Different Co-ordination Behaviour of 1,2-Diaminoethane (en) and Tetracyanonickelate(II) upon Accommodation of Polar Guest Molecules in Their Metal Complex Hosts: Crystal Structures of $[M(en)_2Ni(CN)_4]\cdot 2PhNH_2$ (M = Ni, Cu, Zn or Cd) and $[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]\cdot 4PhOH$[†]

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The single-crystal structures have been determined for aniline and phenol clathrates. Aniline clathrates $[M(en)_2Ni(CN)_4]\cdot 2PhNH_2$ (M = Ni, Cu, Zn or Cd; en = 1,2-diaminoethane) are isomorphous, having monoclinic space group $P2_1/c$ ($Z = 2$). The unit cell parameters a, b, c and β, and R index for the reflections used are: M = Ni, 9.452(3), 10.125(3), 13.440(3) Å and 107.27(2)°, 0.0443 for 1806; for M = Cu, 9.547(4), 10.621(5), 12.746(3) Å and 107.89(2)°, 0.0635 for 1861; for M = Zn, 9.550(3), 10.407(2), 13.026(2) Å and 107.50(1)°, 0.0513 for 1758; and for M = Cd, 9.924(2), 10.545(3), 12.510(1) Å and 107.63(1)°, 0.0456 for 1829. The guest $PhNH_2$ molecules are accommodated among $[-M(en)_2-NC-Ni(CN)_2-CN-]_n$ chains extending along the b axis. The bis(en)-chelated M atoms are linked with *trans*-di-μ-cyano-dicyanonickelate(II) moieties alternately, and adopt an elongated octahedral configuration along the chain. The phenol clathrate $[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]\cdot 4PhOH$ belongs to the triclinic system, space group $P\bar{1}$, with $a = 11.868(1)$, $b = 13.030(1)$, $c = 7.7113(6)$ Å, $\alpha = 105.956(7)$, $\beta = 94.951(8)$, $\gamma = 91.584(9)°$, $Z = 1$ and $R = 0.0410$ for 4095 reflections. Three kinds of crystallographically independent PhOH molecules are enclathrated in the three-dimensional host framework in which the en-chelated Cd atoms are linked with infinite $[{>}Ni{<}(CN-Cd-NC-)_2]_n$ chains and $Cd-NC-Ni(CN)_2-CN-Cd$ and Cd–en–Cd bridges. Interhost, interguest and host–guest hydrogen-bond formation stabilize the whole crystal structures, which are compared with those of $[M(en)_2Ni(CN)_4]$ complexes and the $[Cd(en)Ni(CN)_4]\cdot 2C_6H_6$ clathrate.

With regard to the Hofmann-type and analogous inclusion compounds,[1,2] the Hofmann-en-type $[Cd(en)Ni(CN)_4]\cdot 2G$ ($G = C_4H_5N$, C_4H_4S or C_6H_6) has a host structure similar to that of the Hofmann-type $[Cd(NH_3)_2Ni(CN)_4]\cdot 2G$ ($G = C_4H_5N$, C_4H_4S, C_6H_6 or $PhNH_2$): the guest G molecules are accommodated between the layers of the *catena*-[cadmium(II) tetra-μ-cyanonickelate(II)] network. The NH_3 ligands protrude into the layers in the Hofmann-type compound, but the 1,2-diaminoethane (en) spans the layers at every Cd atom in the Hofmann-en type. Since the Cd-en-Cd span is *ca.* 8.0 Å the latter host cannot accommodate aniline as guest; powder X-ray data suggest that an interlayer distance of *ca.* 8.65 Å (M = Cd, M′ = Pd) is the smallest which can accommodate aniline in the clathrates $[M(NH_3)_2M'(CN)_4]\cdot 2PhNH_2$ (M = Mn, Fe, Co, Ni or Cd; M′ = Ni or Pd).[1] However, when the square-planar $Ni(CN)_4$ is replaced by the tetrahedral $Cd(CN)_4$, both $[Cd(NH_3)_2Cd(CN)_4]$ and $[Cd(en)Cd(CN)_4]$ hosts enclathrate aniline molecules;[3] in the latter, distortion of the en-reinforced three-dimensional host framework and the hydrogen bonds between guests in neighbouring cavities are favourable to the enclathration of aniline molecules. Sopková[4] reported several non-stoichiometric compounds containing aniline and phenol such as $[Ni(en)_2Ni(CN)_4]\cdot 0.14PhNH_2$ and $[Ni(en)_2Pt(CN)_4]\cdot 0.14PhOH$ containing twice as much en in comparison with the Hofmann-en type; little was described of their crystal structures.

We obtained an isostructural series of inclusion compounds $[M(en)_2Ni(CN)_4]\cdot 2PhNH_2$ (M = Ni, Cu, Zn or Cd) as single crystals; a phenol-guest compound $[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]\cdot 4PhOH$ was also prepared under similar conditions. This paper describes their crystal structures in detail.

Experimental

Preparation.—(*a*) $[Ni(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **1** *and* $[Cu(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **2**. To an aqueous solution containing 5 mmol each of $NiCl_2\cdot 6H_2O$ or $CuCl_2\cdot 2H_2O$, $K_2[Ni(CN)_4]\cdot H_2O$ and 10 mmol of en, the appropriate amount of citric acid was added to adjust the pH to 9 in a final volume of *ca.* 100 cm^3. After a small amount of precipitate had been filtered off, the solution was placed on a layer of neat $PhNH_2$ and allowed to stand in a refrigerator at *ca.* 5 °C for a few weeks. Mauve and blue needle-like crystals were obtained for compounds **1** and **2** respectively (Found: C, 46.1; H, 5.80; N, 26.0. $C_{20}H_{30}N_{10}Ni_2$ **1** requires 45.5; H, 5.75; N, 26.5. Found: C, 45.2; H, 5.80; N, 25.5. $C_{20}H_{30}CuN_{10}Ni$ **2** requires C, 45.1; N, 5.70; N, 26.3%).

