1/2	8.3(5)
CCl ^d	0.25	-0.1303(3)	0.6007(3)	1/2	7.9(10)

^a Atom in disorder has been asterisked.

^b Multiplicity.

^c $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

^d Refined with 50% probability each of C and Cl atmos.

which is inclined by 53.2° against the $(10\bar{1})$ plane greater than 25.5° for the former guest. As for the thermal amplitudes of the CN groups in the network, those of C(1) and N(1) on $(10\bar{1})$ are considerably greater than those of C(2) and N(2) on (101) , in particular along the b direction. The inclination of the tn skeletal plane against $(10\bar{1})$ makes the invasion of the tn skeleton more to the latter cavity than to the former. These observations support the idea that the latter cavity is less preferable for the guest to the former one.

3.1.2. $[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 0.5(m\text{-ClC}_6\text{H}_4\text{NH}_2)$, **3-m**

The centrosymmetric space group $Pbam$ was applied. As shown in Figure 2, the structure of **3-m** is obviously different from that of **3-o** but resembles **5-m** [3g]. The 2D network is puckered so much that the dihedral angle δ between the $[\text{CdN}_4]$ and $[\text{NiC}_4]$ planes is 65.5° for the larger bend and 24.5° for the smaller; the angle of 65.5° is the largest among the Hofmann-diam-type structures we have determined so far. Both the skeletal atoms of the tn taking a $cis\text{-}(trans)_3$ (ct_3) conformation and the guest $m\text{-ClC}_6\text{H}_4\text{NH}_2$ are arrayed on the mirror planes at $c = 0$ and $1/2$, respectively. The much puckered 2D network is stacked along the b axis with a

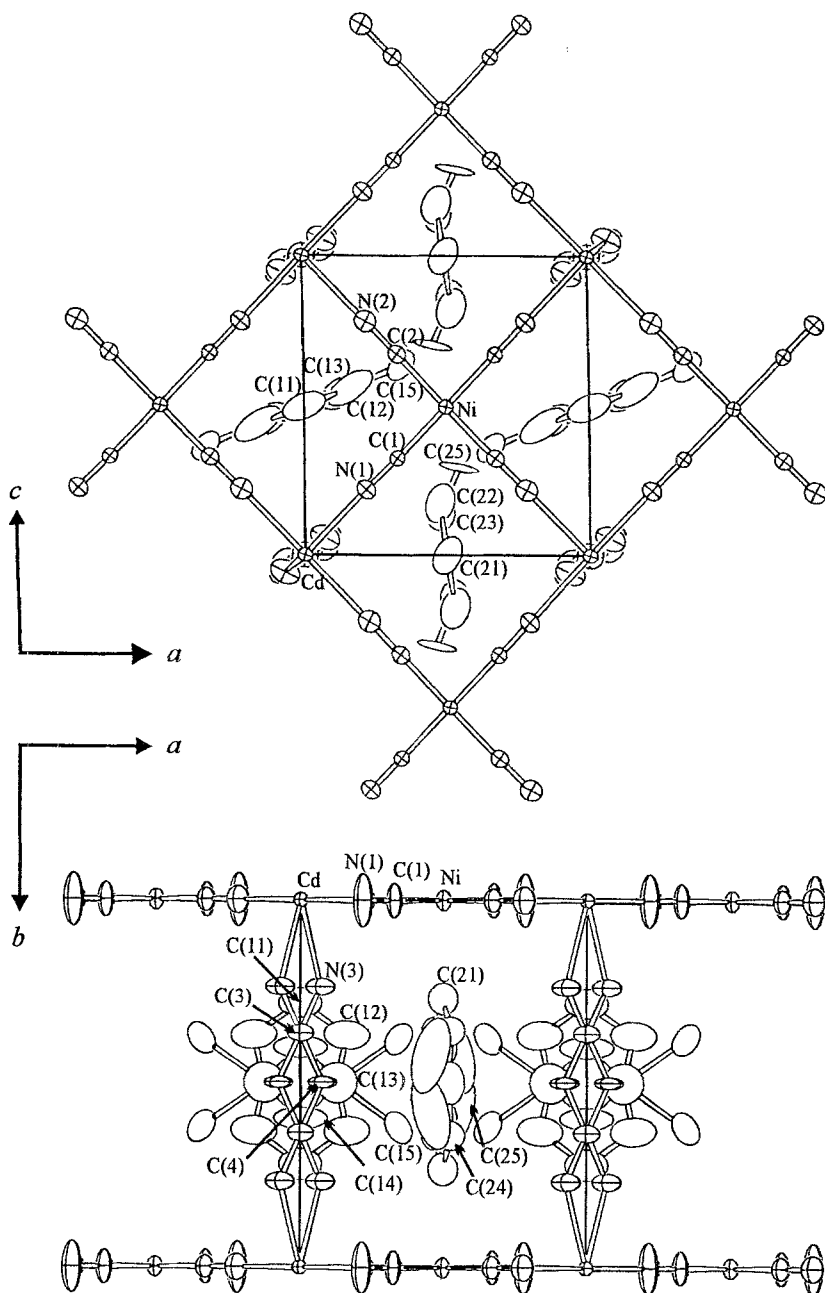


Fig. 1. Structure of **3-o** showing 30% probability thermal ellipsoids. Top: projection along the *b* axis; bottom: projection along the *c* axis. The tn ligand and the guest *o*-MeC₆H₄NH₂ molecules are in disorder.

