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 $[M(en)_2Ni(CN)_4]$ ·2PhNH₂ (M = Ni, Cu, Zn or Cd) and $[{Cd(en)}_2(en){Ni(CN)_4}_2]$ ·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 PhNH₂ 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]\cdot4PhOH belongs to the triclinic system, space group *P*T, with *a* = 11.868(1), *b* = 13.030(1), *c* = 7.7113(6) Å, *a* = 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]-2C₆H₆ clathrate.

With regard to the Hofmann-type and analogous inclusion compounds,^{1,2} the Hofmann-en-type [Cd(en)Ni(CN)₄]·2G $(G = C_4H_5N, C_4H_4S \text{ or } C_6H_6)$ 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 PhNH₂): the guest G molecules are accommodated between the layers of the catena-[cadmium(II) tetra-µ-cyanonickelate(II)] network. The NH₃ ligands protrude into the layers in the Hofmann-type compound, but the 1,2diaminoethane (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 $[M(NH_3)_2M'(CN)_4]$ ·2PhNH₂ (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(NH₃)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. Sopková⁴ reported several non-stoichiometric compounds containing aniline and phenol such as [Ni(en)₂Ni(CN)₄].0.14PhNH₂ and [Ni(en)₂Pt-(CN)₄]·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 $[M(en)_2Ni(CN)_4]$ -2PhNH₂ (M = Ni, Cu, Zn or Cd) as single crystals; a phenol-guest compound $[{Cd(en)}_2(en){Ni-(CN)_4}_2]$ -4PhOH was also prepared under similar conditions. This paper describes their crystal structures in detail.

Experimental

Preparation.—(a) [Ni(en)₂Ni(CN)₄]·2PhNH₂ 1 and [Cu-(en)₂Ni(CN)₄]·2PhNH₂ 2. To an aqueous solution containing 5 mmol each of NiCl₂·6H₂O or CuCl₂·2H₂O, K₂[Ni(CN)₄]·H₂O 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 cm³. After a small amount of precipitate had been filtered off, the solution was placed on a layer of neat PhNH₂ 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. C₂₀H₃₀N₁₀Ni₂ 1 requires 45.5; H, 5.75; N, 26.5. Found: C, 45.2; H, 5.80; N, 25.5. C₂₀H₃₀CuN₁₀Ni 2 requires C, 45.1; N, 5.70; N, 26.3%).

(b) $[Zn(en)_2Ni(CN)_4]$ -2PhNH₂ 3 and $[Cd(en)_2Ni(CN)_4]$ -2PhNH₂ 4. Yellow needles were obtained for both compounds 3 and 4 by procedures similar to the above except that $ZnCl_2$ -2H₂O or $CdCl_2$ -2.5H₂O 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. $C_{20}H_{30}CdN_{10}Ni4$ requires C, 41.3; H, 5.20; N, 24.1%).

(c) $[{Cd(en)}_2(en){Ni(CN)}_4]_2]$ 4 PhOH 5. Using neat PhOH in place of neat PhNH₂ in (b) yellow plate-like crystals of

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

Compound	1	2	3	4	5
Formula	$C_{20}H_{30}N_{10}Ni_2$	C ₂₀ H ₃₀ CuN ₁₀ Ni	$C_{20}H_{30}N_{10}NiZn$	C20H30CdN10Ni	C ₁₈ H ₄₈ Cd ₂ N ₁₄ Ni ₂ O ₄
М	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)	<i>P</i> 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)
$c/\text{\AA}$	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
$D_{\rm m}, D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	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-K α)/cm ⁻¹	15.67	16.63	17.88	16.34	17.86
Crystal size/mm	$0.50 \times 0.40 \times 0.20$	$0.52 \times 0.38 \times 0.18$	$0.50 \times 0.40 \times 0.20$	$0.38 \times 0.28 \times 0.26$	$0.32 \times 0.28 \times 0.20$
hkl ranges	0–13, 0–14,	0–13, 0–14,	0–13, 0–14,	0–13, 0–14,	0-16, -18 to 18 ,
$(4 < 2\theta < 60^{\circ})$	-18 to 18	-17 to 17	-18 to 17	-17 to 16	-10 to 10
Scan width/°	$1.155 + 0.3 \tan \theta$	$1.155 + 0.3 \tan \theta$	$1.155 + 0.3 \tan \theta$	$1.050 + 0.3 \tan \theta$	$0.787 + 0.3 \tan \theta$
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 ⁶	3.3×10^{-4}	9.0×10^{-4}	1.4×10^{-4}	5.5×10^{-4}	2.0×10^{-4}
<i>R</i> , <i>R</i> ′ ^{<i>b</i>}	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 $\Delta \rho/e \ \text{\AA}^{-3}$	+0.40, -0.52	+0.89, -0.69	+0.38, -0.45	+0.65, -0.59	+0.85, -0.58

Table 1 Crystallographic and selected experimental data for compounds 1-5^a

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. Singlecrystal X-ray measurements were carried out at room temperature on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo-K α_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 ($33 \le 2\theta \le 35^\circ$). 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 corrections⁵ were applied for all compounds. An extinction correction was applied only for 5 according to the equation $F_{\rm corr} = F_{\rm c} \{1 - [x(F_{\rm c})^2/$ $\sin\theta$]; x was refined to 1.7(2) × 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 leastsquares 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 76⁶ 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 76⁶ 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 ORTEP⁸ 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 $\pm a$ 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.

^{*a*} Conditions in common: $2\theta - \omega$ 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, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2 / (N_r - N_p)]^{\frac{1}{2}}$.