(*b*) $[Zn(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **3** *and* $[Cd(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **4**. Yellow needles were obtained for both compounds **3** and **4** by procedures similar to the above except that $ZnCl_2\cdot 2H_2O$ or $CdCl_2\cdot 2.5H_2O$ and 50 mmol of en were used (Found C, 44.3; H, 5.65; N, 25.7. $C_{20}H_{30}N_{10}NiZn$ **3** requires C, 44.9; H, 5.65; N, 26.2. Found: C, 42.3; H, 5.30; N, 23.3. $C_{20}H_{30}CdN_{10}Ni$ **4** requires C, 41.3; H, 5.20; N, 24.1%).

(*c*) $[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]\cdot 4PhOH$ **5**. Using neat PhOH in place of neat $PhNH_2$ in (*b*) yellow plate-like crystals of

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Crystallographic and selected experimental data for compounds **1**–**5**[a]

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{20}H_{30}N_{10}Ni_2$	$C_{20}H_{30}CuN_{10}Ni$	$C_{20}H_{30}N_{10}NiZn$	$C_{20}H_{30}CdN_{10}Ni$	$C_{38}H_{48}Cd_2N_{14}Ni_2O_4$
M	527.91	532.76	534.61	581.63	1107.09
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	9.452(3)	9.547(4)	9.550(3)	9.924(2)	11.868(1)
b/Å	10.125(3)	10.621(5)	10.407(2)	10.545(3)	13.030(1)
c/Å	13.440(3)	12.746(3)	13.026(2)	12.510(1)	7.7113(6)
α/°	90	90	90	90	105.956(7)
β/°	107.27(2)	107.89(2)	107.50(1)	107.63(1)	94.951(8)
γ/°	90	90	90	90	91.584(9)
U/Å^3	1228.2(6)	1230.0(7)	1234.8(4)	1247.7(4)	1140.7(2)
Z	2	2	2	2	1
D_m, D_c/g cm^{-3}	1.43(1), 1.43	1.47(2), 1.44	1.42(1), 1.44	1.58(2), 1.55	1.59(1), 1.61
F(000)	552	554	556	592	558
μ(Mo-Kα)/cm^{-1}	15.67	16.63	17.88	16.34	17.86
Crystal size/mm	0.50 × 0.40 × 0.20	0.52 × 0.38 × 0.18	0.50 × 0.40 × 0.20	0.38 × 0.28 × 0.26	0.32 × 0.28 × 0.20
hkl ranges (4 < 2θ < 60°)	0–13, 0–14, −18 to 18	0–13, 0–14, −17 to 17	0–13, 0–14, −18 to 17	0–13, 0–14, −17 to 16	0–16, −18 to 18, −10 to 10
Scan width/°	1.155 + 0.3 tan θ	1.155 + 0.3 tan θ	1.155 + 0.3 tan θ	1.050 + 0.3 tan θ	0.787 + 0.3 tan θ
Transmission factors	0.77–1.00	0.73–1.00	0.81–1.00	0.92–1.00	0.87–1.00
Reflections measured	4102	4177	4126	4105	7101
Unique reflections	2874	2906	2836	2909	6134
N_r[b]	1806	1861	1758	1829	4095
N_p[b]	148	148	148	148	294
g[b]	3.3×10^{-4}	9.0×10^{-4}	1.4×10^{-4}	5.5×10^{-4}	2.0×10^{-4}
R, *R′*[b]	0.0443, 0.0567	0.0635, 0.0955	0.0513, 0.0553	0.0456, 0.0643	0.0410, 0.0438
Goodness of fit[b]	1.881	2.283	2.073	1.776	1.454
$(\Delta/\sigma)_{max}$	0.016	0.007	0.024	0.013	0.017
Maximum, minimum Δρ/e Å^{-3}	+0.40, −0.52	+0.89, −0.69	+0.38, −0.45	+0.65, −0.59	+0.85, −0.58

[a] Conditions in common: 2θ–ω scan. The densities were measured by the flotation method in 1,2-dibromoethane–mesitylene. [b] N_r = Number of used reflections with $|F_o| > 4\sigma(F_o)$, N_p = number of refined parameters, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_r - N_p)]^{\frac{1}{2}}$.

compound **5** were obtained (Found: C, 42.2; H, 4.55; N, 17.1. $C_{38}H_{48}Cd_2N_{14}Ni_2O_4$ requires C, 41.2; H, 4.35; N, 17.7%).* Attempts to obtain crystals of the compounds with M = Ni, Cu or Zn in place of Cd were not successful.

Crystallography.—The crystallographic and selected experimental data for compounds **1**–**5** are listed in Table 1. Single-crystal X-ray measurements were carried out at room temperature on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo-Kα_1 radiation (λ = 0.709 26 Å) from a rotating molybdenum anticathode for each single-crystal specimen coated with epoxy resin. The cell dimensions were refined using 25 reflections (33 ⩽ 2θ ⩽ 35°). Three standard reflections were monitored after every 200 for **4** and **5**, after every 150 for **1** and **3**, and five were monitored after every 150 for **2**: no significant decay was observed. Lorentz, polarization and empirical absorption corrections[5] were applied for all compounds. An extinction correction was applied only for **5** according to the equation $F_{corr} = F_c\{1 - [x(F_c)^2/\sin\theta]\}$; *x* was refined to $1.7(2) \times 10^{-7}$. The Cd and Ni atoms in **4** and **5** were located from Patterson syntheses. All non-H atoms found in the subsequent Fourier and Fourier difference syntheses were refined anisotropically through full-matrix least-squares procedures. The atomic positions found for **4** were applied as an initial model for **1**–**3**. Hydrogen atoms were located, but not refined, at calculated positions and included in the final F_c calculations.

