The Metal Complex Host *catena*-[(1,2-Diaminopropane)-cadmium(II) Tetracyanonickelate(II)] which provides Channel Cavities for Straight- and Branched-chain Aliphatic Guests†

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A number of inclusion compounds $[(pn)Cd(CN)_4Ni]\cdot nG$ (pn = 1,2-diaminopropane; n = 0.3–0.5) have been prepared for various straight-and branched-chain aliphatic guest molecules (G), which are accommodated in the three-dimensional structure of the metal complex host. This structure contains channel cavities surrounded by tetracyanonickelate(II) moieties linked alternately to the Cd which is chelated by the pn. The inclusion compounds are grouped into two types, U- and T-type, according to the shape of the channel revealed by their single-crystal structures. In the monoclinic U-type structure the point-symmetric arrangement of the pn chelate rings provides a snake-like channel, analogous to the spiral ones in urea inclusion compounds, for the straight-chain aliphatic guests pentane, hexane, heptane, diethyl ether, ethane-1,2-diol, 1-bromo-butane and -pentane. In the orthorhombic T-type structure the mirror-symmetric arrangement of the pn chelate rings results in nodal channels, similar to those in thiourea inclusion compounds for 1,1,2,2-tetrachloroethane, 2-chlorobutane, 1,2-dichloropropane, Pr^iOH, 1,2-dichloro- and 1,2-dibromo-ethane and 1,3-dichloropropane. For the straight-line dihalogenoalkane guests the halogen atoms appear to contribute to the preference for the nodal channel by formation of hydrogen bonds with the pn-amino group.

As has been reported preliminarily,[1] the three-dimensional framework of *catena*-[(1,2-diaminopropane)cadmium(II) tetracyanonickelate(II)] provides channel cavities for aliphatic guest molecules, *e.g.* straight- and branched-chain skeletons. In general, straight-chain guests are accommodated in the snake-like U-type cavity, analogous to that observed in inclusion compounds of urea and branched ones in the nodal T-type channel similar to that in inclusion compounds of thiourea.[2] The difference in the channel structures between U and T is due to the geometrical isomerism of the 1,2-diaminopropane (pn) chelate at the Cd atom in the direction of the protrusion into the channel. This paper describes the structural features of these inclusion compounds based on the single-crystal structures determined for fourteen $[(pn)Cd(CN)_4Ni]\cdot nG$ (n = 0.3–0.5, G = aliphatic guest) compounds, seven of the U and seven of the T type. The resemblance with and difference from the urea- and thiourea-host inclusion compounds will be discussed.

Results and Discussion

The inclusion compounds obtained with the general formula $[(pn)Cd(CN)_4Ni]\cdot nG$ are listed in Table 1 along with their elemental analyses. Despite the fact that compounds of normal alkane guests show non-stoichiometric host : guest ratios depending on the methylene chain length, almost stoichiometric n values of *ca.* 0.5 have been observed for some other guests independent of their molecular dimensions. The stoichiometry of the guest will be discussed later in terms of the respective crystal structures.

The crystallographic and selected experimental data are summarised in Table 2; the host structures are illustrated in Fig. 1 for the U type and Fig. 2 for the T type. The inclusion compounds are divided into two groups, one belonging to the monoclinic space group *A*2/*a* (no. 15, unique axis *c*) for the U- and the other to the orthorhombic *Pnma* (no. 62) for the T-type structure. The former space group and monoclinic angle γ have been fixed for the sake of comparison between the U and T structures. The respective unit-cell parameters are similar to one another throughout both U and T: a = *ca.* 14 [13.897(6) for U-5 to 14.183(1) for T-2], b = *ca.* 27 [26.799(1) for T-3 to 27.192(3) Å for T-1], and c = *ca.* 7.6 Å [7.576(4) for U-3 to 7.698(2) Å for T-6], the monoclinic angle γ for U [88.88(3) for U-5 to 91.74(2)° for U-3] deviating by less than 2° from 90°. These inclusion compounds are, to the first approximation, all isostructural: the asymmetric unit of each host is comprised of chemically the same kind and number of atoms in both types U and T. The refined atomic parameters are given for the host atoms of U-4 and T-1 as representatives in Table 3; they are within ± 1% for atoms with the same numberings throughout the U and T structures, leading to little significant differences in the corresponding bond lengths and angles. The atomic parameters for the guest atoms are summarised in Table 4.

The Host Structure.—There are two kinds of square-planar tetracyanonickelate(II) moieties, A and B, centred on crystallographically independent atoms Ni(1) and Ni(2), respectively; Ni(1) and Ni(2) are located at $\frac{1}{4}$, 0, z(= *ca.* 0.36) and $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{4}$ in the *A*2/*a* space group of the U-type structure, and at x(= *ca.* 0.25), $\frac{1}{4}$, z(= *ca.* 0.6) and $\frac{1}{2}$, 0, 0 in the *Pnma* of type T, respectively.

Moiety A makes a doubly bridged one-dimensional (double-1D)[3] extension of $>[Ni\langle(CN\text{–}Cd\text{–}NC)_2\rangle]_\infty$ with the Cd atoms along the c axis of the crystal and its molecular plane almost parallel to the bc plane; these extensions are stacked along the a axis to form the ceiling and floor of the channel. Moiety B spans the Cd atoms on the ceilings and the floors of neighbouring channels, making a folded 'expanded two-dimensional' (expanded-2D)[3] extension along the ac plane, in which the $Ni(CN)_4$ moieties are arranged in a solid-and-blank check pattern. The terms 'double-1D' and 'expanded-2D' have been previously referred to.[3] In the former the Ni atoms are doubly

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Inclusion compounds $[(pn)Cd(CN)_4Ni]\cdot nG$ and their elemental analyses