^{*} 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 PhNH₂ 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

$\begin{split} & \text{Niclow}_{Nicl} V = (Caten)_{Nicl} V = (D_{1})_{Nicl} V = (D_{1$	Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	[Ni(en)2Ni($(N)_4$]·2PhNH ₂ 1			[Cu(en) ₂ Ni	(CN) ₄]•2PhNH ₂ 2		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ni(1)*	0	0	0	Ni*	0	0	0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ni(2)*	0	$\frac{1}{2}$	0	Cu*	0	17	0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1)	-0.0247(5)	0.2935(4)	0.0201(4)	N(1)	-0.0379(7)	õ.2734(4)	0.0441(5)
N(3) 0.1166(5) 0.4432(4) -0.105(4) N(3) 0.0482(5) 0.4427(5) -0.1009(4) C(1) -0.0155(6) 0.1800(4) 0.0150(3) N(4) 0.2336(5) 0.0057(4) 0.0169(4) C(2) 0.0771(7) 0.0493(5) C(1) 0.0658(7) 0.0449(5) C(14) 0.313(10) 0.272(7) 0.2247(6) 0.210(6) C(11) 0.0658(10) 0.272(7) 0.2247(6) 0.210(6) C(11) 0.0658(10) 0.272(7) 0.2247(7) 0.2478(6) 0.210(6) C(11) 0.0658(10) 0.272(7) 0.2247(7) 0.210(6) C(11) 0.0658(10) 0.272(7) 0.2247(7) 0.2247(7) 0.210(7) C(12) 0.374(7) 0.2272(7) 0.247(7) 0.224(7) 0.1276(1) 0.057(7) 0.234(7) 0.2247(7) 0.224(7) 0.2126(7) 0.212(7) 0.2126(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.234(7) 0.242(7) 0.134(7) 0.2126(7) 0.2252(7)<	N(2)	0.1206(7)	0.0650(6)	-0.1778(5)	N(2)	0.1381(7)	0.0836(5)	-0.1702(5)
N(4) 0.2100(5) 0.466(c4) 0.1080(4) N(4) 0.2036(6) 0.500(4) 0.1080(4) C(1) -0.0185(6) 0.0150(4) C(1) -0.0446(5) C(3) 0.2527(9) 0.4116(7) -0.058(7) C(3) 0.2527(7) 0.4380(5) 0.0490(5) C(4) 0.3113(0) 0.2727(7) 0.2341(7) C(11) 0.618(9) 0.2722(6) 0.2121(6) N(11) 0.8133(10) 0.2237(7) 0.2341(7) C(11) 0.6682(14) 0.1332(9) C(13) 0.4410(15) 0.1327(7) 0.2341(7) C(14) 0.4582(14) 0.1232(10) 0.1276(11) 0.0358(12) 0.1736(11) 0.3347(7) 0.238(12) C(16) 0.462(14) 0.1282(8) 0.1332(9) C(15) 0.4470(15) 0.1472(9) 0.128(14) Ni* 0 0 0 C(4* 0 1 0.0334(7) 0.0138(3) N(1) 0.0127(7) 0.238(6) 0.128(6) 0.328(5) N(1) 0.0328(1) 0.0338(5) N(1) 0.0127(7) 0.238(6) 0.4138(8) 0.0435(5) N(1) 0.0236(7) 0.2126(6)<	N(3)	0.1166(5)	0.4534(4)	-0.1065(4)	N(3)	0.0982(6)	0.4427(5)	-0.1106(4)
$ \begin{array}{ccccc} C(1) & -0.0185(6) & 0.180(4) & 0.0150(4) & C(1) & -0.0246(6) & 0.0163(5) & 0.0287(4) \\ C(2) & 0.0771(7) & 0.0171(5) & -0.0190(5) & C(2) & 0.0870(7) & 0.0492(6) & -0.0199(4) \\ C(3) & 0.2588(7) & 0.4193(6) & -0.0440(5) & C(3) & 0.2527(7) & 0.04116(7) & -0.054(7) \\ N(11) & 0.8047(10) & 0.2722(6) & 0.2121(6) & N(11) & 0.8057(10) & 0.2727(7) & 0.234(7) \\ C(12) & 0.5746(12) & 0.1665(7) & 0.2108(6) & C(11) & 0.0665(10) & 0.2520(6) & 0.2208(7) \\ C(12) & 0.5746(12) & 0.1628(7) & 0.2132(9) & C(13) & 0.4410(15) & 0.1472(9) & 0.1276(11) \\ C(14) & 0.3622(14) & 0.1428(8) & 0.1332(9) & C(15) & 0.4777(13) & 0.2700(7) & 0.1384(7) \\ C(14) & 0.3622(14) & 0.1324(9) & 0.2854(9) & C(15) & 0.4777(13) & 0.2708(8) & 0.2956(7) \\ C(16) & 0.0038(11) & 0.304(7) & 0.2872(6) & C(16) & 0.0612(11) & 0.057(8) & 0.2956(7) \\ C(16) & 0.0038(11) & 0.304(7) & 0.2872(6) & C(16) & 0.0612(11) & 0.057(8) & 0.2956(7) \\ N(1) & -0.026(7) & 0.226(4) & 0.0338(5) & N(1) & -0.026(7) & 0.2762(5) & 0.0435(6) \\ N(3) & 0.1137(6) & 0.4443(5) & -0.115(4) & N(3) & 0.1258(6) & 0.0466(6) & -0.1614(6) \\ N(3) & 0.1137(6) & 0.4443(5) & -0.115(4) & N(3) & 0.1258(6) & 0.0435(6) & -0.1210(4) \\ N(4) & 0.2129(5) & 0.0508(5) & C(12) & 0.097(8) & 0.0498(6) & -0.1614(6) \\ N(3) & 0.1137(6) & 0.0443(6) & -0.0168(5) & C(2) & 0.097(8) & 0.0498(6) & -0.0161(6) \\ C(1) & -0.026(7) & 0.175(15) & 0.0229(5) & C(1) & -0.0167(6) & 0.0108(6) & -0.0101(6) \\ C(2) & 0.0585(8) & 0.0443(6) & -0.0168(5) & C(2) & 0.097(8) & 0.0498(6) & -0.01614(6) \\ N(11) & 0.071(12) & 0.204(9) & 0.2134(7) & C(13) & 0.4258(7) & 0.4490(7) \\ N(11) & 0.071(12) & 0.204(9) & 0.2124(7) & C(13) & 0.4258(1) & 0.0498(6) & -0.0101(6) \\ C(13) & 0.258(13) & 0.0148(1) & 0.1278(10) & C(13) & 0.4258(1) & 0.0398(1) & 0.0378(1) \\ O.130 & 0.458(16) & 0.1484(1) & 0.1278(10) & C(13) & 0.458(13) & 0.1958(1) & 0.0378(1) \\ O.130 & 0.458(16) & 0.1484(1) & 0.1278(1) & 0.278(13) & 0.2790(8) & 0.490(7) \\ N(11) & 0.478(11) & 0.2548(1) & 0.258(1) & 0.2128(7) & C(13) & 0.458(1) & 0.0378(1) & 0.2378(7) \\ N(11) & 0.478(10) & 0.3924(7) $	N(4)	0.2100(5)	0.4966(4)	0.1080(3)	N(4)	0.2036(6)	0.5005(4)	0.1080(4)