TABLE IV. Atomic parameters for $[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot 1.5(p\text{-MeC}_6\text{H}_4\text{NH}_2)$, **5-p**.

Atom	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^2$ ^a
Cd	0.17144(2)	0.20196(1)	0.06316(3)	2.151(4)
Ni	0.42307(4)	0.223208(3)	0.56365(6)	2.346(8)
N(1)	0.2842(3)	0.1923(2)	0.2907(5)	4.07(8)
N(2)	0.5534(3)	0.2786(3)	0.2773(6)	4.22(8)
N(3)	0.5553(3)	0.2810(3)	0.8378(5)	4.04(8)
N(4)	0.2903(3)	0.1821(2)	0.8398(5)	3.72(7)
N(5)	0.2119(4)	0.3014(2)	0.0053(7)	4.11(8)
N(6)	0.3694(3)	0.6029(2)	-0.0921(7)	3.77(8)
C(1)	0.3377(3)	0.2067(2)	0.3952(5)	3.11(7)
C(2)	0.5045(3)	0.2623(2)	0.3894(5)	3.03(7)
C(3)	0.5068(3)	0.2612(2)	0.7328(5)	2.98(7)
C(4)	0.3406(3)	0.2008(2)	0.7345(5)	2.74(6)
C(5)	0.3055(4)	0.3217(3)	0.0723(9)	4.51(10)
C(6)	0.3462(5)	0.3783(2)	-0.0150(10)	4.82(12)
C(7)	0.2883(4)	0.4368(2)	0.0001(7)	3.81(9)
C(8)	0.3498(4)	0.4902(8)	-0.0628(8)	3.78(9)
C(9)	0.3021(3)	0.5533(2)	-0.0419(6)	3.23(7)
C(11)	0.3427(7)	0.5320(4)	0.4328(12)	7.3(2)
C(12)	0.3881(7)	0.4758(4)	0.4213(11)	7.0(2)
C(13)	0.3397(6)	0.4205(4)	0.4602(9)	6.6(2)
C(14)	0.2426(8)	0.4251(5)	0.5141(9)	7.5(2)
C(15)	0.1966(9)	0.4761(6)	0.5383(13)	9.1(3)
C(16)	0.2475(9)	0.5346(5)	0.4918(13)	9.5(3)
CN(17) ^b	0.3943(10)	0.5855(5)	0.3940(18)	12.6(4)
CN(18) ^b	0.1938(11)	0.3545(7)	0.5594(13)	12.6(4)
CN(20) ^b	-0.0013(9)	0.3682(7)	0.872(23)	13.0(4)
C(21)	-0.0019(7)	0.4385(7)	0.0464(13)	9.3(3)
C(22)	0.0260(9)	0.4779(7)	0.1581(13)	10.0(4)
C(23)	0.0369(7)	0.5442(7)	0.1073(14)	9.8(3)

^a $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$.

^b Refined with 50% probability each of C and N atoms.

shift of $a/4$ so as to give a nodal structure to the interlayer space. The guest is accommodated in the antinodal zone limiting the number of available cavities to 0.5 per formula unit of the host, similar to the case of **9-o** [3h].

The guest $m\text{-ClC}_6\text{H}_4\text{NH}_2$ disordered in the cavity centered at 0, 1/2, 1/2 (site symmetry: $2/m$) gives the overlapped image of two orientations inverted to each other about the cavity center. The tentative assignments were possible for the respective skeletal atoms based on the electron densities in the Fourier-difference synthesis; the Cl was averaged with a C on the aromatic ring. The refinement