			Analysis (%)*			
Code	Guest, G	*n*	C	H	N	Halogen
U-1	$CH_3(CH_2)_3CH_3$	0.5	29.10 (29.60)	4.00 (4.20)	21.80 (21.80)	
U-2	$CH_3(CH_2)_4CH_3$	0.36	28.70 (28.15)	3.95 (4.00)	22.10 (22.10)	
U-3	$CH_3(CH_2)_5CH_3$	0.32	28.55 (29.00)	3.90 (4.00)	22.05 (22.05)	
U-4	OEt_2	0.5	27.60 (28.00)	3.90 (3.90)	21.65 (21.75)	
U-5	$HOCH_2CH_2OH$	0.5?	22.35 (25.25)	3.35 (3.45)	21.00 (22.10)	
U-6	$CH_3(CH_2)_3Br$	0.5?	23.85 (25.85)	3.25 (3.50)	19.60 (20.10)	6.30 (9.55)
U-7	$CH_3(CH_2)_4Br$	0.36	26.00 (25.45)	3.40 (3.35)	20.60 (21.10)	7.55 (7.20)
T-1	$Cl_2CHCHCl_2$	0.5	22.00 (22.20)	2.75 (2.55)	19.55 (19.40)	16.50 (16.35)
T-2	MeCHClEt	0.5	27.20 (27.35)	3.70 (3.70)	21.40 (21.25)	4.45 (4.50)
T-3	$MeCHClCH_2Cl$	0.5	24.95 (25.15)	3.20 (3.25)	20.95 (20.70)	8.45 (8.75)
T-4	MeCHOHMe	0.5?	25.80 (26.90)	3.65 (3.70)	21.70 (22.15)	
T-5	$ClCH_2CH_2Cl$	0.5	24.00 (24.10)	3.00 (3.00)	21.20 (21.10)	8.55 (8.90)
T-6	$BrCH_2CH_2Br$	0.5	21.70 (21.70)	2.75 (2.75)	19.25 (18.95)	15.75 (18.05)
T-7	$Cl(CH_2)_3Cl$	0.5	25.10 (25.15)	3.35 (3.25)	20.60 (20.70)	8.55 (8.75)

* Calculated values in parentheses.

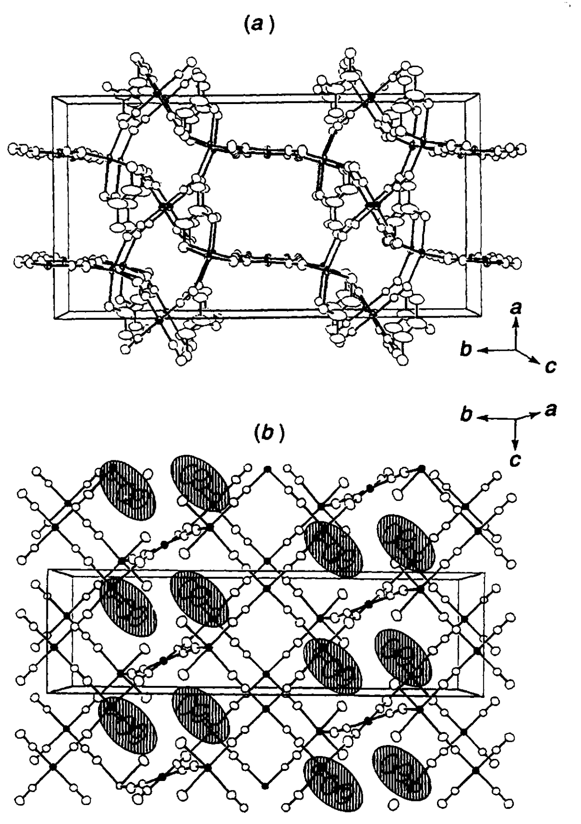
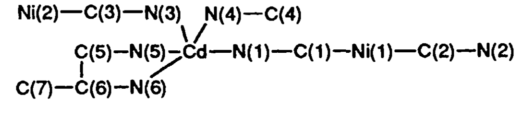


Fig. 1 The U-type host structure. (*a*) A view along the *c* axis. (*b*) A view along the *a* axis in the range of *ca.* 0.7*a*, 1.2*b* and 3*c*, shading indicates approximate van der Waals spaces for the pn chelate rings; the Cd and Ni atoms are shown as solid ellipsoids. Atomic numbering is in the sequence below.



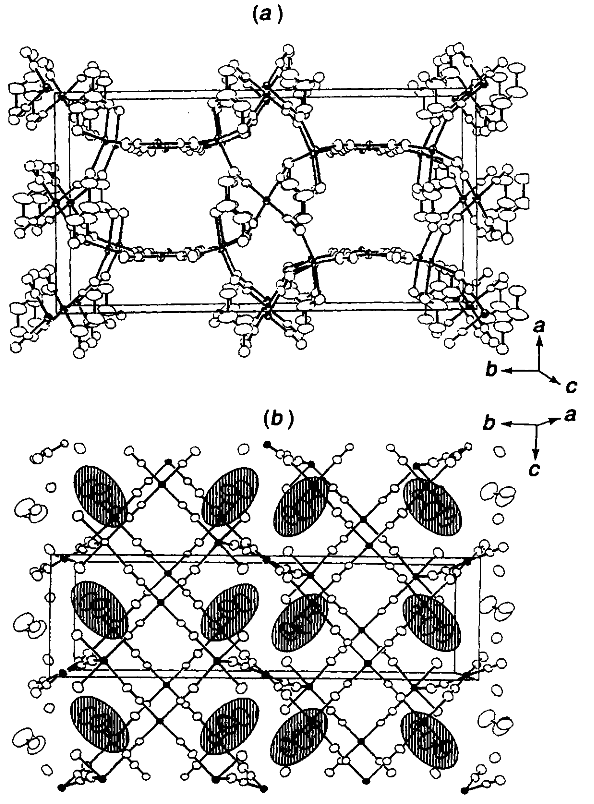
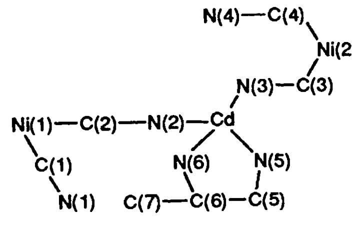


Fig. 2 The T-type host structure. Details as in Fig. 1. Atomic numbering is in the sequence below.



bridged successively by a couple of –CN–Cd–NC moieties to give a one-dimensional array. In the latter the $Ni(CN)_4$ moieties are linked by Cd atoms at every N-terminal to give a two-dimensional network of Ni–CN–Cd–NC–Ni edges. Thus, the two types of extensions interconnected at each Cd atom together comprise the three-dimensional host framework with channels extending along the *c* axis; the six-co-ordination of the Cd is accomplished with two N atoms from each moiety A and B and two from the bidentate pn ligand.