All the calculations were performed with the program SHELX 76[6] on a HITAC M-680H computer in the Computer Centre of the Institute for Molecular Science, Okazaki. Atomic scattering factors were taken from ref. 7 for Cd, Cu, Ni and Zn, and from SHELX 76[6] for C, H, N and O.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

The refined atomic parameters for compounds **1**–**4** are listed in Table 2, and for **5** in Table 3. The ORTEP[8] views of the structures of **4** and **5** are shown in Figs. 1 and 2. Compounds **1**–**3** are isostructural with **4**. Interatomic distances and angles are summarized in Table 4 for **1**–**4**, and in Table 5 for **5**.

Structures of Compounds **1**–**4**.—The space group $P2_1/c$ was uniquely determined from the systematic absences; compounds **1**–**4** are isostructural with one another. The host complex has a chain structure of $[-M(en)_2-NC-Ni(CN)_2-CN-]_n$, in which the $Ni(CN)_4^{2-}$ behaves as a bidentate bridging ligand through the N atoms of the CN groups in *trans* positions between the chelated $M(en)_2^{2+}$ moieties. The catenation mode of the $Ni(CN)_4$ may be denoted as *trans*-one-dimensional.[2b] The infinite chain involves protrusion of the en-chelate rings from the octahedral M at $0,\frac{1}{2},0$ along the ±*a* direction and that of the terminal CN from the square-planar Ni along the $\pm(a - c)$ direction so that the cavities for the guest aniline molecules in the interchain space are centred approximately at $\frac{1}{2},\frac{1}{4},\frac{1}{4}$ and the equivalent positions in the $P2_1/c$ space group.

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* The analytical results contain some discrepancies from the required values probably due to insufficient washing of the products before the analysis; however, too much washing sometimes caused decomposition of the products which are unstable under ambient conditions, gradually liberating the guest molecules. The discrepancies do not indicate guest-deficient compositions: the C:H:N ratios in the found values suggest excessive amounts of the guest aromatic molecules adsorbed on the products. The occupancy factors refined for the guests in the structure refinement were all greater than unity: 1.029(8), 1.074(10), 1.047(8) and 1.051(10) for $PhNH_2$ in **1**, **2**, **3** and **4**, and 1.053(6), 1.089(8) and 1.107(11) for PhOH-1, -2 and -3 in **5**.

Table 2 Final atomic coordinates for compounds **1–4**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
$[Ni(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **1**				$[Cu(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **2**			
Ni(1)*	0	0	0	Ni*	0	0	0
Ni(2)*	0	½	0	Cu*	0	½	0
N(1)	−0.0247(5)	0.2935(4)	0.0201(4)	N(1)	−0.0379(7)	0.2734(4)	0.0441(5)
N(2)	0.1206(7)	0.0650(6)	−0.1778(5)	N(2)	0.1381(7)	0.0836(5)	−0.1702(5)
N(3)	0.1166(5)	0.4534(4)	−0.1065(4)	N(3)	0.0982(6)	0.4427(5)	−0.1106(4)
N(4)	0.2100(5)	0.4966(4)	0.1080(3)	N(4)	0.2036(6)	0.5005(4)	0.1080(4)
C(1)	−0.0185(6)	0.1809(4)	0.0150(4)	C(1)	−0.0246(6)	0.1683(5)	0.0287(4)
C(2)	0.0771(7)	0.0371(5)	−0.1109(5)	C(2)	0.0879(7)	0.0492(6)	−0.1059(4)
C(3)	0.2688(7)	0.4139(6)	−0.0440(5)	C(3)	0.2527(9)	0.4116(7)	−0.0541(7)
C(4)	0.3227(7)	0.4983(6)	0.0496(5)	C(4)	0.3113(9)	0.4958(6)	0.0473(7)
N(11)	0.8047(10)	0.2722(6)	0.2121(6)	N(11)	0.8133(10)	0.2727(7)	0.2341(7)
C(11)	0.6618(9)	0.2478(6)	0.2108(6)	C(11)	0.6665(10)	0.2520(6)	0.2203(7)
C(12)	0.5746(12)	0.1665(7)	0.1314(7)	C(12)	0.5903(12)	0.1750(7)	0.1334(7)
C(13)	0.4258(14)	0.1428(8)	0.1332(9)	C(13)	0.4410(15)	0.1472(9)	0.1276(11)
C(14)	0.3682(14)	0.1954(11)	0.2089(10)	C(14)	0.3729(17)	0.2008(14)	0.2058(12)
C(15)	0.4602(13)	0.2749(9)	0.2854(9)	C(15)	0.4577(13)	0.2730(9)	0.2835(9)
C(16)	0.6028(11)	0.3034(7)	0.2872(6)	C(16)	0.6012(11)	0.3057(8)	0.2936(7)
$[Zn(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **3**				$[Cd(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **4**			
Ni*	0	0	0	Ni*	0	0	0
Zn*	0	½	0	Cd*	0	½	0
N(1)	−0.0286(7)	0.2826(4)	0.0338(5)	N(1)	−0.0267(7)	0.2762(5)	0.0435(6)
N(2)	0.1340(8)	0.0777(7)	−0.1714(5)	N(2)	0.1538(8)	0.0846(6)	−0.1614(6)
N(3)	0.1137(6)	0.4443(5)	−0.1115(4)	N(3)	0.1256(6)	0.4325(5)	−0.1210(4)
N(4)	0.2129(5)	0.5000(5)	0.1103(4)	N(4)	0.2314(6)	0.5015(5)	0.1156(4)
C(1)	−0.0206(7)	0.1751(5)	0.0229(5)	C(1)	−0.0167(6)	0.1696(6)	0.0312(5)
C(2)	0.0851(8)	0.0442(6)	−0.1068(5)	C(2)	0.0974(8)	0.0491(6)	−0.1001(6)
C(3)	0.2662(8)	0.4105(8)	−0.0479(7)	C(3)	0.2700(8)	0.4039(8)	−0.0507(7)
C(4)	0.3210(7)	0.4982(8)	0.0485(6)	C(4)	0.3233(7)	0.4988(7)	0.0440(7)
N(11)	0.8071(12)	0.2801(9)	0.2235(7)	N(11)	0.8128(11)	0.3028(10)	0.2316(8)
C(11)	0.6676(10)	0.2548(9)	0.2169(8)	C(11)	0.6794(11)	0.2659(9)	0.2212(9)
C(12)	0.5821(16)	0.1737(9)	0.1326(7)	C(12)	0.6046(13)	0.1853(8)	0.1343(7)
C(13)	0.4358(16)	0.1483(11)	0.1328(12)	C(13)	0.4653(13)	0.1515(10)	0.1241(10)
C(14)	0.3278(18)	0.2053(13)	0.2122(10)	C(14)	0.3805(23)	0.1950(13)	0.1994(11)
C(15)	0.4639(15)	0.2807(13)	0.2865(10)	C(15)	0.4659(13)	0.2709(13)	0.2787(13)
C(16)	0.6040(13)	0.3093(9)	0.2921(7)	C(16)	0.6074(13)	0.3147(8)	0.2988(7)