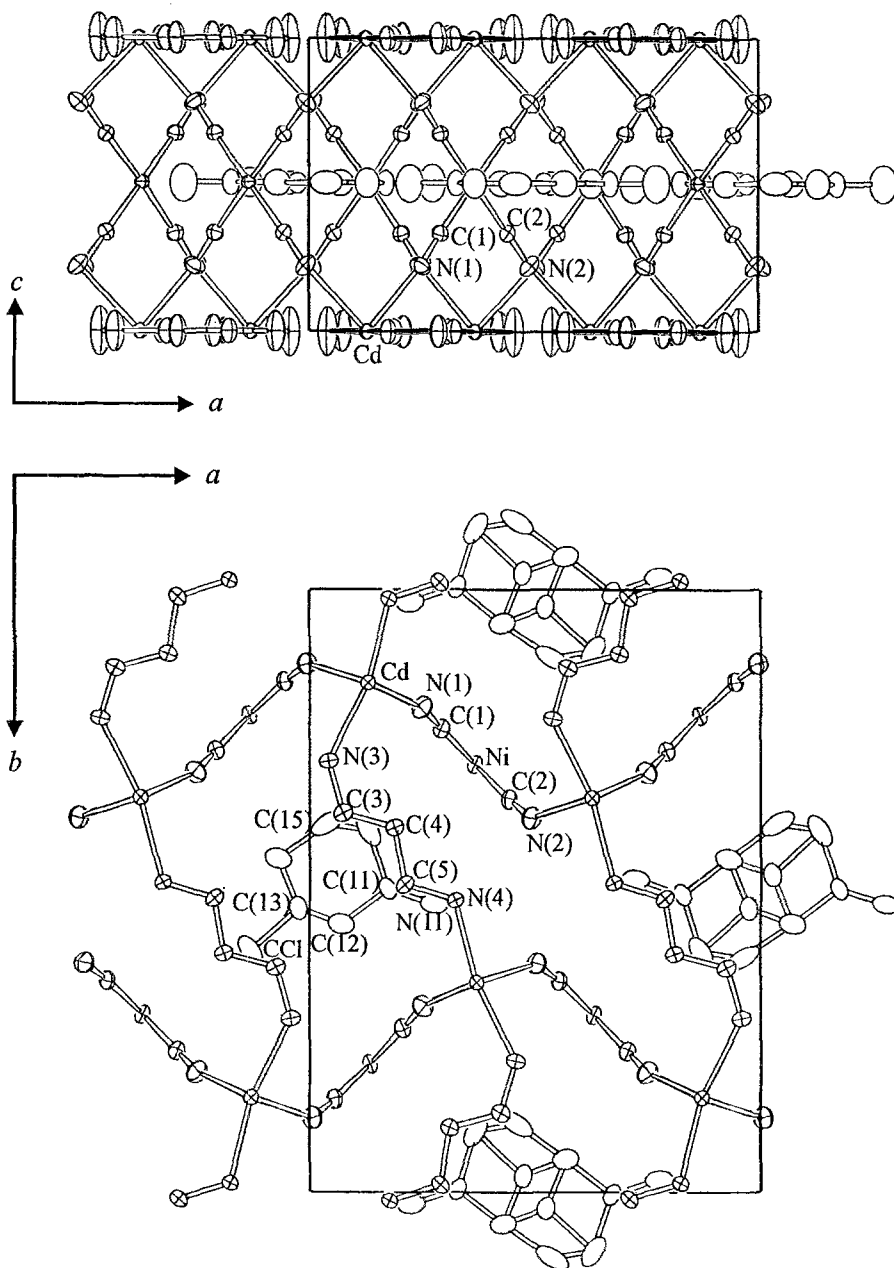


Fig. 2. Structure of **3-m** showing 30% probability thermal ellipsoids. Top: projection along the *b* axis; bottom: projection along the *c* axis. The disordered guest *m*-C₆H₄NH₂ molecule with atomic notations is shown in one possible orientation.

TABLE V. Atomic parameters for $[\text{Cd}(\text{dahpn})\text{Ni}(\text{CN})_4] \cdot 1.5(2\text{-MeC}_6\text{H}_6\text{N})$, **7-q**.

Atom ^a	G ^b	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^{2c}$
Cd	0.50	0.22742(3)	0.23669(2)	0	2.447(6)
Ni	0.50	0.48286(6)	0.20845(3)	1/2	2.40(1)
N(1)	1.00	0.3277(3)	0.2053(2)	0.2206(6)	4.02(8)
N(2)	1.00	0.6309(3)	0.2286(2)	0.2175(6)	4.21(9)
N(3)	0.50	0.3325(5)	0.3034(2)	0	4.1(1)
N(4)	0.50	0.3664(5)	0.6658(2)	0	4.0(1)
C(1)	1.00	0.3866(3)	0.2042(2)	0.3281(5)	2.87(8)
C(2)	1.00	0.5766(3)	0.2183(2)	0.3249(5)	2.87(8)
C(3)	0.50	0.2779(7)	0.3512(3)	0	4.5(2)
C(4)	0.50	0.3498(6)	0.3940(3)	0	4.6(2)
C(5)	0.50	0.2876(7)	0.4409(3)	0	5.6(2)
C(6)	0.50	0.3609(8)	0.4852(3)	0	5.7(2)
C(7)	0.50	0.2974(8)	0.5318(3)	0	6.0(2)
C(8)	0.50	0.3669(6)	0.5760(3)	0	4.3(2)
C(9)	0.50	0.3042(6)	0.6219(3)	0	4.1(2)
C(10)	0.50	0.750(3)	0.442(4)	1/2	79(6)
N(11)	0.50	0.5556(10)	0.4314(4)	1/2	9.7(3)
C(12)	0.50	0.636(2)	0.3972(6)	1/2	13.7(6)
C(13)	0.50	0.601(2)	0.3453(5)	1/2	13.0(6)
C(14)	0.50	0.490(2)	0.3340(5)	1/2	15.1(6)
C(15)	0.50	0.3223(15)	0.3503(8)	1/2	12.7(6)
C(16)	0.50	0.241(2)	0.3911(7)	1/2	13.7(7)
C(17)	0.50	0.268(2)	0.4421(13)	1/2	25.3(12)
C(18)	0.50	0.3784(12)	0.4468(5)	1/2	8.9(4)
C(19)	0.50	0.4489(13)	0.4161(4)	1/2	9.0(4)
C(20)	0.50	0.421(2)	0.3635(5)	1/2	14.8(7)
C(21)*	0.25	0.003(4)	0.405(3)	-0.193(6)	15(2)
C(22)	1.00	-0.0096(10)	0.4140(11)	-0.084(5)	29(2)
C(23)	1.00	-0.0051(12)	0.4614(9)	-0.170(5)	37(2)
C(24)	0.50	0	1/2	-0.116(5)	25(2)

^a Atom in disorder has been asterisked.^b Multiplicity.^c $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

discriminating between the Cl and C so far applied never gave any acceptable convergence.