The difference between the U- and T-type structures is brought about by the difference in arrangements of the pn ligand protruding from the Cd atom into the channel. In U the pn is arranged point-symmetrically, *i.e.* the pn rising up from the Cd atom at *x*, *y*, *z* on the floor is correlated through the inversion

Table 2 Crystallographic and selected experimental data for $[(\mathrm{pn})\mathrm{Cd}(\mathrm{CN})_4\mathrm{Ni}]\cdot n\mathrm{G}$

(*a*) U type: monoclinic, space group *A*2/*a* (no. 15, unique axis *c*), *Z* = 4, scan mode 2θ–ω, scan range 4.0 < 2θ < 60.0°

Compound	U-1	U-2	U-3	U-4	U-5	U-6	U-7
G	C_5H_{12}	C_6H_{14}	C_7H_{16}	OEt_2	$HOCH_2CH_2OH$	$CH_3(CH_2)_3Br$	$CH_3(CH_2)_4Br$
n	0.5	0.36	0.32	0.5	0.5?	0.5?	0.36
M	385.39	380.32	380.36	386.38	380.35	417.80	404.40
a/Å	14.075(1)	13.987(2)	14.014(5)	13.961(3)	13.897(6)	14.116(5)	14.082(3)
b/Å	27.026(3)	26.971(2)	26.963(5)	26.998(3)	26.890(5)	26.839(4)	26.943(7)
c/Å	7.612(1)	7.595(2)	7.576(4)	7.589(3)	7.607(1)	7.642(1)	7.602(3)
γ/°	89.82(1)	91.74(1)	91.74(2)	89.16(1)	88.88(3)	90.19(3)	90.43(3)
U/Å^3	2829.5(1)	2863.6(7)	2862(2)	2860(1)	2842(1)	2895(1)	2884(1)
D_m,D_c/g cm^{-3}	1.75(1), 1.77	1.75(2), 1.76	1.77(2), 1.77	1.77(1), 1.79	1.79(1), 1.78	1.91(1), 1.92	1.87(1), 1.86
F(000)	1528	1504	1508	1528	1496	1632	1578.88
Crystal size (mm)	0.50 × 0.20 × 0.45	0.30 × 0.20 × 0.20	0.45 × 0.30 × 0.30	0.20 × 0.10 × 0.20	0.30 × 0.20 × 0.30	0.30 × 0.05 × 0.40	0.30 × 0.30 × 0.35
Diffractometer[a]	AFC5S	AFC5R	AFC5R	AFC5R	AFC5S	AFC5S	AFC5S
μ(Mo-Kα)/cm^{-1}	27.58	27.95	27.99	28.00	28.19	41.31	37.31
Scan width/°	1.313 + 0.3tanθ	1.103 + 0.3tanθ	1.155 + 0.35tanθ	0.892 + 0.3tanθ	1.523 + 0.3tanθ	1.155 + 0.3tanθ	1.523 + 0.3tanθ
Reflections	4764	4587	4584	4583	4683	4601	4591
N_o[b]	3485	3177	3344	2911	2899	2757	3251
N_p[b]	182	173	173	173	182	173	173
R, *R'*[b]	0.033, 0.037	0.041, 0.046	0.040, 0.044	0.050, 0.054	0.045, 0.049	0.087, 0.141	0.084, 0.136
Goodness of fit[b]	3.375	4.252	3.896	5.245	4.516	13.91	12.067
Δ/e.s.d.[c] host	0.02	0.01	0.02	0.03	0.01	0.02	0.02
guest	0.02	0.09	0.24	0.70	0.23	0.02	0.62
Maximum residual/e Å^{-3}	0.8	0.8	0.6	0.9	0.7	1.8	2.0

(*b*) T type: orthorhombic, space group *Pnma* (no. 62), *Z* = 8

Compound	T-1	T-2	T-3	T-4	T-5	T-6	T-7
G	$Cl_2CHCHCl_2$	MeCHClEt	$MeCHClCH_2Cl$	MeCHOHMe	$ClCH_2CH_2Cl$	$BrCH_2CH_2Br$	$Cl(CH_2)_3Cl$
n	0.5	0.5	0.5	0.5?	0.5	0.5	0.5
M	433.24	395.60	405.81	379.37	398.80	443.23	405.81
a/Å	14.061(1)	14.183(1)	14.104(3)	14.157(3)	13.916(3)	13.981(3)	14.104(7)
b/Å	27.192(3)	26.983(2)	26.799(1)	26.699(2)	26.638(2)	26.685(4)	26.654(6)
c/Å	7.590(1)	7.615(1)	7.657(1)	7.586(2)	7.631(4)	7.698(2)	7.645(6)
U/Å^3	2901.9(5)	2914(1)	2893.8(6)	2867.5(9)	2892(2)	2872(1)	2874(2)
D_m, D_c/g cm^{-3}	1.96(2), 1.98	1.80(2), 1.80	1.85(1), 1.86	1.75(1), 1.76	1.87(1), 1.87	2.052(1), 2.05	1.88(1), 1.88
F(000)	1688	1560	1592	1496	1560	1704	1592
Crystal size (mm)	0.40 × 0.10 × 0.30	0.30 × 0.10 × 0.50	0.10 × 0.10 × 0.40	0.30 × 0.10 × 0.40	0.80 × 0.40 × 0.10	0.10 × 0.10 × 0.30	0.45 × 0.25 × 0.10
Diffractometer[a]	AFC5	AFC5S	AFC5S	AFC5R	AFC5R	AFC5S	AFC5R
μ(Mo-Kα)/cm^{-1}	31.29	28.38	29.50	27.91	30.17	55.41	29.71
Scan mode	2θ–ω	ω	2θ–ω	ω	ω	2θ–ω	ω
Scan range/°	3.0 < 2θ < 60.0	4.0 < 2θ < 60.0	4.0 < 2θ < 60.0	4.0 < 2θ < 60.0	5.0 < 2θ < 60.0	4.0 < 2θ < 60.0	5.0 < 2θ < 60.0
Scan width/°	1.30 + 0.3tanθ	0.588 + 0.3tanθ	0.672 + 0.3tanθ	0.882 + 0.3tanθ	1.05 + 0.3tanθ	0.882 + 0.3tanθ	1.134 + 0.3tanθ
Reflections	4816	4806	4775	4761	4691	4736	3777
N_o[b]	2373	2680	2379	2820	2875	2489	2382
N_p[b]	191	191	191	182	164	164	164
R,*R'*[b]	0.068, 0.094	0.057, 0.061	0.060, 0.068	0.050, 0.053	0.061, 0.071	0.065, 0.072	0.064, 0.077
Goodness of fit[b]	8.080	4.765	5.495	3.637	5.083	5.876	6.013
Δ/e.s.d.[c] host	0.03	0.04	0.02	0.14	0.11	0.01	0.03
guest	0.43	0.33	0.49	0.31	0.04	0.07	0.32
Maximum residual/e Å^{-3}	2.7	1.5	1.5	0.7	2.1	2.0	2.5