* Special position at the inversion centre; multiplicity = 0.5.

Table 3 Final atomic coordinates for compound **5**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cd	0.245 62(3)	0.194 12(3)	0.112 75(4)	O(11)	0.244 4(4)	0.712 2(4)	0.490 5(6)
Ni(1)[a,b]	0	0	½	C(11)	0.235 3(4)	0.740 8(4)	0.671 0(7)
Ni(2)[a,b]	½	½	0	C(12)	0.148 7(5)	0.809 0(4)	0.732 7(9)
N(1)	0.148 4(3)	0.090 2(3)	0.275 1(5)	C(13)	0.136 0(5)	0.839 5(5)	0.915 7(9)
N(2)	0.132 4(4)	0.127 1(3)	0.843 1(5)	C(14)	0.207 2(6)	0.805 4(5)	1.035 3(9)
N(3)	0.358 9(4)	0.303 1(3)	−0.012 1(6)	C(15)	0.293 7(6)	0.739 4(5)	0.970 9(9)
N(4)	0.424 2(4)	0.600 7(4)	0.365 7(6)	C(16)	0.308 3(5)	0.705 0(4)	0.786 8(8)
N(5)	0.120 6(4)	0.326 2(3)	0.227 3(6)	O(21)[a,c]	0.018 9(9)	0.640 6(8)	0.331 1(12)
N(6)	0.339 7(4)	0.292 1(4)	0.392 7(6)	C(21)	0.011 9(7)	0.574 9(5)	0.166 5(9)
N(7)	0.350 3(4)	0.043 9(4)	0.020 2(7)	C(22)	0.103 9(6)	0.553 3(6)	0.072 3(9)
C(1)	0.093 6(4)	0.055 7(3)	0.361 4(5)	C(23)	0.094 1(6)	0.478 6(7)	−0.094 6(9)
C(2)	0.081 8(4)	0.080 9(3)	0.711 5(5)	O(31)[c,d]	0.313 3(29)	−0.062 8(22)	0.517 7(34)
C(3)	0.412 1(4)	0.376 6(4)	−0.011 5(6)	O(32)[c,e]	0.356 4(15)	0.122 8(16)	0.622 1(22)
C(4)	0.454 6(4)	0.562 8(4)	0.229 8(7)	C(31)	0.395 2(13)	−0.041 4(10)	0.491 4(16)
C(5)	0.182 7(8)	0.405 3(6)	0.390 6(9)	C(32)	0.417 1(12)	0.067 3(9)	0.573 0(12)
C(6)	0.264 0(7)	0.361 7(7)	0.493 2(9)	C(33)	0.525 2(13)	0.109 3(7)	0.580 9(12)
C(7)	0.474 0(4)	0.052 1(4)	0.040 8(7)				

[a] Multiplicity 0.5. [b] Special position at the inversion centre. [c] Atom in disorder. [d] Multiplicity 0.23(1). [e] Multiplicity 0.27(1).