3.1.3. $[\text{Cd}(\text{dapt})\text{Ni}(\text{CN})_4] \cdot 1.5(p\text{-MeC}_6\text{H}_4\text{NH}_2)$, **5-p**

The centrosymmetric space group $P2_1/a$ was uniquely applied from the observed systematic absences. As shown in Figure 3, the host structure of **5-p** is similar

to that of **3-m**. However, owing to the monoclinic distortion of the unit cell, the 2D network is stacked with a slight shift along both the *a* and *c* directions. The puckering of the 2D network is not so great as that in **3-m**, the δ angles being 41.2° and 16.3° . The skeleton of the daptn taking a *trans-gauche-(trans)*₄ (tgt₄) conformation is less slanted than the tn in **3-m** but inclined against the *ab* plane. The less distorted host structure produces the two crystallographically independent cavities, one centered at *ca.* $1/4, 1/2, 1/2$ (general position) and the other at $0, 1/2, 0$ (special position: $\bar{1}$), so that the number of the cavities available for the guest increases to 1.5. The guest *p*-MeC₆H₄NH₂ molecule in the former cavity is clipped by the daptn pillars with its aromatic plane almost parallel to the skeletal plane of the daptn pillars, whereas that in the latter is almost vertical to the daptn skeletal plane. Discrimination between the CH₃ and NH₂ groups was practically impossible, although it is crystallographically possible for the molecule at the general position; the relevant atoms were refined as an equal probability of C and N.

3.1.4. [Cd(dahpn)Ni(CN)₄] \cdot 1.5(2-MeC₉H₆N), **7-q**

The centrosymmetric space group *Pbam* was applied. The host structure of **7-q** is topologically the same as those of **3-m** and **5-p**, as shown in Figure 4. The puckering of the 2D network with the δ angles of 43.2° and 25.7° is marginally greater than that in **5-p**; however, the dahpn pillar taking an all-*trans* (t₈) conformation is parallel to the *b* axis. Two crystallographically independent cavities are given in the host structure: one centered at $1/2, 1/2, 1/2$ ($2/m$) and the other at $0, 1/2, 0$ ($2/m$). The skeletons of the dahpn and the guest 2-MeC₉H₆N in the former cavity are all arranged on the mirror planes at $c = 0$ and $1/2$, respectively. The guest skeleton in the latter cavity is also approximately on the *bc* plane.

The array of the puckered 2D networks bridged by the almost vertical dahpn pillar brings about the relative expansion of the former cavity and the compression of the latter along the *b* axis. The expanded cavity, approximately surrounded by four dahpn pillars at the sides and two Ni(CN)₄ moieties at the top and the bottom, is large enough to accommodate a couple of the guests. The guest in the compressed cavity is in disorder related with the site symmetry $2/m$. Since the guests in the former cavity occupy the space corresponding to two cavity units along the *a* axis, the final stoichiometry between the host and guest becomes 1.5.

3.2. DISCUSSION

In Table VI the Hofmann-type clathrate [Cd(NH₃)₂Ni(CN)₄] \cdot 2C₆H₆ and the Hofmann-diam-type ones [Cd(diam)Ni(CN)₄] \cdot *x*G whose single crystal structures have been available are listed with the space group, form of the 2D network, conformation of the diam skeleton and the dihedral angle δ between the [CdN₄] and [NiC₄] planes. Although the number of cavities in a unit cell of the Hofmann-type is 2, let us consider a $2 \times$ enlarged structure in volume along the *ab* plane, involving four