[a] Rigaku AFC5S and AFC5: graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) from a sealed tube with a scan rate of 8° min^{-1} (4° min^{-1} for T-3) at ambient temperature. Rigaku AFC5R: graphite-monochromated Mo-Kα radiation (λ = 0.709 26 Å) from a rotating anode with a scan rate of 32° min^{-1} at ambient temperature. [b] N_o = Number of reflections used with $|F_o| > 3\sigma(F_o)$, N_p = Number of refined parameters, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $w = 1$; goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$. [c] Maximuim shift/e.s.d. in the final cycle.

centre $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ to the pn hanging down from the Cd at $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$ on the ceiling in the channel extending along [220]. Hence a guest molecule accommodated in the channel gives a centrosymmetric image in the structure refinement irrespective of the real molecular structure. In the T-type structure the pn ligands are arranged mirror-symmetrically; each of the channels is bisected by the mirror plane at $b = \frac{1}{4}$ or $\frac{3}{4}$. Hence a mirror-symmetric image of the guest is given in the T channel. As the projections along the *a* axis in Figs. 1 and 2 show, the point-symmetric arrangement of the pn in the U-type structure results in a snake-like bending of the channel, whereas the mirror-symmetric arrangement in T results in a nodal channel.

Although the period of the node in structure T is the *c* dimension of the crystal, *ca.* 7.6 Å, the length of the snake-like channel in the U-type structure is greater (*ca.* 8.5 Å) due to the slant of the channel against the *c* axis. The height of the channel along the *a* axis is found to be approximately 3.6 Å ($=\frac{a}{2} - 3.4$ Å) by estimating the thickness of the tetracyanonickelate to be 3.4 Å, but expanded considerably in the region between the openings of the meshes on the ceiling and floor of the channel. Hence the channel in the U-type structure also has a nodal character. The width of the channel in the U-type structure is approximated to 4.9 Å by subtracting twice the van der Waals radius of N (1.55 Å) from the distance of 8.037(5) Å between N(4) of the cyanide ion in moiety B and N(6) of the ph ligand. In the T-type structure the channel is most narrow between N(6) and N(6′) at the node, *ca.* 3.6 Å, and the widest between N(5) and N(5′) at the antinode, *ca.* 7.4 Å.

Little distortion has been observed for the square-planar moieties, but the co-ordination sphere about the Cd atom is considerably distorted from a regular octahedron in both U- and T-type structures. The Cd–N bond lengths range from 2.20(2) Å for Cd–N(1) in U-6 to 2.452(5) Å for Cd–N(3) in U-1, the N(*i*)–Cd–N(*j*) angles from 74.8(6)° for N(5)–Cd–N(6) to 102.3(6)° for N(2)–Cd–N(6) in T-1. Although the Ni(1)–C–N–Cd sequence is almost linear, the Cd–N–C angles associated with Ni(2) deviate by 24–37° from 180°. No significant correlation has been observed between the distortion and the guest.

Table 3 Refined atomic parameters for the host atoms in U-4 and T-1

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) $[(pn)Cd(CN)_4Ni]\cdot 0.5OEt_2$ U-4			
Cd	0.284 03(2)	0.134 62(1)	−0.126 13(4)
Ni(1)	$\frac{1}{4}$	0	0.365 30(9)
Ni(2)	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$
N(1)	0.261 4(3)	0.078 6(1)	0.086 8(5)
N(2)	0.240 8(3)	−0.078 6(1)	0.644 7(5)
N(3)	0.332 5(3)	0.197 4(2)	0.088 4(6)
N(4)	0.632 7(3)	0.169 2(1)	0.133 0(6)
N(5)	0.324 2(3)	0.193 2(2)	−0.348 4(6)
N(6)	0.450 8(3)	0.124 7(1)	−0.168 6(5)
C(1)	0.256 3(3)	0.048 7(1)	0.192 5(5)
C(2)	0.244 5(3)	−0.048 6(2)	0.538 4(5)
C(3)	0.395 5(3)	0.217 4(2)	0.152 1(6)
C(4)	0.581 2(3)	0.199 5(2)	0.176 6(6)
C(5)	0.426 2(5)	0.192 0(4)	−0.371(1)
C(6)	0.482 9(5)	0.158 6(4)	−0.304(1)
C(7)	0.588 8(4)	0.159 0(3)	−0.338 9(9)
(*b*) $[(pn)Cd(CN)_4Ni]\cdot 0.5Cl_2CHCHCl_2$ T-1			
Cd	0.218 94(4)	0.114 14(2)	0.130 75(7)
Ni(1)	0.248 9(1)	$\frac{1}{4}$	0.624 1(2)
Ni(2)	$\frac{1}{2}$	0	0
N(1)	0.249 0(6)	0.171 4(3)	0.905(1)
N(2)	0.242 1(6)	0.170 7(2)	0.345 2(9)
N(3)	0.667 0(5)	0.051 5(3)	0.162(1)
N(4)	0.399 6(5)	0.080 3(3)	0.126(1)
N(5)	0.176 5(5)	0.057 0(3)	−0.099(1)
N(6)	0.056 3(5)	0.129 5(3)	0.080 0(9)
C(1)	0.249 0(6)	0.201 4(3)	0.798(1)
C(2)	0.246 5(6)	0.200 8(3)	0.451 3(9)
C(3)	0.604 3(6)	0.031 6(3)	0.099(1)
C(4)	0.420 1(5)	0.050 2(3)	0.080 7(9)
C(5)	0.075 3(8)	0.060 4(6)	−0.123(2)
C(6)	0.025 5(8)	0.098 6(7)	−0.064(2)
C(7)	−0.079 6(7)	0.100 5(6)	−0.104(2)

Array of the Guest Molecules.—Since the diffraction data provide support for the same space groups, *A*2/*a* for U and the *Pnma* for T, in each type of structure, a statistical distribution related to the inversion centre in U or the mirror plane in T is inevitable for those guests the molecular symmetries of which cannot be correlated with the symmetry elements in the channel. Hence, the guest is generally disordered to a greater or lesser extent in the refined crystal structure. The images of the guest molecules shown in Fig. 3 for the U-type and in Fig. 4 for the T-type structures should be regarded as those enforced by the respective space groups applied in the structure refinements. In addition to the disorder, the thermal amplitudes for the guest atoms are always extremely large suggesting that the guest molecules have a great degree of freedom in terms of thermal motion in the channel cavities. Relatively large thermal amplitudes have also been observed for the C atoms of the pn chelate ring in the host.