$\begin{array}{ccccccc} C(2) & 0.0771(7) & 0.0371(5) & -0.1109(5) & C(2) & 0.0879(7) & 0.0492(6) & -0.1059(4) \\ C(3) & 0.2288(7) & 0.0493(6) & 0.0449(65) & C(4) & 0.3113(9) & 0.9258(6) & 0.0473(7) \\ C(1) & 0.6818(9) & 0.2478(6) & 0.2121(6) & N(11) & 0.6658(10) & 0.2520(6) & 0.2234(7) \\ C(11) & 0.6618(9) & 0.2478(6) & 0.2121(6) & N(11) & 0.6658(10) & 0.2520(6) & 0.2234(7) \\ C(13) & 0.4582(14) & 0.1428(8) & 0.1332(9) & C(13) & 0.4410(15) & 0.1472(9) & 0.1234(7) \\ C(13) & 0.4582(14) & 0.1428(8) & 0.1332(9) & C(13) & 0.4410(15) & 0.1472(9) & 0.1236(11) \\ C(16) & 0.6028(11) & 0.3034(7) & 0.2834(9) & C(16) & 0.6012(11) & 0.307(8) & 0.2396(7) \\ C(16) & 0.6028(11) & 0.3034(7) & 0.2834(9) & C(16) & 0.6012(11) & 0.307(8) & 0.2396(7) \\ C(16) & 0.6028(11) & 0.3034(7) & 0.2834(9) & C(16) & 0.6012(11) & 0.307(8) & 0.2396(7) \\ N(1) & -0 & 0 & 0 & N^{*} & 0 & 0 \\ N(1) & -0.0286(7) & 0.2834(9) & 0.0338(5) & N(1) & -0.0267(7) & 0.2752(5) & 0.0435(6) \\ N(2) & -0.0286(7) & 0.2836(4) & 0.0338(5) & N(1) & -0.0267(7) & 0.2752(5) & 0.0435(6) \\ N(3) & 0.1137(6) & 0.04443(5) & -0.1115(4) & N(3) & 0.1256(6) & 0.0357(5) & 0.1126(4) \\ N(4) & 0.2129(5) & 0.5000(5) & 0.1103(4) & N(4) & 0.2314(6) & 0.5015(5) & 0.1126(4) \\ N(4) & 0.2129(5) & 0.5000(5) & 0.1103(4) & N(4) & 0.2314(6) & 0.5015(5) & 0.1126(4) \\ N(4) & 0.2129(5) & 0.5000(5) & 0.1103(4) & N(4) & 0.2314(6) & 0.5015(5) & 0.1126(4) \\ N(4) & 0.2129(5) & 0.5000(5) & 0.1103(4) & N(4) & 0.2314(6) & 0.5015(5) & 0.1126(4) \\ N(4) & 0.2129(5) & 0.5000(5) & 0.1103(4) & N(4) & 0.2314(8) & 0.0491(6) & -0.1001(6) \\ C(1) & 0.2662(8) & 0.4498(8) & 0.0497(7) & C(3) & 0.2790(8) & 0.4091(8) & -0.007(7) \\ C(4) & 0.321(07) & 0.4982(8) & 0.0485(6) & C(11) & 0.6794(11) & 0.2587(7) & 0.409(7) \\ C(3) & 0.2582(16) & 0.1125(7) & C(12) & 0.0496(13) & 0.1353(8) & 0.1134(7) \\ C(13) & 0.3278(13) & 0.2124(9) & 0.2231(7) & C(13) & 0.4587(11) & 0.3287(10) & 0.231(6) \\ C(11) & 0.676(10) & 0.2384(8) & 0.2035(13) & 0.2125(17) & C(13) & 0.4587(11) & 0.2587(13) & 0.1387(10) & 0.2377(13) \\ C(13) & 0.3278(13) & 0.2032(13) & 0.2257(13)$	C(1)	-0.0185(6)	0.1809(4)	0.0150(4)	C(1)	-0.0246(6)	0.1683(5)	0.0287(4)
$ \begin{array}{ccccc} C(3) & 0.2688(7) & 0.4136(6) & -0.0440(5) & C(3) & 0.2527(9) & 0.4116(7) & -0.0541(7) \\ V(11) & 0.8047(10) & 0.2722(6) & 0.2121(6) & N(11) & 0.8133(10) & 0.2727(7) & 0.2341(7) \\ V(11) & 0.6618(9) & 0.2478(6) & 0.2108(6) & C(110) & 0.6665(10) & 0.2520(6) & 0.2230(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) & 0.2088(14) & 0.2088(10) \\ C(16) & 0.6028(11) & 0.3047(7) & 0.2872(6) & C(15) & 0.4577(13) & 0.2730(9) & 0.2835(9) \\ C(16) & 0.6028(11) & 0.304(7) & 0.2872(6) & C(16) & 0.6012(11) & 0.307(8) & 0.2936(7) \\ Zneny_N(1CN)_{a})_{2}PhNH_{a} J & & & & & & & & & & \\ Icm_{1} & 0 & 0 & 0 & & & & & & & & & & & & & $	C(2)	0.0771(7)	0.0371(5)	-0.1109(5)	C(2)	0.0879(7)	0.0492(6)	-0.1059(4)
$\begin{array}{ccccc} C(4) & 0.3227(7) & 0.4938(6) & 0.0496(5) & C(4) & 0.3113(0) & 0.4958(6) & 0.0473(7) \\ C(11) & 0.6618(9) & 0.2722(6) & 0.2121(6) & N(11) & 0.6133(10) & 0.2520(6) & 0.2234(7) \\ C(13) & 0.4582(14) & 0.1665(7) & 0.1314(7) & C(12) & 0.5903(12) & 0.1750(7) & 0.134(7) \\ C(13) & 0.4582(14) & 0.1954(11) & 0.2089(10) & C(13) & 0.4410(15) & 0.1472(9) & 0.1276(11) \\ C(16) & 0.6028(11) & 0.3034(7) & 0.2854(9) & C(15) & 0.457(13) & 0.2370(9) & 0.2835(9) \\ C(16) & 0.6028(11) & 0.3034(7) & 0.2854(9) & C(16) & 0.6012(11) & 0.307(8) & 0.2936(7) \\ (Zn(en)_2Ni(CN)_4)_2PhNH_2 J & & & & & & & \\ \hline N^+ & 0 & 0 & 0 & & & & & & & & & & & & & $	C(3)	0.2688(7)	0.4139(6)	-0.0440(5)	C(3)	0.2527(9)	0.4116(7)	- 0.0541(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4)	0.3227(7)	0.4983(6)	0.0496(5)	C(4)	0.3113(9)	0.4958(6)	0.0473(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(11)	0.8047(10)	0.2722(6)	0.2121(6)	N(11)	0.8133(10)	0.2727(7)	0.2341(7)