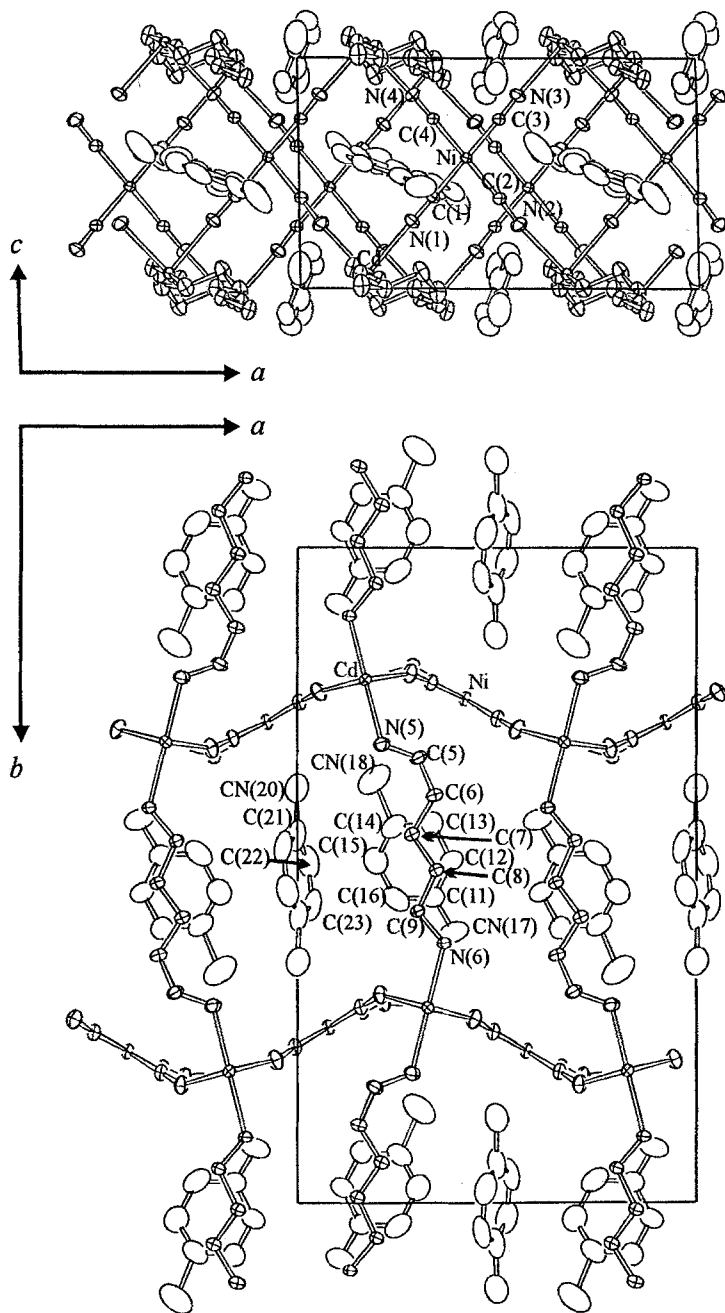


Fig. 3. Structure of **5-p** showing 30% probability thermal ellipsoids. Top: projection along the *b* axis; bottom: projection along the *c* axis. The CH₃ and NH₂ groups of the guest *p*-MeC₆H₄NH₂ molecule have not been discriminated.

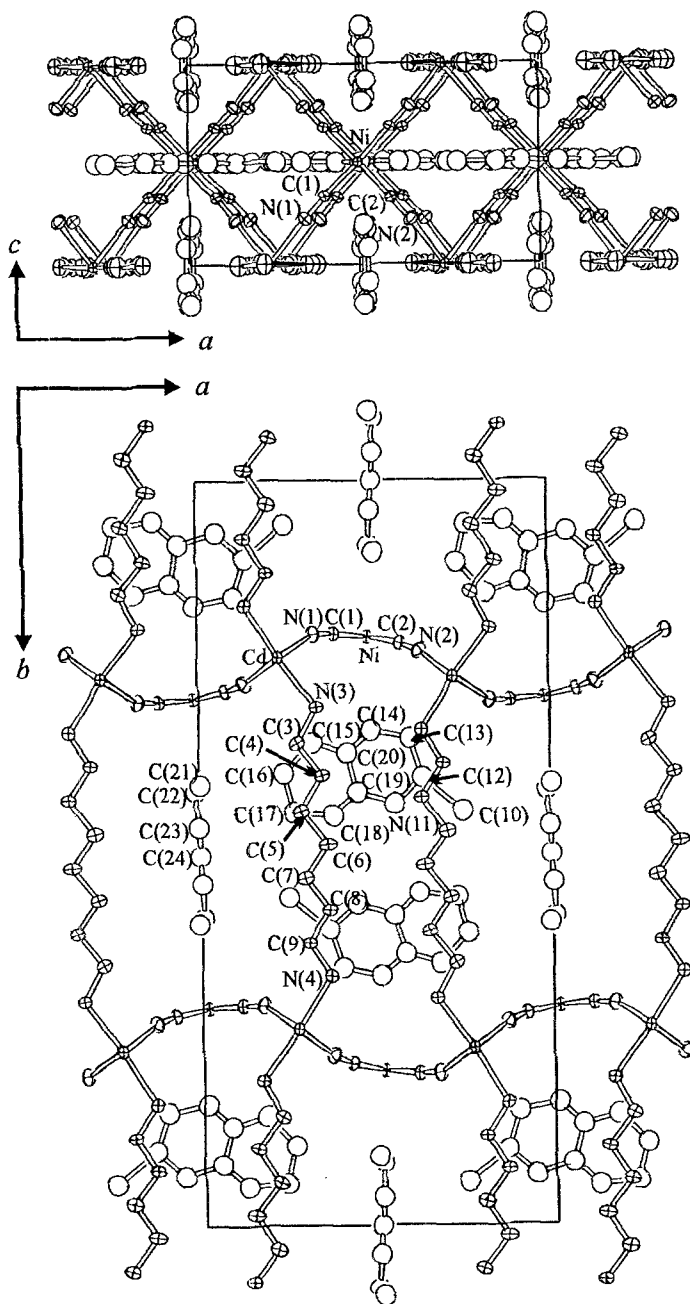


Fig. 4. Structure of 7-*q* showing 30% probability thermal ellipsoids. Top: projection along the *b* axis; bottom: projection along the *c* axis. The guest 2-MeC₉H₆N molecule in the cavity centered at 0, 1/2, 0 is in disorder; isotropic spheres of 8.0 Å² for the atoms of the guest molecules.