The straight-chain molecules in U-type structures. By the analogy with normal alkanes in the inclusion compound of urea,[2] straight-chain alkane molecules of carbon number *m* can be approximated to an ellipsoidal column with long (*ca.* 5.3 Å) and short (*ca.* 4 Å) diameters and length 1.256 (m − 1) + 4.0 Å.

The peaks observed in the Fourier map for pentane in U-1 are assigned to a pair of molecules taking the all-*trans* skeletal conformation distributed statistically with an equal probability by sharing the central and the terminal C atoms in common; the central C is on the centre of inversion at $\frac{1}{2}$, 0, $\frac{1}{2}$ [Fig. 3(*a*)].

Table 4 Refined parameters for the guest molecules

Code	Atom	*G**	*X*/*a*	*Y*/*b*	*Z*/*c*
U-1	GC(1)	1	0.5224(7)	0.0447(6)	0.204(2)
	GC(21)	*0.5*	0.513(1)	0.0063(5)	0.314(2)
	GC(22)	*0.5*	0.5080(9)	0.0366(5)	0.383(3)
	GC(3)	0.5	$\frac{1}{2}$	0	$\frac{1}{2}$
U-2	GC(1)	*0.71*	0.503(2)	−0.0066(8)	0.372(6)
	GC(2)	*0.71*	0.509(1)	0.0334(9)	0.298(6)
	GC(3)	*0.71*	0.518(2)	0.0180(9)	0.070(5)
U-3	GC(1)	*0.63*	0.507(1)	−0.0066(7)	0.370(6)
	GC(2)	*0.63*	0.509(1)	0.0302(8)	0.294(6)
	GC(3)	*0.63*	0.528(1)	0.0169(7)	0.068(4)
U-4	GO	0.5	0.499(2)	−0.012(1)	0.062(3)
	GC(1)	1	0.528(2)	0.020(1)	0.144(3)
	GC(2)	1	0.517(1)	0.030(1)	0.290(5)
U-5	GO(1)	*0.5*	0.484(2)	−0.0206(7)	0.379(7)
	GO(2)	*0.5*	0.547(2)	0.003(1)	0.088(5)
	GC(1)	*0.5*	0.514(2)	0.037(2)	0.319(7)
	GC(2)	*0.5*	0.542(2)	0.027(2)	0.201(6)
U-6	GBr	*0.5*	0.4906(7)	0.0049(5)	0.390(2)
	GC(1)	1	0.492(4)	0.052(3)	0.200(9)
	GC(2)	1	0.525(2)	0.009(1)	0.041(8)
U-7	GC(1)	*0.71*	$\frac{1}{2}$	0	$\frac{1}{2}$
	GC(2)	*0.71*	0.497(2)	0.007(2)	0.382(7)
	GC(3)	*0.71*	$\frac{1}{2}$	0	0
T-1	GCl(1)	0.5	−0.0064(9)	$\frac{1}{4}$	0.2155(9)
	GCl(2)	0.5	−0.0192(7)	$\frac{1}{4}$	0.780(1)
	GCl(3)	1	−0.0148(5)	0.1713(2)	0.4967(9)
	GC(1)	0.5	−0.046(6)	$\frac{1}{4}$	0.453(9)
	GC(2)	0.5	0.013(9)	$\frac{1}{4}$	0.56(1)
T-2	GCl(1)	*0.5*	−0.008(2)	0.1848(7)	0.495(3)
	GC(1)	0.5	−0.018(1)	$\frac{1}{4}$	0.807(3)
	GC(2)	0.5	−0.005(3)	$\frac{1}{4}$	0.61(1)
	GC(3)	0.5	−0.053(2)	$\frac{1}{4}$	0.42(1)
	GC(4)	0.5	−0.007(3)	$\frac{1}{4}$	0.205(4)
T-3	GCl(1)	0.5	−0.0237(6)	$\frac{1}{4}$	0.826(1)
	GCl(2)	*0.5*	0.000(1)	0.3150(6)	0.507(2)
	GC(1)	*0.5*	−0.009(3)	0.272(1)	0.613(7)
	GC(2)	0.5	−0.056(1)	$\frac{1}{4}$	0.456(6)
	GC(3)	0.5	−0.022(1)	$\frac{1}{4}$	0.250(3)
T-4	GO	*0.5*	−0.020(2)	0.199(1)	0.442(5)
	GC(1)	0.5	−0.049(2)	$\frac{1}{4}$	0.0339(7)
	GC(2)	0.5	0.034(3)	$\frac{1}{4}$	0.23(1)
	GC(3)	0.5	−0.015(3)	$\frac{1}{4}$	0.556(9)
T-5	GCl(1)	0.5	−0.0236(6)	$\frac{1}{4}$	0.185(1)
	GCl(2)	0.5	−0.0092(6)	$\frac{1}{4}$	0.735(2)
T-6	GBr(1)	0.5	−0.0191(4)	$\frac{1}{4}$	0.1936(9)
	GBr(2)	0.5	−0.0094(3)	$\frac{1}{4}$	0.764(1)
T-7	GCl(1)	0.5	0.0548(8)	$\frac{1}{4}$	0.149(1)
	GCl(2)	0.5	0.0052(9)	$\frac{1}{4}$	0.700(2)

* *G* = Multiplicity; those due to the disorder are in italics.