$\begin{array}{cccccc} C(12) & 0.5746(12) & 0.1665(7) & 0.1314(7) & C(12) & 0.590(12) & 0.1750(7) & 0.1334(7) \\ C(13) & 0.4258(14) & 0.1954(11) & 0.2089(10) & C(14) & 0.3721(7) & 0.2008(14) & 0.2058(12) \\ C(15) & 0.4602(13) & 0.2734(9) & 0.2834(9) & C(15) & 0.4577(13) & 0.2730(9) & 0.2835(9) \\ C(16) & 0.60228(11) & 0.3034(7) & 0.2872(6) & C(16) & 0.6012(11) & 0.3057(8) & 0.2936(7) \\ (Zn(en),Ni(CN)_{a}]-2PhNH_{3} & & & & & & & & & & \\ C(den),Ni(CN)_{a}]-2PhNH_{3} & & & & & & & & & & & & & & & & \\ N^{*} & 0 & 0 & 0 & & & & & & & & & & & & & $	C(11)	0.6618(9)	0.2478(6)	0.2108(6)	C(11)	0.6665(10)	0.2520(6)	0.2203(7)
$\begin{array}{cccccc} C(13) & 0.4258(14) & 0.14328(8) & 0.1332(9) & C(13) & 0.4410(15) & 0.1472(9) & 0.1276(11) \\ C(14) & 0.3682(14) & 0.1954(11) & 0.2058(10) & C(14) & 0.3729(17) & 0.2008(14) & 0.2058(12) \\ C(15) & 0.4602(13) & 0.2749(9) & 0.2854(9) & C(15) & 0.4577(13) & 0.2730(9) & 0.2335(9) \\ C(16) & 0.6028(11) & 0.3037(7) & 0.2872(6) & C(16) & 0.6012(11) & 0.3057(8) & 0.2936(7) \\ Zn(en)_1Ni(CN)_4]_2PhNH_3 3 & & & & & & & & & & & & & & & & & &$	C(12)	0.5746(12)	0.1665(7)	0.1314(7)	C(12)	0.5903(12)	0.1750(7)	0.1334(7)
$\begin{array}{ccccc} 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) & 0.2734(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)_2]N(CN)_1]_2PhNH_2 & & & & & & & & & \\ Iccc(en)_2[Ni(CN)_1]_2PhNH_2 & & & & & & & & & \\ Iccc(en)_2[Ni(CN)_1]_2PhNH_2 & & & & & & & & & & & \\ Iccc(en)_2[Ni(CN)_1]_2PhNH_2 & & & & & & & & & & & & & & & \\ N^* & 0 & 0 & 0 & & & & & & & & & & & & & $	C(13)	0.4258(14)	0.1428(8)	0.1332(9)	C(13)	0.4410(15)	0.1472(9)	0.1276(11)
$\begin{array}{cccccc} 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) \\ \hline Zn(en)_2Ni(CN)_1_2PhNH_2 3 & & & & & & & & \\ \hline Ni^* & 0 & 0 & 0 & & & & & & & & & & \\ \hline Ni^* & 0 & 0 & 0 & & & & & & & & & & & \\ \hline Ni^* & 0 & 0 & & & & & & & & & & & & & \\ \hline Ni^* & 0 & 0 & & & & & & & & & & & & & & \\ \hline Ni^* & 0 & 0 & & & & & & & & & & & & & & \\ \hline Ni^* & 0 & 0 & & & & & & & & & & & & & & & $	C(14)	0.3682(14)	0.1954(11)	0.2089(10)	C(14)	0.3729(17)	0.2008(14)	0.2058(12)
$ \begin{array}{ccccc} C(16) & 0.6028(11) & 0.3034(7) & 0.2872(6) & C(16) & 0.012(11) & 0.3057(8) & 0.2936(7) \\ [Zn(en)_2Ni(CN)_1]_2PhNH_3 & [Cd(en)_2Ni(CN)_1]_2PhNH_3 & [C$	C(15)	0.4602(13)	0.2749(9)	0.2854(9)	C(15)	0.4577(13)	0.2730(9)	0.2835(9)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	C(16)	0.6028(11)	0.3034(7)	0.2872(6)	C(16)	0.6012(11)	0.3057(8)	0.2936(7)
$ \begin{array}{c ccccc} \mathbf{N}_{1}^{*} & 0 & 0 & 0 & \mathbf{N}_{1}^{*} & 0 & 0 & 0 \\ \hline \mathbf{X}_{2}^{*} & 0 & \frac{1}{2} & 0 & \mathbf{C}_{4}^{*} & 0 & \frac{1}{2} & 0 \\ \mathbf{N}_{1}(1) & -0.02667(7) & 0.2826(4) & 0.0338(5) & \mathbf{N}_{1}(1) & -0.0267(7) & 0.2752(5) & 0.0435(6) \\ \mathbf{N}_{2}(2) & 0.1340(8) & 0.0777(7) & -0.1714(5) & \mathbf{N}_{1}(2) & 0.0526(6) & 0.4325(5) & -0.1210(4) \\ \mathbf{N}_{4}(1) & 0.2129(5) & 0.5000(5) & 0.1103(4) & \mathbf{N}_{4}(1) & 0.2314(6) & 0.5015(5) & 0.1156(4) \\ \mathbf{N}_{4}(1) & 0.0206(7) & 0.1751(5) & 0.0224(5) & \mathbf{C}_{1}(1) & -0.0167(6) & 0.1696(6) & 0.0312(5) \\ \mathbf{C}_{1}(2) & 0.0851(8) & 0.0442(6) & -0.1068(5) & \mathbf{C}_{1}(2) & 0.0974(8) & 0.0498(6) & -0.0607(7) \\ \mathbf{C}_{4}(4) & 0.3210(7) & 0.4982(8) & 0.0485(6) & \mathbf{C}_{4}(4) & 0.3233(7) & 0.4988(7) & 0.0490(1) \\ \mathbf{C}_{1}(1) & 0.6071(12) & 0.2801(9) & 0.2235(7) & \mathbf{N}_{1}(1) & 0.8128(11) & 0.3028(10) & 0.2316(8) \\ \mathbf{C}_{1}(1) & 0.6676(10) & 0.2548(9) & 0.2169(8) & \mathbf{C}_{1}(1) & 0.6794(11) & 0.2659(9) & 0.2216(9) \\ \mathbf{C}_{1}(2) & 0.5821(6) & 0.1737(9) & 0.1328(7) & \mathbf{C}_{1}(2) & 0.6964(13) & 0.1853(8) & 0.1343(7) \\ \mathbf{C}_{1}(3) & 0.4388(16) & 0.1483(11) & 0.1328(12) & \mathbf{C}_{1}(3) & 0.4653(13) & 0.1515(10) & 0.1241(10) \\ \mathbf{C}_{1}(4) & 0.3207(13) & 0.2285(10) & \mathbf{C}_{1}(1) & 0.3652(3) & 0.1990(13) & 0.2787(13) \\ \mathbf{C}_{1}(6) & 0.6040(13) & 0.3093(9) & 0.2921(7) & \mathbf{C}_{1}(1) & 0.6074(13) & 0.3147(8) & 0.2988(7) \\ \mathbf{S}_{1}(1)^{**} & 0 & 1 & \mathbf{C}_{1}(2) & 0.444 & \mathbf{C}_{1}(1) & 0.2353(4) & 0.7408(4) & 0.671 & \mathbf{C}_{1}(7) \\ \mathbf{N}_{1}(2)^{**} & \frac{1}{2} & \frac{1}{2} & 0 & \mathbf{C}_{1}(2) & 0.1487(5) & 0.8090(4) & 0.72278(13) \\ \mathbf{N}_{1}(1)^{**} & 0 & 0 & \frac{1}{4} & \mathbf{C}_{1}(1) & 0.2353(4) & 0.7408(4) & 0.671 & \mathbf{C}_{1}(7) \\ \mathbf{N}_{1}(2)^{**} & \frac{1}{2} & \frac{1}{2} & 0 & \mathbf{C}_{1}(2) & 0.1487(5) & 0.8090(4) & 0.73278(9) \\ \mathbf{N}_{1}(1) & 0.1388(4) & 0.0090(23) & 0.2751(5) & \mathbf{C}_{1}(13) & 0.1487(5) & 0.8090(4) & 0.73278(13) \\ \mathbf{N}_{1}(1) & 0.1328(4) & 0.0077(3) & 0.22751(5) & \mathbf{C}_{1}(3) & 0.1487(5) & 0.8090(4) & 0.73278(9) \\ \mathbf{N}_{1}(1) & 0.1484(3) & 0.0090(23) & 0.2751(5) & \mathbf{C}_{1}(3) & 0.1383(5) & 0.7050(4) & 0.7586$	$[Zn(en)_2Ni($	CN) ₄]·2PhNH ₂ 3			[Cd(en) ₂ Ni	$(CN)_4$]·2PhNH ₂ 4		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Ni*	0	0	0	Ni *	0	0	0
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Zn *	0	$\frac{1}{2}$	0	Cd*	0	$\frac{1}{2}$	0
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	N(1)	-0.0286(7)	õ.2826(4)	0.0338(5)	N(1)	-0.0267(7)	õ.2762(5)	0.0435(6)
N(3) 0.1137(6) 0.4443(5) -0.115(4) N(3) 0.1256(6) 0.4325(5) -0.120(4) N(4) 0.2129(5) 0.5015(5) 0.1156(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) 0.5015(5) 0.01156(4) C(2) 0.0851(8) 0.0442(6) -0.1068(5) C(2) 0.0974(8) 0.0493(8) -0.0507(7) C(3) 0.2200(8) 0.4105(8) -0.0479(7) C(3) 0.3223(7) 0.4988(7) 0.0440(7) N(11) 0.812(11) 0.3028(10) 0.2235(7) N(11) 0.3128(11) 0.3028(10) 0.2213(8) C(11) 0.6676(10) 0.2548(9) 0.2169(8) C(11) 0.6653(13) 0.1123(1) 0.2128(1) 0.213(1) 0.2124(10) C(13) 0.4453(13) 0.1235(10) 0.2124(10) C(14) 0.328(51) 0.279(13) 0.279(13) 0.279(13) 0.279(13) 0.279(13) 0.279(13) 0.279(7) C(14) 0.3247(8) 0.2025(13) 0.12941(10) 0.26459(13) 0.1205(13)	N(2)	0.1340(8)	0.0777(7)	-0.1714(5)	N(2)	0.1538(8)	0.0846(6)	-0.1614(6)
N(4) 0.2129(5) 0.5000(5) 0.1133(4) N(4) 0.2314(6) 0.5015(5) 0.1156(6) 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) -0.0485(5) C(2) 0.0974(8) 0.0493(8) -0.0507(7) C(3) 0.2662(8) 0.4105(8) -0.0479(7) C(3) 0.2700(8) 0.4039(8) -0.0507(7) N(11) 0.871(12) 0.2801(9) 0.2235(7) N(11) 0.8128(1) 0.0258(9) 0.2212(9) C(12) 0.5821(16) 0.1737(9) 0.2169(8) C(11) 0.6759(11) 0.2258(9) 0.2212(9) C(13) 0.4358(16) 0.1483(11) 0.1326(7) C(14) 0.3805(23) 0.1515(10) 0.1241(10) O(14) 0.3320(13) 0.2122(10) C(14) 0.3805(23) 0.1950(13) 0.1994(11) C(15) 0.4639(15) 0.2807(13) 0.2285(10) C(15) 0.4659(13) 0.2787(13) C(16) 0.6040(13) 0.3093(9) 0.2921(7) C(16) 0.6074(13) 0.3147	N(3)	0.1137(6)	0.4443(5)	-0.1115(4)	N(3)	0.1256(6)	0.4325(5)	-0.1210(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(4)	0.2129(5)	0.5000(5)	0.1103(4)	N(4)	0.2314(6)	0.5015(5)	0.1156(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1)	-0.0206(7)	0.1751(5)	0.0229(5)	C(1)	-0.0167(6)	0.1696(6)	0.0312(5)
$\begin{array}{cccccc} C(3) & 0.26c2(8) & 0.4105(8) & -0.0479(7) & C(3) & 0.2700(8) & 0.4039(8) & -0.0507(7) \\ C(4) & 0.3210(7) & 0.4982(8) & 0.0485(6) & C(4) & 0.3233(7) & 0.4988(7) & 0.0440(7) \\ N(11) & 0.8071(12) & 0.2801(9) & 0.2235(7) & N(11) & 0.8128(11) & 0.3028(10) & 0.2316(8) \\ C(11) & 0.6676(10) & 0.2548(9) & 0.2169(8) & C(11) & 0.6794(11) & 0.2659(9) & 0.2212(9) \\ C(12) & 0.5821(16) & 0.1737(9) & 0.1326(7) & C(12) & 0.6046(13) & 0.1853(8) & 0.1334(7) \\ C(13) & 0.4358(16) & 0.1483(11) & 0.1328(12) & C(13) & 0.4655(13) & 0.1515(10) & 0.1241(10) \\ C(14) & 0.3278(18) & 0.2053(13) & 0.2122(10) & C(14) & 0.3805(23) & 0.1950(13) & 0.1994(11) \\ C(15) & 0.4639(15) & 0.2807(13) & 0.2805(10) & C(15) & 0.4659(13) & 0.2709(13) & 0.2787(13) \\ C(16) & 0.6040(13) & 0.3093(9) & 0.2921(7) & C(16) & 0.6074(13) & 0.3147(8) & 0.2988(7) \\ \end{array}$ * 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 Oldow 0.111 & 0.245 4(4) & 0.712 2(4) & 0.490 5(6) \\ Ni(1)^{a,b} & 0 & 0 & \frac{1}{2} & C(11) & 0.235 3(4) & 0.740 8(4) & 0.671 0(7) \\ Ni(2)^{a,b} & \frac{1}{4} & \frac{1}{2} & 0 & C(12) & 0.148 7(5) & 0.899 0(4) & 0.732 7(9) \\ N(1) & 0.148 (4) & 0.090 2(3) & 0.275 1(5) & C(13) & 0.136 0(5) & 0.839 5(5) & 0.915 7(9) \\ N(1) & 0.148 (4) & 0.303 1(3) & -0.012 1(6) & C(15) & 0.297 7(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) & 0.297 7(6) & 0.805 4(5) & 1.035 3(9) \\ N(3) & 0.358 9(4) & 0.303 1(3) & -0.012 1(6) & C(16) & 0.018 9(9) & 0.640 6(8) & 0.331 1(12) \\ N(6) & 0.339 7(4) & 0.292 1(4) & 0.327 7(6) & C(21) & 0.011 9(7) & 0.574 9(5) & 0.166 5(9) \\ N(5) & 0.120 6(4) & 0.352 7(6) & C(21) & 0.011 9(7) & 0.574 9(5) & 0.166 5(9) \\ N(5) & 0.120 6(4) & 0.535 7(3) & 0.361 4(5) & C(23) & 0.091 1(6) & 0.478 6(7) & -0.094 6(9) \\ C(1) & 0.093 8(4) & 0.052 7(3) & 0.327 7(6) & C(31) & 0.395 2(13) & -0.041 4(10) & 0.491 4(16) \\ C(5) & 0.182 7(8) & 0.405 3(6) & 0.229 8(7) & C(31) & 0.395 2(13) & -0.041 4(10) & 0.491 4(16) \\	C(2)	0.0851(8)	0.0442(6)	-0.1068(5)	C(2)	0.0974(8)	0.0491(6)	-0.1001(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3)	0.2662(8)	0.4105(8)	-0.0479(7)	C(3)	0.2700(8)	0.4039(8)	-0.0507(7)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	C(4)	0.3210(7)	0.4982(8)	0.0485(6)	C(4)	0.3233(7)	0.4988(7)	0.0440(7)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	N(11)	0.8071(12)	0.2801(9)	0.2235(7)	N(11)	0.8128(11)	0.3028(10)	0.2316(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(11)	0.6676(10)	0.2548(9)	0.2169(8)	C(11)	0.6794(11)	0.2659(9)	0.2212(9)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12)	0.5821(16)	0.1737(9)	0.1326(7)	C(12)	0.6046(13)	0.1853(8)	0.1343(7)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C(13)	0.4358(16)	0.1483(11)	0.1328(12)	C(13)	0.4653(13)	0.1515(10)	0.1241(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(14)	0.3278(18)	0.2053(13)	0.2122(10)	C(14)	0.3805(23)	0.1950(13)	0.1994(11)
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) ^{<i>a.b</i>} 0 0 $\frac{1}{2}$ C(11) 0.235 3(4) 0.740 8(4) 0.671 0(7) Ni(2) ^{<i>a.b</i>} $\frac{1}{2}$ $\frac{1}{2}$ 0 C(12) 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) 0.338 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) 0.422 (4) 0.600 7(4) 0.365 7(6) C(16) 0.308 3(5) 0.705 0(4) 0.788 (8) N(5) 0.120 6(4) 0.326 2(3) 0.227 3(6) O(21) ^{<i>a.c</i>} 0.018 9(9) 0.640 6(8) 0.331 1(12) N(6) 0.339 7(4) 0.029 2 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) 0.0723 3(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) 0.0723 (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) ^{<i>c.d</i>} 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) ^{<i>c.e</i>} 0.356 4(15) 0.122 8(16) 0.622 1(22) C(3) 0.412 1(4) 0.376 6(4) -0.011 5(6) O(32) ^{<i>c.e</i>} 0.356 4(15) 0.122 8(16) 0.622 1(22) C(4) 0.454 6(4) 0.552 1(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) * Multiplicity 0.5. ^b Special position at the inversion centre. ^c Atom in disorder. ^d Multiplicity 0.23(1). ^e Multiplicity 0.27(1).	C(15)	0.4639(15)	0.2807(13)	0.2865(10)	C(15)	0.4659(13)	0.2709(13)	0.2787(13)
* 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) ^{<i>a</i>,<i>b</i>} 0 0 $\frac{1}{2}$ C(11) 0.235 3(4) 0.740 8(4) 0.671 0(7) Ni(2) ^{<i>a</i>,<i>b</i>} $\frac{1}{2}$ 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) 0.322 2(3) 0.227 3(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 5(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) 0.356 (64) -0.011 5(6) O(32) ^{c,d} 0.313 3(29) -0.062 8(22) 0.517 7(34) C(3) 0.412 1(4) 0.356 (64) -0.011 5(6) O(32) ^{c,d} 0.313 3(29) -0.062 8(22) 0.517 7(34) C(3) 0.412 1(4) 0.365 (64) -0.011 5(6) O(32) ^{c,d} 0.313 3(29) -0.062 8(22) 0.517 7(34) C(3) 0.412 1(4) 0.356 (64) -0.011 5(6) O(32) ^{c,d} 0.313 2(9) -0.062 8(22) 0.517 7(34) C(3) 0.412 1(4) 0.356 (64) -0.011 5(6) O(32) ^{c,d} 0.313 2(9) -0.062 8(22) 0.517 7(34) C(3) 0.412 1(4) 0.356 (64) -0.011 5(6) O(32) ^{c,d} 0.313 2(9) -0.062 8(22) 0.517 7(34) C(3) 0.412 1(4) 0.356 (64) -0.011 5(6) O(32) ^{c,d} 0.313 2(9) -0.062 8(22) 0.517 7(34) 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) 0.330 (69) 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) * Multiplicity 0.5, ^b Special position at the inversion centre, ^c Atom in disorder, ^d Multiplicity 0.23(1), ^c Multiplicity 0.27(C(16)	0.6040(13)	0.3093(9)	0.2921(7)	C(16)	0.6074(13)	0.3147(8)	0.2988(7)