TABLE VI. Structural features and the dihedral angle δ between $[\text{CdN}_4]$ and $[\text{NiC}_4]$ planes of the Hofmann-diam-type series.

Compound*, code	Space group	2D network	Diam skeleton	$\delta/^\circ$	Ref.
$[\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4] \cdot 2\text{C}_6\text{H}_6$, 0	$P4/m$	Flat	-	0	3f, 9d
$[\text{Cd}(\text{en})\text{Ni}(\text{CN})_4] \cdot 2\text{C}_6\text{H}_6$, 2	$P4/mmm$	Flat	$t_3?$	0	2, 3f
$[\text{Cd}(\text{mea})\text{Ni}(\text{CN})_4] \cdot 2\text{C}_6\text{H}_6$, 2'	$P4/mmm$	Flat	$t_3?$	0	11
$[\text{Cd}(1\text{-pn})\text{Ni}(\text{CN})_4] \cdot 1.5\text{C}_6\text{H}_6$, 2''	$P422$	Flat	$t_3?$	0	10
$[\text{Cd}(d1\text{-pn})\text{Ni}(\text{CN})_4] \cdot 1.5\text{C}_6\text{H}_6$, 2'''	$P4/mmm$	Flat	$t_3?$	0	10
$[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 1.72(o\text{-MeC}_6\text{H}_4\text{NH}_2)$, 3-0	$P2/m$	Flat	$t_4?$	0	Present work
$[\text{Cd}(\text{tn})\text{Ni}(\text{CN})_4] \cdot 0.5(m\text{-ClC}_6\text{H}_4\text{NH}_2)$, 3-m	$Pbam$	Puckered	ct_3	24.5, 65.5	Present work
$[\text{Cd}(\text{dabtn})\text{Ni}(\text{CN})_4] \cdot \text{C}_4\text{H}_5\text{N}$, 4-pyr	$P2/m$	Puckered	t_3	35.8	3c
$[\text{Cd}(\text{dabtn})\text{Ni}(\text{CN})_4] \cdot 1.5\text{C}_6\text{H}_5\text{NH}_2$, 4-a	$P\bar{1}$	Puckered	tct_3	7.4, 47.4	3c
$[\text{Cd}(\text{dabtn})\text{Ni}(\text{CN})_4] \cdot 1.5(o\text{-MeC}_6\text{H}_4\text{NH}_2)$, 4-0	$P\bar{1}$	Puckered	tct_3	6.4, 40.9	3g
$[\text{Cd}(\text{dabtn})\text{Ni}(\text{CN})_4] \cdot \text{C}_6\text{H}_5\text{NMe}_2$, 4-d	$P2_1/m$	Puckered	tct_3	28.8	3c
$[\text{Cd}(\text{dabtn})\text{Ni}(\text{CN})_4] \cdot (2, 5\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_2)$, 4-x	$P2_1/m$	Puckered	tct_3	41.2	3a
$[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot o\text{-MeC}_6\text{H}_4\text{NH}_2$, 5-0	$P4/mmm$	Flat	?	0	3g
$[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot m\text{-MeC}_6\text{H}_4\text{NH}_2$, 5-m	$Pbam$	Puckered	ct_3ct	24.2, 63.1	3g
$[\text{Cd}(\text{daptn})\text{Ni}(\text{CN})_4] \cdot 1.5(p\text{-MeC}_6\text{H}_4\text{NH}_2)$, 5-p	$P2_1/a$	Puckered	tgt_4	42.1, 16.3	Present work
$[\text{Cd}(\text{dahxn})\text{Ni}(\text{CN})_4] \cdot o\text{-MeC}_6\text{H}_4\text{NH}_2$, 6-0	$P2/m$	Puckered	t_7	13.9	3b
$[\text{Cd}(\text{dahxn})\text{Ni}(\text{CN})_4] \cdot m\text{-MeC}_6\text{H}_4\text{NH}_2$, 6-m	$P\bar{1}$	Puckered	t_7	36.3	3d
$[\text{Cd}(\text{dahxn})\text{Ni}(\text{CN})_4] \cdot p\text{-MeC}_6\text{H}_4\text{NH}_2$, 6-p	$P2/m$	Puckered	t_7	37.7	3d
$[\text{Cd}(\text{dabtn})\text{Ni}(\text{CN})_4] \cdot (2, 4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_2)$, 6-x	$P2/m$	Puckered	t_7	38.3	3d
$[\text{Cd}(\text{dahpn})\text{Ni}(\text{CN})_4] \cdot 1.5(2\text{-MeC}_9\text{H}_6\text{N})$, 7-q	$Pbam$	Puckered	t_8	43.2	Present work
$[\text{Cd}(\text{daotn})\text{Ni}(\text{CN})_4] \cdot \text{PhMe}$, 8-t	$P2/m$	Puckered	t_9	41.5	3i
$[\text{Cd}(\text{daotn})\text{Ni}(\text{CN})_4] \cdot o\text{-MeC}_6\text{H}_4\text{NH}_2$, 8-0	$P2/m$	Puckered	t_9	40.5	3g
$[\text{Cd}(\text{daotn})\text{Ni}(\text{CN})_4] \cdot p\text{-MeC}_6\text{H}_4\text{NH}_2$, 8-p	$P\bar{1}$	Puckered	t_9	42.9	3g
$[\text{Cd}(\text{daotn})\text{Ni}(\text{CN})_4] \cdot \text{C}_6\text{H}_{13}\text{OH}$, 8-h	$P2/m$	Puckered	t_9	40.7	3e
$[\text{Cd}(\text{danon})\text{Ni}(\text{CN})_4] \cdot 0.5(o\text{-Me}_2\text{C}_6\text{H}_4)$, 9-0	$P\bar{1}$	Puckered	g_2t_8	51.4, 32.5	3h