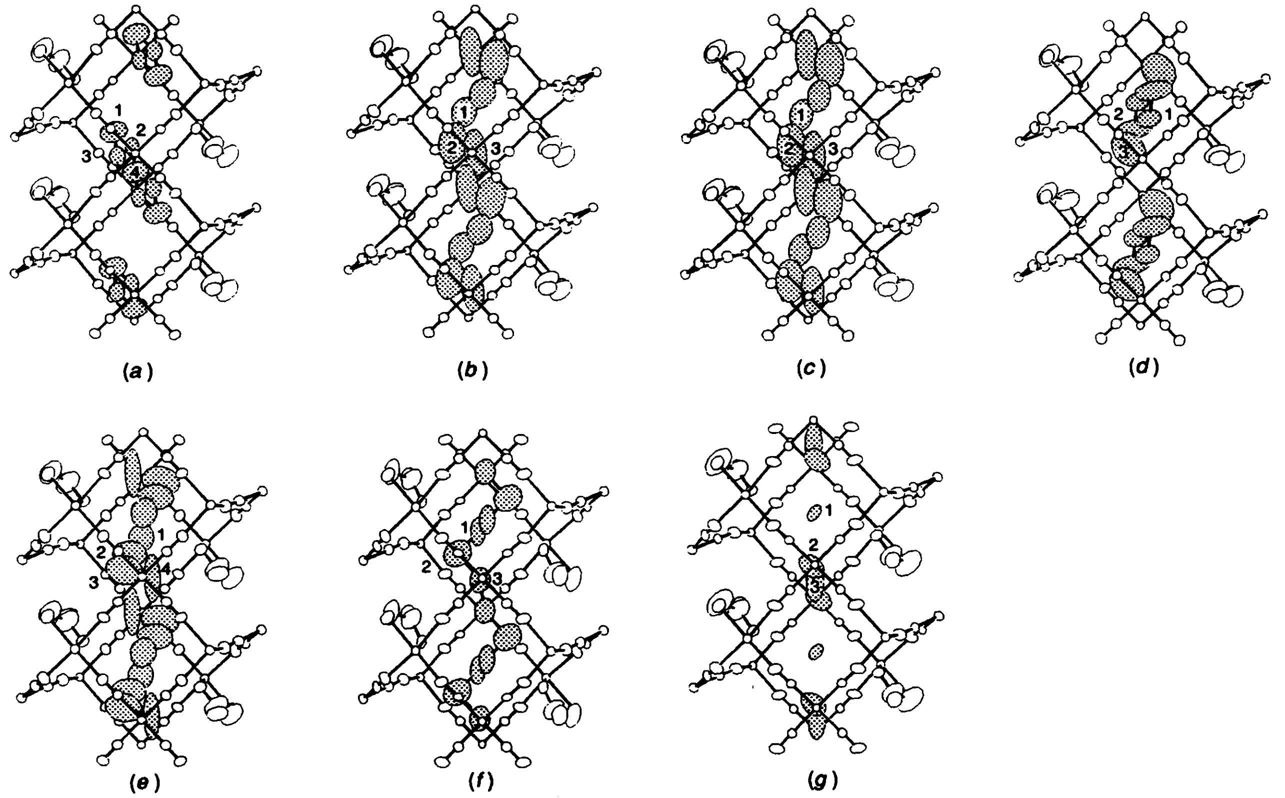


Fig. 3 Images of the guest molecules in the U-type structures: (*a*) pentane [1 = GC(1), 2 = GC(21), 3 = GC(22), 4 = GC(3)], (*b*) hexane [1 = GC(3), 2 = GC(2), 3 = GC(1)], (*c*) heptane [1 = GC(3), 2 = GC(2), 3 = GC(1)], (*d*) diethyl ether [1 = GO, 2 = GC(1), 3 = GC(2)], (*e*) ethane-1,2-diol (ethylene glycol) [1 = GO(2), 2 = GC(2), 3 = GC(1), 4 = GO(1)], (*f*) 1-bromobutane [1 = GC(2), 2 = GC(1), 3 = GBr] and (*g*) 1-bromopentane [1 = GC(3), 2 = GC(2), 3 = GC(1)]