Hydrogen bonds are suggested between the host complex chains and between the host and the guest. Atom N(2) of the terminal CN group on the Ni in one chain is almost within hydrogen-bonding distance between the en NH_2 groups, N(3) and N(4), chelated to the M in the adjacent chain; additionally the NH_2 group of the guest aniline, N(11), is directed toward N(2). One of the en NH_2 groups, N(3), may also form a hydrogen bond with N(11). The respective distances between the N atoms in **1–4** are 3.294(7), 3.355(7), 3.391(8) and 3.619(8) for N(2)···N(3), 3.292(9), 3.214(9), 3.254(9) and 3.24(1) for N(2)···N(4), 3.35(1), 3.28(1), 3.35(1) and 3.45(1) for N(2)···N(11), and 3.304(9), 3.70(1), 3.40(1) and 3.25(1) Å for N(3)···N(11). Some of these appear to be too long for hydrogen bonds, although the critical distance, *e.g.* 3.3 Å, is

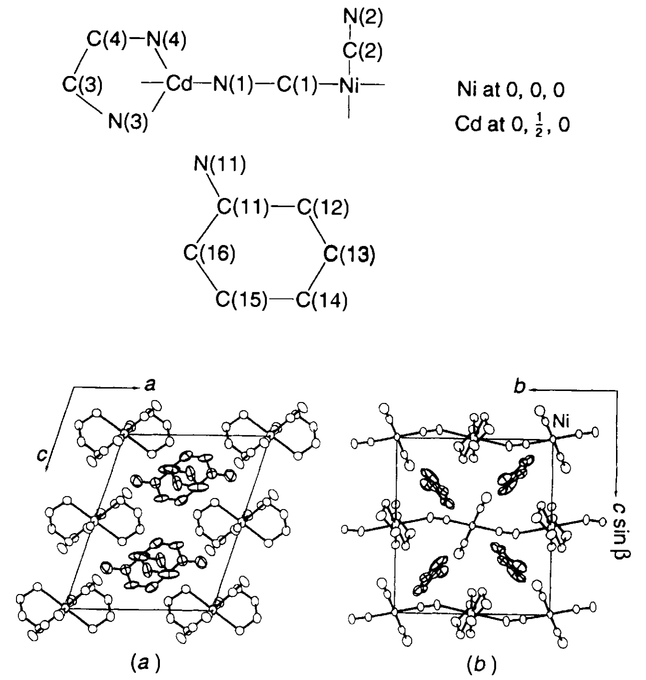

Fig. 1 Projections of [Cd(en)$_2$Ni(CN)$_4$]·2PhNH$_2$ **4** along (*a*) the *b* axis and (*b*) the *a* axis; 30% probability ellipsoids. Anisotropic peripheries have been shown for the guest aniline molecules. The atomic numbering is shown at the top

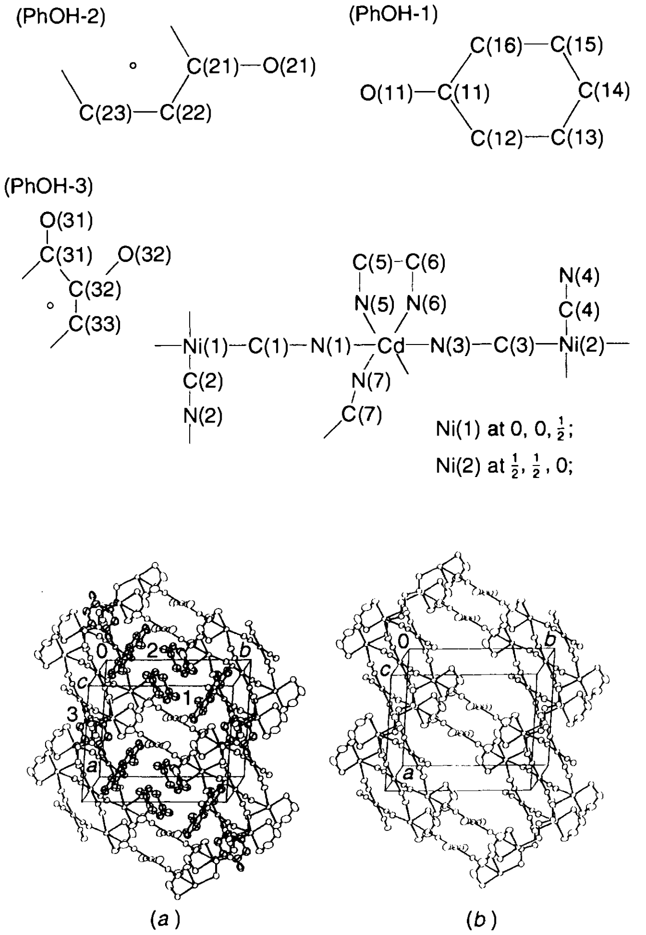

Fig. 2 Perspective views of [{Cd(en)$_2$}(en){Ni(CN)$_4$}$_2$]·4PhOH **5** (*a*) with the phenol guest molecules 1–3 and (*b*) without the guests; 30% probability ellipsoids. The atomic numbering is shown at the top; $\bar{1}$ (○) at 0, ½, 0 for PhOH-2 and at ½, 0, ½ for PhOH-3

Table 4 Selected interatomic distances (Å) and angles (°) for compounds **1**–**4**