* Abbreviations are as follows: en = 1,2-diaminoethane; mea = 2-aminoethanol; pn = 1,2-diaminopropane; tn = 1,3-diaminopropane; dabtn = 1,4-diaminobutane; daptn = 1,5-diaminopentane; dahxn = 1,6-diaminohexane; dahpn = 1,7-diaminoheptane; daotn = 1,8-diaminooctane; danon = 1,9-diaminononane.

cavity units, in order to discuss the number of cavities available for the guest in the Hofmann-diam-type series; the enlarged structure has been exemplified in Figure 1 (the *ac* plane of **3-o** corresponds to the *ab* plane of the tetragonal structure).

In the host structures of the methylene number 2, i.e., from **2** to **2'''** in the lines of Table VI, the 2D network is flat with the tetragonal symmetries similar to the Hofmann-type **0**; the host structures are substantially the same as one another. In the Hofmann-pn-type [10] one of the four cavity units is occupied by two methyl groups of the 1,2-diaminopropane (pn) ligands at random to decrease *x* to 1.5.

Although **3-o** and **5-o** have the flat 2D network, the network is puckered to a greater or lesser extent upon increasing the methylene chain length in the diam above 2. The dihedral angle δ , which should be an index showing the extent of the puckering, is larger than 60° in the extremely distorted hosts of **3-m** and **5-m**. In the even-*n* hosts the values are less than 48° .

The number of cavities available for the guest, being equal to $2x$ for the four in total in the expanded structure, appears to be related to the puckering of the 2D network, the conformation of the diam skeleton, and the shape of the guest molecule. The flat network and the vertical *tn* pillar in **3-o** are substantially the same as those in the **2**-family, though the unit cell is slightly distorted to the monoclinic $P2/m$ with $a \approx b$ and $\beta = 91.03(2)^\circ$. However, as is obvious in Figure 1, the guest molecules suffer much steric repulsion between those in the fully occupied cavity and the partly occupied one in **3-o** with the ratio of 1.00(2):0.72(2) based on the refined occupancies, or even with the ratio of *ca.* 1:0.5 suggested from the analytical results. The thermal ellipsoids of C(1) and N(1) elongated along the *b* axis suggest that the apparently flat 2D network might be an average of puckered ones in disorder. Although the structure has been refined with an acceptable convergence (see Table I), it is still doubtful that **3-o**, as well as **5-o**, keep a completely flat 2D network; an apparently high symmetry ($P4/mmm$) with the extremely high disorders in the interlayer moieties was observed in the structure of **5-o** [3g]

The diam skeleton in the all-*trans* conformation with even-*n* (**4-pyr**, all of the **6**- and **8**-families) always bridges between the 2D networks slantwise and occupies two cavity units, leading to $x = 1$; the unit cell symmetry becomes $P2/m$ or $P\bar{1}$ slightly distorted from $P2/m$. The skeletons of the diam and the guest are arrayed along the respective mirror planes in the $P2/m$ unit cell or pseudo-mirror planes in the $P\bar{1}$ cell. The cavity has a channel character along the mirror plane but with a rather narrow opening between the cavities due to the puckering of the 2D network. The guest is surrounded by four diam pillars in the interlayer cavity.

The structure of **3-m** resembles that of **5-m** in the extremely puckered 2D network and the diam skeleton arrayed along the mirror plane. The guest skeleton is on an adjacent mirror plane in **3-m** but statistically distributed about the mirror plane in **5-m**. In the former the guest is surrounded by four *tn* pillars but in the latter the guest is clipped by a couple of *daptn* pillars. The *tn* span with the *ct*₃ conformation is too short to clip the guest between two pillars; the longer *daptn*

span allows accommodation of two guests for the four cavities in **5-m** ($x = 1$). The value of $x = 0.5$ in **3-m** is discussed with **9-o** below.