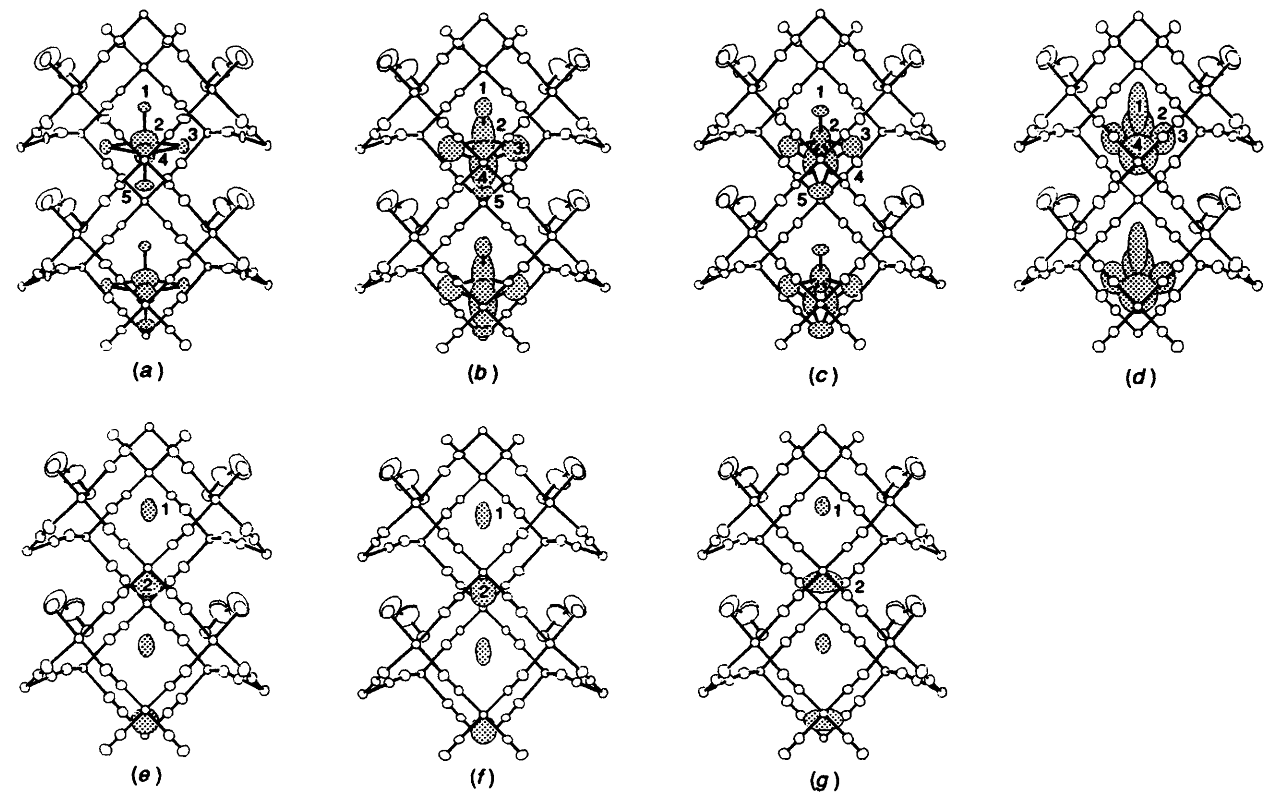


Fig. 4 Images of the guest molecules in the T-type structures: (*a*) 1,1,2,2-tetrachloroethane [1 = GCl(1), 2 = GC(1), 3 = GCl(3), 4 = GC(2), 5 = GCl(2)], (*b*) 2-chlorobutane [1 = GC(4), 2 = GC(3), 3 = GCl, 4 = GC(2), 5 = GC(1)], (*c*) 1,2-dichloropropane [1 = GC(1), 2 = GC(2), 3 = GCl(2), 4 = GC(1), 5 = GCl(1)], (*d*) Pr^{i}OH [1 = GC(2), 2 = GC(1), 3 = GO, 4 = GC(1)], (*e*) 1,2-dichloroethane [1 = GCl(1), 2 = GCl(2)], (*f*) 1,2-dibromoethane [1 = GBr(1), 2 = GBr(2)] and (*g*) 1,3-dichloropropane [1 = GCl(1), 2 = GCl(2)]

Although pentane was observed as the discrete molecule in the channel of U-1, giving a stoichiometric coefficient $n = 0.5$, hexane in U-2 and heptane in U-3 [Fig. 3(*b*) and 3(*c*)] are observed as polymethylene chains of six C atoms in length without any cut-off between molecules. Increases of *ca.* 14 and 28% in length for hexane and heptane from that of pentane are reasonable for decreases in n to *ca.* 0.36 and 0.32, respectively (see Table 1).

Diethyl ether with a five-atom skeleton in U-4 [Fig. 3(*d*)] is observed as a discrete molecule, like pentane in U-1. The central oxygen (GO), however, is distributed statistically about the inversion centre at $\frac{1}{2}$, 0, 0, *i.e.* the centre of gravity of the molecule is displaced by $\frac{1}{2}$ along the c axis from that of pentane in U-1. In other words, the diethyl ether is accommodated in the region sandwiched by the mesh openings, but the pentane by the crossings of the Ni(1)(CN–Cd)$_4$ (moiety A) doubly bridged one-dimensional extensions. The distance of 3.20(3) Å between GO and N(6) of the pn suggests a hydrogen bond stabilising the guest at this position. As for the ethane-1,2-diol in U-5 [Fig. 3(*e*)], a pair of discrete molecules is distributed separately about the inversion centre $\frac{1}{2}$, 0, 0. Although hydrogen bonds N–H $\cdots$ O between the pn nitrogen in the host and the terminal OH groups of the guest can be imagined, ambiguities remain in the molecular structure, distribution, and the stoichiometry; the analytical results are rather non-stoichiometric.

The 1-bromobutane molecule in U-6 gives a point-symmetrically distributed pair of Br atoms about $\frac{1}{2}$, 0, 0 at both sides of the butane skeleton which is centred at $\frac{1}{2}$, 0, $\frac{1}{2}$. The guest should adopt random orientations with respect to the bromine terminal. If it takes up an ordered orientation, the crystal symmetry should be lowered by losing at least the inversion centres from the *A*2/*a* space group. Such a lowering of the symmetry was not observed. The 1-bromopentane in U-7 appears to be disordered to such an extent that only four peaks appeared on the Fourier map. They were assigned tentatively to C atoms; no peaks could be assigned to Br. The analytical results supporting $n = 0.36$ similar to that for hexane in U-2 are reasonable for 1-bromopentane with a six-atom skeleton.

The guest molecules in T-type structures. Owing to the nodal character of the T-type structure, the stoichiometry of one guest in one loop is established for all the examined guests except for Pr^{i}OH in T-4. However, highly disordered structures with unusual molecular shapes and extremely large thermal amplitudes have been observed for the guests in the antinodal region of the channel, where considerable freedom of motion may be allowed; the unusual shapes are partly due to the symmetry elements of the *Pnma* space group. In the cases of the three dihalogenoalkanes in T-5, -6 and -7 [Fig. 4(*e*)–4(*g*)], no definite peaks could be found for the skeletal C atoms; the atomic parameters were refined only for the halogen atoms.

Except for MeCHClEt in T-2 and Pr^{i}OH in T-4, each of the guests has a terminal halogen atom, which is located in the vicinity of the node within a hydrogen-bond distance of the pn nitrogen atoms N(6) and N(6'). It appears that the opening between the loops is blocked with the halogen atom, the thermal amplitude of which is in general smaller than those of the atoms in the antinodal region. The blocking effect of the halogen atom may contribute to the preference of the straight-chain dihalogenoalkanes for the nodal rather than the snake-like channel. In T-5 to -7 the halogen atom at the pn nitrogen side has a smaller thermal amplitude than that at the antinodal side. Hence, the halogen atom at the head of the chain blocks the opening *via* hydrogen bonds involving the pn nitrogen atoms; the chain in the antinodal region undergoes thermal motion to such an extent that no atomic positions are observable, but the tail halogen is forced to move about the narrower region in the vicinity of the node so as to give observable atomic positions.

The atomic positions observed for Pr^{i}OH give an unusual molecular structure [Fig. 4(*d*)]. It appears that the OH group, distributed about the mirror plane, does not participate in any hydrogen bonds. The analytical results are ambiguous as to the occupation of the guest in the loop. However, the structure refinement assuming $n = 0.5$ gave the best convergence among the T-group compounds.

Comparison with Inclusion Compounds of Urea and Thiourea.—The common factor for the present and the urea and thiourea inclusion compounds is that the guest stabilises the host structure selectively. Although we examined more than fifty aliphatic species with various chain lengths and alicyclic ones,* single crystals suitable for X-ray crystallography have so far been obtained only for guests with relatively short chain lengths, as described above. The channels in the present U- and T-type structures have greater nodal character than those of the urea and thiourea inclusion compounds due to the doubly bridged one-dimensional $>[\mathrm{Ni}\langle(\mathrm{CN{-}Cd{-}NC})_2\rangle]_\infty$ mesh structures at the top and bottom of the channel. In other words, the cavities in these structures provide cages in which the guest is imprisoned as defined for clathrates by Palin and Powell.[4] In this respect the present structures are more specific for short-chain guests than are the channels in the urea and the thiourea host structures; heptane is the shortest normal alkane to stabilise the urea host structure of c dimension *ca.* 11.0 Å along the channel.