	1	**2**	**3**	**4**
Ni–C(1)	1.856(4)	1.906(5)	1.866(6)	1.849(6)
Ni–C(2)	1.881(6)	1.863(6)	1.867(7)	1.871(7)
M–N(1)	2.130(4)	2.593(5)	2.336(5)	2.454(5)
M–N(3)	2.103(4)	2.005(5)	2.138(5)	2.345(5)
M–N(4)	2.083(4)	1.966(5)	2.107(5)	2.313(5)
C(1)–N(1)	1.144(6)	1.180(6)	1.134(7)	1.143(8)
C(2)–N(2)	1.130(7)	1.128(7)	1.134(8)	1.142(8)
N(3)–C(3)	1.489(8)	1.433(9)	1.485(9)	1.468(9)
N(4)–C(4)	1.499(7)	1.443(9)	1.489(8)	1.460(9)
C(3)–C(4)	1.481(9)	1.55(1)	1.51(1)	1.52(1)
N(11)–C(11)	1.37(1)	1.34(1)	1.34(1)	1.35(1)
C(11)–C(12)	1.41(1)	1.40(1)	1.43(1)	1.40(1)
C(12)–C(13)	1.43(1)	1.40(1)	1.42(2)	1.40(1)
C(13)–C(14)	1.40(2)	1.46(2)	1.47(2)	1.51(2)
C(14)–C(15)	1.39(2)	1.32(2)	1.34(2)	1.35(2)
C(15)–C(16)	1.37(1)	1.35(1)	1.35(1)	1.43(2)
C(16)–C(11)	1.42(1)	1.39(1)	1.42(1)	1.46(1)
N(2) ··· N(3^{I})	3.294(7)	3.355(7)	3.391(8)	3.619(8)
N(2) ··· N(4^{II})	3.292(9)	3.214(9)	3.254(9)	3.24(1)
N(2) ··· N(11^{III})	3.35(1)	3.28(1)	3.35(1)	3.45(1)
N(3) ··· N(11^{IV})	3.304(9)	3.70(1)	3.40(1)	3.25(1)
C(1)–Ni–C(2)	87.7(2)	88.0(3)	88.2(3)	88.3(3)
N(1)–M–N(3)	88.0(2)	88.6(2)	88.7(2)	88.0(2)
N(1)–M–N(4)	90.7(2)	90.9(2)	90.8(2)	91.2(2)
N(3)–M–N(4)	83.5(2)	87.1(2)	83.1(2)	77.6(2)
M–N(1)–C(1)	163.9(4)	150.3(5)	156.4(5)	153.6(6)
Ni–C(1)–N(1)	175.7(4)	178.1(5)	176.6(6)	175.6(6)
Ni–C(2)–N(2)	176.8(5)	177.1(6)	176.3(7)	176.7(7)
M–N(3)–C(3)	106.9(3)	108.6(4)	107.4(4)	106.8(4)
M–N(4)–C(4)	108.2(3)	107.2(4)	108.3(4)	107.6(4)
N(3)–C(3)–C(4)	110.8(5)	108.6(6)	110.9(6)	112.2(6)
N(4)–C(4)–C(3)	108.6(5)	110.5(6)	109.5(5)	110.9(5)
N(11)–C(11)–C(12)	118.1(9)	116.8(9)	120(1)	122(1)
N(11)–C(11)–C(16)	121.1(8)	118.4(9)	120(1)	120(1)
C(12)–C(11)–C(16)	120.8(8)	124.8(9)	120(1)	119(1)
C(11)–C(12)–C(13)	116.3(9)	115(1)	116(1)	120(1)
C(12)–C(13)–C(14)	123(1)	121(1)	123(1)	126(1)
C(13)–C(14)–C(15)	118(1)	118(1)	116(2)	107(2)
C(14)–C(15)–C(16)	122(1)	125(1)	126(1)	133(2)
C(11)–C(16)–C(15)	119.9(8)	116.5(9)	120(1)	115(1)

Symmetry operations I $-x$, $y - \frac{1}{2}$, $-z - \frac{1}{2}$; II x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; III $x - 1$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; IV $-x + 1$, $-y + 1$, $-z$.

rather arbitrary. The fact is that the N ··· N interatomic distances depend on M and that hydrogen-bond formation is most plausible between N(2) and N(4) for all the structures.

Structure of Compound **5**.—The host structure in Fig. 2 is built up of two kinds of Ni(CN)$_4$ moieties centred on Ni(1) and Ni(2) respectively, and of en ligands, one being chelating and the other bridging to the respective Cd atoms. The en-chelated Cd(en) moieties are linked to Ni(1)(CN)$_4$ to form an infinite {〉Ni〈 [CN–Cd(en)–NC–]$_2$}$_n$ extension along the *c* axis of the crystal, in which Ni(1) is on the inversion centre at 0, 0, ½. By depicting the square-planar Ni(CN)$_4$ as X, the infinite extension of XXX ··· involving a Cd(en) at every corner is seen as a doubly bridged one-dimensional extension.[2b] One Cd(en) at *x*, *y*, *z* is linked through the μ-*trans*-NC–Ni(2)(CN)$_2$–CN– moiety to the Cd(en) in the neighbouring unit cell related by the inversion centre at ½, ½, 0 where the Ni(2) is located. The Cd(en) is additionally linked through the bridging en to another Cd(en) at 1 − *x*, −*y*, −*z*. Hence, six-co-ordination of the Cd is accomplished with two N atoms from the chelating en, one from the bridging en, two from the CN groups in the double-one-dimensional extension and one from the μ-*trans*-NC–Ni(CN)$_2$–CN– linkage. Eventually a complicated three-dimensional