Table 3 Final atomic coordinates for compound 5 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) ^{<i>a.b.</i>} 0 0 $\frac{1}{2}$ C(11) 0.235 3(4) 0.740 8(4) 0.671 0(7) Ni(2) ^{<i>a.b.</i>} $\frac{1}{2}$ 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 7(6) C(21) 0.011 9(7) 0.573 9(5) 0.166 5(9) N(7) 0.350 3(4) 0.043 9(4) 0.020 2(7) C(22) 0.103	* Special pos	sition at the inversion	on centre; multiplic	ity = 0.5.				
Table 3 Final atomic coordinates for compound 5Atom X/a Y/b Z/c Cd0.245 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) ^{<i>a.b.</i>} 00 $\frac{1}{2}$ C(11)0.235 3(4)0.740 8(4)0.671 0(7)Ni(2) ^{<i>a.b.</i>} $\frac{1}{2}$ $\frac{1}{2}$ 0C(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) ^{<i>a.c.</i>} 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(23)0.094 1(6)0.478 6(7) $-0.094 6(9)$ 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) ^{<i>c.d.</i>} 0.335 2(13) $-0.041 4(10)$ 0.491 4(16)C(5)0.182 7(8)0.405 3(6)0.390 6(9)<						<u> </u>		<u> </u>
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)**b00 $\frac{1}{2}$ C(11) $0.235\ 3(4)$ $0.740\ 8(4)$ $0.671\ 0(7)$ Ni(2)**b $\frac{1}{2}$ $\frac{1}{2}$ 0C(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) $0.358\ 9(4)$ $0.303\ 1(3)$ $-0.012\ 1(66)$ 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) $0.018\ 9(9)$ $0.640\ 6(8)$ $0.331\ 1(12)$ N(6) $0.339\ 7(4)$ $0.292\ 1(4)$ $0.302\ 2(7)$ C(22) $0.103\ 9(6)$ $0.553\ 3(6)$ $0.072\ 3(9)$ C(1) $0.093\ 5(4)$ $0.043\ 9(4)$ $0.020\ 2(7)$ C(23) $0.094\ 1(6)$ $0.478\ 6(7)$ $-0.094\ 6(9)$ C(1) $0.093\ 5(4)$ $0.055\ 7(3)$ $0.361\ 4(5)$ C(23)	Table 3 Fin	nal atomic coordina	ites for compound	•				
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 $\frac{1}{2}$ C(11) $0.235\ 3(4)$ $0.740\ 8(4)$ $0.671\ 0(7)$ Ni(2) a,b $\frac{1}{2}$ 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) $0.120\ 6(4)$ $0.326\ 2(3)$ $0.227\ 3(6)$ C(21) $0.018\ 9(9)$ $0.640\ 6(8)$ $0.331\ 1(12)$ N(6) $0.339\ 7(4)$ $0.292\ 1(4)$ $0.302\ 2(7)$ C(22) $0.013\ 9(6)$ $0.553\ 3(6)$ $0.072\ 3(9)$ C(1) $0.093\ 6(4)$ $0.055\ 7(3)$ $0.361\ 4(5)$ C(23) $0.094\ 1(6)$ $0.478\ 6(7)$ $-0.046\ 6(9)$ N(7) $0.350\ 3(4)$ $0.080\ 9(3)$ $0.711\ 5(5)$ $O(31)\ c^{cd}$ $0.313\ 3(29)$ $-0.062\ 8(22)$ $0.517\ 7(34)$ C(3) $0.412\ 1(4)$ $0.376\ 6(4)$ $-0.011\ 5(6)$ $O(32)\ c^{cd}$ $0.356\ 4(15)$ $0.122\ 8(16)$ $0.622\ 1(22)$ C(4) $0.452\ $	Atom	X /a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cd	0.24562(3)	0.194 12(3)	0.112 75(4)	O(11)	0.2444(4)	0.712.2(4)	0.490 5(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$Ni(1)^{a,b}$	0	0	1	cân	0.2353(4)	0.740 8(4)	0.6710(7)
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) $0.264 0(7)$ $0.361 7(7)$ <td< td=""><td>$Ni(2)^{a,b}$</td><td>1</td><td>1</td><td>$\dot{0}$</td><td>$\tilde{C}(12)$</td><td>0.148 7(5)</td><td>0.809 0(4)</td><td>0.7327(9)</td></td<>	$Ni(2)^{a,b}$	1	1	$\dot{0}$	$\tilde{C}(12)$	0.148 7(5)	0.809 0(4)	0.7327(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 0.23(1). " Multiplicity 0.27(1).	N(I)	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(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) $0.474 0(4)$ $0.052 1(4)$ $0.040 8(7)$ $0.525 2(13)$ $0.109 3(7)$ $0.580 9(12)$	N(2)	0.1324(4)	0.127 1(3)	0.843 1(5)	C(14)	0.207 2(6)	0.805 4(5)	1.035 3(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) $0.417 1(12)$	N(3)	0.358 9(4)	0.303 1(3)	-0.0121(6)	C(15)	0.293 7(6)	0.739 4(5)	0.970 9(9)
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) $0.081 8(4)$ $0.080 9(3)$ $0.711 5(5)$ $O(31)^{c.d}$ $0.313 3(29)$ $-0.062 8(22)$ $0.517 (34)$ 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 $0.23(1)$. "Multiplicity $0.27(1)$.	N(4)	0.4242(4)	0.600 7(4)	0.365 7(6)	C(16)	0.308 3(5)	0.705 0(4)	0.786 8(8)