The effective span length between the networks is elongated in **5-p**, **4-a**, and **4-o** with the less slanted pillars of the daptn (tgt_4) and dabtn (tct_3), respectively. The less slanted pillar occupies only one of the four cavity units so that one more cavity becomes available for the guest with the more slender shape, p -MeC₆H₄NH₂, PhNH₂ and o -MeC₆H₄NH₂, which guests are clipped by the diam pillars in parallel in the channel cavity and vertically in another channel. This effect is remarkable in **7-q**: the t_8 skeleton is almost vertical to the network elongating the interlayer distance enough to accommodate a couple of the guest 2-MeC₉H₆N molecules in the wider cavity and one in the narrower cavity.

The danon pillar appears to be too long to accommodate the guest o -Me₂C₆H₄ in a host structure like **7-q**. One of the channels separated by the array of the danon pillars is invaded by the highly twisted skeleton of the g_2t_8 conformation in full, i.e., the channel collapses at one side and that at another side only accommodates the guests. In **3-m** collapse of the cavity occurs along the nodal channel alternately. The deformation of both structures leads to $x = 0.5$.

The host structures of odd- n skeleton vary remarkably even among only two **3**- and three **5**-families; for $n = 7$ and 9 , only one each of well-defined structures have been available. In other words, the relevant guest selects the host structure strictly in the odd- n family. In the attempts to prepare clathrates of other guests under similar experimental conditions, single crystals have been obtained with the composition Cd(diam)₂Ni(CN)₄· x H₂O ($x = 0$ or 1) for tn, daptn, dahpn and danon. Their structures will be reported elsewhere [12].

References

1. (a) T. Iwamoto: 'The Hofmann-type and related inclusion compounds' Ch. 2 in *Inclusion Compounds* Vol. 1, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London (1984), pp. 29–57. (b) T. Iwamoto: 'Inclusion compounds of multi-dimensional cyanometal complex hosts' Ch. 6 in *Inclusion Compounds* Vol. 5, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, Oxford (1991), pp. 172–212.
2. T. Miyoshi, T. Iwamoto and Y. Sasaki: *Inorg. Chim. Acta* **6**, 59 (1972).
3. (a) S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **2**, 341 (1984). (b) T. Hasegawa, S. Nishikiori, and T. Iwamoto: *J. Incl. Phenom.* **2**, 351 (1984). (c) S. Nishikiori and T. Iwamoto: *Inorg. Chem.* **25**, 788 (1986). (d) T. Hasegawa and T. Iwamoto: *J. Incl. Phenom.* **6**, 143 (1988). (e) T. Hasegawa and T. Iwamoto: *J. Incl. Phenom.* **6**, 549 (1988). (f) S. Nishikiori, T. Kitazawa, R. Kuroda, and T. Iwamoto: *J. Incl. Phenom.* **7**, 369 (1989). (g) S. Nishikiori, T. Hasegawa, and T. Iwamoto: *J. Incl. Phenom.* **11**, 137 (1991). (h) M. Hashimoto, T. Kitazawa, T. Hasegawa, and T. Iwamoto: *J. Incl. Phenom.* **11**, 153 (1991). (i) T. Hasegawa, S. Franzen, D. Lambright, D. H. Oh, S. Balasubramanian, B. Hedman and K. O. Hodgson: *Inorg. Chem.* **30**, 1441 (1991).
4. M. Hashimoto, T. Hasegawa, H. Ichida, and T. Iwamoto: *Chem. Lett.* 1397 (1989); M. Hashimoto and T. Iwamoto: *Chem. Lett.* 1531 (1990).
5. A. T. C. North, D. C. Phillips, and F. S. Mathews: *Acta Crystallogr. Sect. A* **24**, 351 (1968).
6. T. Sakurai and K. Kobayashi: *Rep. Inst. Phys. Chem. Res.* **55**, 69 (1979).
7. *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–98, Kynoch Press, Birmingham, 1974 (Distr. Kluwer Academic Publ. Group, Dordrecht).

8. C. K. Johnson: ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1976).
9. (a) R. Kuroda and Y. Sasaki: *Acta Crystallogr., Sect. B* **30**, 687 (1974). (b) H. M. Powell and J. H. Rayner: *Nature (London)* **163**, 566 (1949); J. H. Rayner and H. M. Powell: *J. Chem. Soc.* 319 (1952). (c) T. Miyoshi, T. Iwamoto, and Y. Sasaki: *Inorg. Chim. Acta* **7**, 9 (1973). (d) Y. Sasaki: *Bull. Chem. Soc. Jpn.* **42**, 2412 (1969).
10. S. Nishikiori, T. Iwamoto, and Y. Yoshino: *Bull. Chem. Soc. Jpn.* **53**, 2236 (1980).
11. S. Nishikiori and T. Iwamoto: *Chem. Lett.* 1755 (1981); *Bull. Chem. Soc. Jpn.* **56**, 3246 (1983).
12. H. Yuge, A. Mamada, M. Asai, S. Nishikiori, and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, in press.