Table 5 Selected interatomic distances (Å) and angles (°) for compound **5**

N(1)–C(1)	1.868(4)	C(1)–N(1)	1.136(5)	C(11)–C(12)	1.405(7)	O(31)–C(31)	1.05(3)
Ni(1)–C(2)	1.855(4)	C(2)–N(2)	1.136(5)	C(12)–C(13)	1.380(8)	O(32)–C(32)	1.05(2)
Ni(2)–C(3)	1.869(4)	C(3)–N(3)	1.131(6)	C(13)–C(14)	1.369(9)	C(31)–C(32)	1.39(1)
Ni(2)–C(4)	1.869(5)	C(4)–N(4)	1.124(6)	C(14)–C(15)	1.393(9)	C(32)–C(33)	1.37(1)
Cd–N(1)	2.414(4)	N(5)–C(5)	1.508(8)	C(15)–C(16)	1.394(8)	C(33)–C(31^{IV})	1.36(2)
Cd–N(2^{I})	2.313(4)	C(5)–C(6)	1.42(1)	C(16)–C(11)	1.373(7)	N(4) ⋯ O(11)	2.711(7)
Cd–N(3)	2.371(4)	N(6)–C(6)	1.418(8)	O(21)–C(21)	1.32(1)	N(4) ⋯ N(6^{V})	3.275(7)
Cd–N(5)	2.339(4)	N(7)–C(7)	1.460(6)	C(21)–C(22)	1.36(1)	N(6) ⋯ O(32)	3.19(2)
Cd–N(6)	2.351(4)	C(7)–C(7^{II})	1.505(7)	C(22)–C(23)	1.377(9)	O(1) ⋯ O(21)	2.86(1)
Cd–N(7)	2.325(4)	O(11)–C(11)	1.353(6)	C(23)–C(21^{III})	1.41(1)	O(11) ⋯ O(31^{VI})	2.97(3)

C(1)–Ni(1)–C(2)	90.6(2)	Ni(1)–C(1)–N(1)	178.4(4)	C(12)–C(13)–C(14)	120.8(6)
C(3)–Ni(2)–C(4)	89.2(2)	Ni(1)–C(2)–N(2)	177.5(4)	C(13)–C(14)–C(15)	119.4(6)
N(1)–Cd–N(2^{I})	95.0(1)	Ni(2)–C(3)–N(3)	177.6(4)	C(14)–C(15)–C(16)	121.7(6)
N(1)–Cd–N(3)	172.3(1)	Ni(2)–C(4)–N(4)	178.0(5)	C(11)–C(16)–C(15)	117.2(6)
N(1)–Cd–N(5)	85.2(1)	Cd–N(1)–C(1)	169.1(4)	O(21)–C(21)–C(22)	121.9(8)
N(1)–Cd–N(6)	87.7(2)	Cd–N(2^{I})–C(2^{I})	170.6(4)	O(21)–C(21)–C(23^{III})	117.6(8)
N(1)–Cd–N(7)	84.8(2)	Cd–N(3)–C(3)	155.9(4)	C(21)–C(22)–C(23)	119.9(7)
N(2^{I})–Cd–N(3)	92.6(1)	Cd–N(5)–C(5)	107.5(4)	C(22)–C(21)–C(23^{III})	120.4(6)
N(2^{I})–Cd–N(5)	93.0(2)	Cd–N(6)–C(6)	109.5(4)	C(22)–C(23)–C(21^{III})	119.7(7)
N(2^{I})–Cd–N(6)	168.7(2)	Cd–N(7)–C(7)	121.2(3)	O(31)–C(31)–C(32)	108(3)
N(2^{I})–Cd–N(7)	86.5(2)	N(5)–C(5)–C(6)	115.5(6)	O(31)–C(31)–C(33^{IV})	127(2)
N(3)–Cd–N(5)	95.4(2)	N(6)–C(6)–C(5)	116.0(6)	O(32)–C(32)–C(31)	126(2)
N(3)–Cd–N(6)	85.0(2)	N(7)–C(7)–C(7^{II})	113.2(4)	O(32)–C(32)–C(33)	116(1)
N(3)–Cd–N(7)	94.7(2)	O(11)–C(11)–C(12)	116.8(5)	C(32)–C(31)–C(33^{IV})	124(1)
N(5)–Cd–N(6)	76.2(2)	O(11)–C(11)–C(16)	121.0(5)	C(31)–C(32)–C(33)	118(1)
N(5)–Cd–N(7)	169.9(2)	C(12)–C(11)–C(16)	122.2(5)	C(32)–C(33)–C(31^{IV})	118(1)
N(6)–Cd–N(7)	104.7(2)	C(11)–C(12)–C(13)	118.6(6)		

Symmetry operations: I $x, y, z - 1$; II $-x + 1, -y, -z$; III $-x, -y + 1, -z$; IV $-x + 1, -y, -z + 1$; V $-x + 1, -y + 1, -z + 1$: VI $x, y + 1, z$.

framework is formed involving three kinds of cavities each accommodating one phenol molecule.

Phenol molecule 1 (PhOH-1) is located on general positions between the square mesh of the double-one-dimensional linkage and the $Ni(2)(CN)_4$ moiety, with its aromatic ring almost perpendicular to the mesh; there are two such molecules in the unit cell. Molecule 2 (PhOH-2), sandwiched by the en chelate rings, takes a disorder related to the inversion centre at 0, $\frac{1}{2}$, 0. Molecule 3 (PhOH-3), sandwiched by the bridging en ligands, takes a disorder related to another inversion centre at $\frac{1}{2}$, 0, $\frac{1}{2}$. In addition to the disorder caused by the inversion centre, two O atoms of PhOH-3, O(31) and O(32), were observed independently with an occupancy ratio 23:27. The hydrogen bonds involving the OH groups of the PhOH molecules, O(11), O(21) and O(31), the NH_2 group of en, N(6), and the terminal N of the $Ni(2)(CN)_4$, N(4), have O(11) ⋯ O(21), O(11) ⋯ O(31), N(4) ⋯ O(11), N(6) ⋯ O(32) and N(4) ⋯ N(6) distances ranging from 2.7 to 3.3 Å.