Generally host and guest are incommensurate with each other along the axis of the channel in channel-cavity inclusion compounds; incommensurateness along the lateral directions is also probable. As a number of single-crystal studies[2,5] on the urea and thiourea inclusion compounds have shown, it is rather difficult to obtain definite atomic positions for the guest molecule crystallographically, although remarkable progress has recently been made in discriminating the host and guest in their periodicities not only along the channel but also about the interchannel arrangement of the guest molecules in urea as host.[6,7] Except for hexane in U-2 and heptane in U-3, the guest molecules in the present U series are accommodated almost stoichiometrically and have been observed as discrete moities albeit with a greater or lesser extent of disorder. In addition to the cage-like character of the channel, the host–guest interaction involving hydrogen bonding may favour the stoichiometric retention of guests with appropriate dimensions and functional groups and their observation as discrete moieties in the present U and T channels.

Another fact to be noted is the structural variation of the metal complex host [(pn)Cd(CN)$_4$Ni] upon change of the guest molecule. The difference between the U- and T-type structures is more analogous to the structural variations described by Otto[5c] for urea inclusion compounds of α,ω-dihalogenoalkanes than to that between the urea and thiourea inclusion compounds. The crystal system was reported to be rhombohedral for 1,4-, 1,5-

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* Normal alkanes C_nH_{2n+2} (n = 8–12) did not give well developed single crystals, although the formation of microcrystalline substances has been observed. The compounds $Me_2CHCHMe_2$, $CH_2{=}CHCH{=}CH_2$, $O(CH_2CH_2)_2O$, HCO_2H, $MeCO_2H$, $NC(CH_2)_4CN$, CH_2Cl_2, CCl_4, CH_2Br_2, CBr_4, $MeCHClCH_2CH_2Cl$, MeCHClCHClMe, CH_2ICH_2I, $CH_2{=}CHClCHCl{=}CH_2$, *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, 1,3- and 1,5-*cyclo*-C_8H_{12} and dicyclopentadiene did not give any crystalline substances. During the preparation of this manuscript, single crystals of T-type (Bu^{t}OH, Me_2CO and CMe_4) and U-type [$CH_3(CH_2)_5Br$] inclusion compounds were obtained; their structures will be reported elsewhere. Powder diffraction data for limited amounts of powdery products suggest U-type structures for $C_7H_{13}OH$ and T-type structures for $CHCl_3$, $MeCHCl_2$, $CH_2ClCHCl_2$, CH_2ClCH_2Cl and $CCl_2{=}CCl_2$ inclusion compounds.

† It seems desirable to reinvestigate the structural variations of the urea–α,ω-dihalogenoalkane inclusion compounds in comparison with later results for inclusion compounds of $Br(CH_2)_nBr$ (n = 7–12) in ref. 7(*c*) which reported that the host keeps its hexagonal symmetry regardless of changes of the guest based on the discrimination of the periodic repeat distance between the host and the guest.

and 1,6-dichloroalkanes but monoclinic for 1,6-dibromohexane as the guest; the variations were interpreted in terms of the deformation of the host from the ideal hexagonal structure.† As for the present metal complex host, under experimental conditions quite similar to those we employed, non-substituted small aromatic molecules such as pyrrole, thiophene and benzene give Hofmann pn-type clathrates, $[(pn)Cd(CN)_4Ni]\cdot 1.5G$.[8] From the single-crystal structure of the pyrrole clathrate, the host complex has a structure substantially similar to that of Hofmann's benzene clathrate $[(NH_3)_2Ni(CN)_4Ni]\cdot 2C_6H_6$:[9,10] the two-dimensionally extended $CdNi(CN)_4$ networks are stacked with the pillars of the ambidentate pn between the Cd atoms. When the aromatic guest has a substituent such as methyl or nitro, the host adopts a channel structure like those in the present U- or T-type structures. Thus there is a wide range of selectivity of the guest for the $[(pn)Cd(CN)_4Ni]$ host structure. Aromatic guest inclusion compounds of U and T types will be reported elsewhere.[11]

On the Chiralities of the pn and of the Guests.—The pn chelate rings in the U- and T-type structures are almost coplanar with regard to the skeletal atoms. The skeletal atoms C(5), C(6) and C(7) deviate little from the plane defined by Cd, N(5) and N(6): the deviations are within ± 0.2 Å except for 0.4 Å for C(6) in U-6. Moreover, the thermal parameters are so large that significant discrimination was impossible between the δ and λ conformations of the pn chelate ring. We attempted to prepare the clathrates using L-pn and racemic mixtures of 2-chlorobutane (T-2) and 1,2-dichloropropane (T-3). The results of the structure analyses completely coincided with those for T-2 and T-3 prepared using DL-pn. Chiral recognition of the guests appears not to be practical in these T-type structures.

Experimental

Preparation.—Single crystals of the inclusion compounds were obtained by leaving aqueous solutions containing the host in contact with the neat phase of the guest species in a refrigerator for a few days; yellow plate-like crystals were obtained at the interface between the aqueous and organic phases and the bottom of the aqueous phase. Aqueous solutions were prepared by the procedure reported for the Hofmann pn-type clathrates,[8] but the pH was adjusted to 8.0 for the U and to 8.0–9.0 for the T group using citric acid. The pH appears to be critical in order to obtain well developed crystals. The presence of the guest in the product was ascertained by infrared spectrometry. The crystals gradually liberate the guest under ambient conditions. Thermal gravimetry indicated that the liberation of the guest is not accomplished in a single stage but is accompanied with thermal decomposition of the host.

Crystallography.—All the crystals subjected to X-ray analysis were coated with acrylate resin in order to prevent spontaneous decomposition in the ambient atmosphere. Some details of the experimental conditions are summarised in Table 2. Three representative reflections were monitored at regular intervals throughout the data collection on the four-circle automated diffractometer. Although a few crystals showed decay to a small extent, the corrections were limited to Lorentz polarisation and absorption. The density was measured by the flotation technique in a carbon tetrachloride–bromoform mixture.

All the calculations for the structure refinement were carried out on a HITAC M680/682H computer at the computer centre of this University using the programs in UNICS III[12] including ORTEP[13] and their local versions; atomic scattering factors for neutral atoms were taken from ref. 14, including real dispersion corrections. The heavy-atom method was applied to determine the positions of Cd and Ni. Successive Fourier and Fourier-difference syntheses and block-diagonal least-squares procedures were applied to refine all the non-hydrogen atoms anisotropically with units weights.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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