Comparison of the Structures among the Aniline Clathrates and the Host Complexes.—Isostructural series of $[M(en)_2M'(CN)_4]_n$ metal complexes without guests are known for M = Ni **1′**, Cu **2′** and Zn **3′** with M′ = Ni,[9] and M = Ni with M′ = Pd,[10] having a one-dimensional chain of [-M(en)$_2$-*trans*-NC-Ni (or Pd)(CN)$_2$-CN-]$_n$, which are also isostructural with the one-dimensional chain of the present host complex of the aniline clathrates, although $[Cd(en)_2Ni(CN)_4]_n$ **4′** has a zigzag chain of [-Cd(en)$_2$-*cis*-NC-Ni(CN)$_2$-CN-]$_n$ with the *cis*-one-dimensional $Ni(CN)_4$ moiety.[11]

The *trans*-one-dimensional catenation chain in compounds **1′**–**3′** bends at every N of M–N–C with angle δ of 155.6(4)° for **1′**, 123.6(4)° for **2′** and 148.0(7)° for **3′** so as to form intrachain hydrogen bonds between the terminal N of the unidentate CN group and the NH_2 group of the chelating en. Each of the octahedral MN_6 co-ordination spheres is elongated along the chain, in particular for **2′** due to the Jahn–Teller effect on the Cu^{2+}. The elongation of the Cu–N bond and the bending of Cu–N–C angle in **2′** causes the formation of interchain hydrogen bonds, reducing U/Z to 334 Å^3 in comparison with 342 and 345 Å^3 for **1′** and **3′**. Disorder in the conformation of the en chelate ring was reported for **1′** and **3′** but not for **2′**. Calculated from literature data,[9] the interchain N ⋯ N distances between the CN and en are 3.278(7), 3.343(7), 3.442(9) and 3.490(8) Å for **1′**, 3.116(6) and 3.218(4) Å for **2′**, and 3.331(9) and 3.40(1) Å for **3′**, although the interchain hydrogen bonds were not discussed in the original literature.

Accommodation of aniline molecules in the interchain space makes the *trans*-one-dimensional catenation chain straight for **1**–**3**, and in the case of **4** the *cis*-one-dimensional form in **4′** becomes *trans*; no disorder has been observed for the conformation of the en chelate ring. Upon accommodation of the guest, the M–N bond along the chain increases to a small extent: Ni–N by 0.004, Cu–N by 0.060 and Zn–N by 0.059 Å; the angle δ increases to 163.9(4), 150.4(5) and 156.4(5)°. The distortion of the one-dimensional chain is reduced and the crystal packing appears to be stabilized with the formation of hydrogen bonds between the host and the guest in addition to the interchain ones.

Comparison of the Structures among $[Cd(en)_2Ni(CN)_4]\cdot 2PhNH_2$ **4**, $[\{Cd(en)\}_2(en)\{Ni(CN)_4\}_2]\cdot 4PhOH$ **5** *and* $[Cd(en)Ni(CN)_4]\cdot 2C_6H_6$ **6**.—The inclusion compounds **4**, **5** and the known[2] Hofmann-en-type $[Cd(en)Ni(CN)_4]\cdot 2C_6H_6$ **6** have the same molar ratio of $CdNi(CN)_4$: guest = 1 : 2 but differ in the content of en; they are all prepared under similar experimental conditions. However, the resulting crystal structures are quite different and accompanied with a change in the $CdNi(CN)_4$: en ratio from 1 : 2 to 2 : 3 to 1 : 1. As for the co-ordination of the en ligand to the Cd, it is chelating in **4**, chelating and singly bridging in **5** and a *catena*-single-one-dimensional linkage builder in **6**. The $Ni(CN)_4$ acts as a *catena-trans*-one-dimensional linkage builder in **4**, *catena*-doubly-one-dimensional and *trans*-bridging ligand in **5**, and *catena*-tetra-close-two-dimensional linkage builder in **6**, respectively. The differences in the host structures are deduced from the interaction of the host with the guest molecules, *i.e.* the guest determines the host structure.

With regard to the guest molecules, differences are seen in the absence or presence of a substituent group: no substituent in compound **6** but acidic OH in **5** and basic NH_2 in **4**. The polar substituents in **4** and **5** are favourable to the formation of hydrogen bonds with the host and/or neighbouring guest. Although the aniline in **4** as well as in **1–3** is accommodated in the cavity in a considerably different way from that of the Hofmann-en-type compounds, the host structure of **5** partially resembles that of the latter. Molecule PhOH-3 is trapped between a couple of the bridging en ligands, and PhOH-1 is capped with the mesh of doubly-one-dimensional $[\rangle Ni \langle (CN{-}Cd{-}NC{-})_2]$ at one side, whereas the C_6H_6 in **6** is clipped with a couple of bridging en ligands and capped with the close-two-dimensional meshes at both sides, top and bottom. These arrangements and orientations of the guest phenol molecules are fixed with the host–guest and interguest hydrogen-bond formation.

Hofmann's benzene, aniline and phenol compounds $Ni(CN)_2 \cdot NH_3 \cdot G$ $[= Ni(NH_3)_2Ni(CN)_4 \cdot 2G]$ where G = C_6H_6, $PhNH_2$ or $PhOH \cdot H_2O$ were reported as anomalous nickel compounds because the neutral, basic and acidic aromatic hydrocarbons had resulted in similar compositions.[12] After the single-crystal structure had been determined for the benzene compound,[13] powder X-ray diffraction data indicated that the Hofmann-type aniline compounds were isostructural to the benzene one;[2] the Hofmann-type phenol compounds may also be assumed to be isostructural.

In contrast with the Hofmann-type compounds, the difference in the chemical functionality among the three aromatic guests leads to differences in the crystal structures of **4–6** where the $(NH_3)_2$ ligands in the Hofmann-type $[Cd(NH_3)_2Ni(CN)_4] \cdot 2G$ are replaced by one en for C_6H_6, 1.5 en for PhOH and 2 en for $PhNH_2$.

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