N(6) $0.3397(4)$ $0.2921(4)$ $0.3927(6)$ C(21) $0.0119(7)$ $0.5749(5)$ $0.1665(9)$ N(7) $0.3503(4)$ $0.0439(4)$ $0.0202(7)$ C(22) $0.1039(6)$ $0.5533(6)$ $0.0723(9)$ C(1) $0.0936(4)$ $0.0557(3)$ $0.3614(5)$ C(23) $0.0941(6)$ $0.4786(7)$ $-0.0946(9)$ C(2) $0.0818(4)$ $0.0809(3)$ $0.7115(5)$ $O(31)^{c.d}$ $0.3133(29)$ $-0.0628(22)$ $0.5177(34)$ C(3) $0.4121(4)$ $0.3766(4)$ $-0.0115(6)$ $O(32)^{c.e}$ $0.3564(15)$ $0.1228(16)$ $0.6221(22)$ C(4) $0.4526(4)$ $0.2298(7)$ C(31) $0.3952(13)$ $-0.0414(10)$ $0.4914(16)$ C(5) $0.1827(8)$ $0.4053(6)$ $0.3906(9)$ C(32) $0.4171(12)$ $0.0673(9)$ $0.5730(12)$ C(6) $0.2640(7)$ $0.3617(7)$ $0.4932(9)$ C(33) $0.5252(13)$ $0.1093(7)$ $0.5809(12)$ C(7) $0.4740(4)$ $0.0521(4)$ $0.0408(7)$ $0.3252(13)$ $0.1093(7)$ $0.5809(12)$ C(7) $0.4740(4$	N(5)	0.120.6(4)	0.3262(3)	0.227 3(6)	$O(21)^{a,c}$	0.018 9(9)	0.640 6(8)	0.331 1(12)
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) $0.474 0(4)$ $0.052 1(4)$ $0.040 8(7)$ $0.109 3(7)$ $0.580 9(12)$ $0.109 3(7)$ $0.580 9(12)$	N(6)	0.339 7(4)	0.292 1(4)	0.392 7(6)	Č(21)	0.0119(7)	0.574 9(5)	0.166 5(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). Multiplicity 0.27(1).	N(7)	0.350 3(4)	0.043 9(4)	0.0202(7)	C(22)	0.103 9(6)	0.553 3(6)	0.072 3(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 $0.27(1)$.	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(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 $0.27(1)$.	C(2)	0.081 8(4)	0.080 9(3)	0.711 5(5)	$O(31)^{c,d}$	0.313 3(29)	-0.0628(22)	0.517 7(34)
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 $0.23(1)$. Multiplicity $0.27(1)$.	C(3)	0.412 1(4)	0.376 6(4)	-0.0115(6)	O(32) ^{c,e}	0.356 4(15)	0.122 8(16)	0.622 1(22)
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) $0.474\ 0(4)$ $0.052\ 1(4)$ $0.040\ 8(7)$ $0.575\ 0(12)$ a' Multiplicity 0.5 . b' Special position at the inversion centre. c' Atom in disorder. a' Multiplicity $0.23(1)$. c' Multiplicity $0.27(1)$.	C(4)	0.454 6(4)	0.562 8(4)	0.229 8(7)	C(31)	0.395 2(13)	-0.0414(10)	0.491 4(16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	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(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).	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)
^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).	C(7)	0.474 0(4)	0.052 1(4)	0.040 8(7)	` '		- ()	
	^a Multiplicity	0.5. ^b Special posit	tion at the inversion	centre. ^c Atom in disc	rder. ^d Multiplicity	0.23(1). ^e Multinli	city 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 NH₂ groups, N(3) and N(4), chelated to the M in the adjacent chain; additionally the NH₂ group of the guest aniline, N(11), is directed toward N(2). One of the en NH₂ 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 $[Cd(en)_2Ni(CN)_4]$ -2PhNH₂ 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



(PhOH-3)





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; $\overline{I}(\bigcirc)$ at 0, $\frac{1}{2}$, 0 for PhOH-2 and at $\frac{1}{2}$, 0, $\frac{1}{2}$ 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)		
$N(2) \cdots N(3^{i})$	3.294(7)	3.355(7)	3.391(8)	3.619(8)		
$N(2) \cdots N(4^n)$	3.292(9)	3.214(9)	3.254(9)	3.24(1)		
$N(2) \cdots N(11^{m})$	3.35(1)	3.28(1)	3.35(1)	3.45(1)		
$N(3) \cdots N(11^{W})$	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 $N \cdots N$ 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 $\langle [CN-Cd(en)-NC-]_2 \}_n$ extension along the c axis of the crystal, in which Ni(1) is on the inversion centre at 0, 0, $\frac{1}{2}$. By depicting the square-planar Ni(CN)₄ as X, the infinite extension of XXX \cdots 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 $\frac{1}{2}$, $\frac{1}{2}$, 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-onedimensional 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) Ni(1)-C(2) Ni(2)-C(3) Ni(2)-C(4) Cd-N(1) Cd-N(2 ¹) Cd-N(3) Cd-N(3) Cd-N(5) Cd-N(6) Cd-N(7)	1.868(4) 1.855(4) 1.869(4) 1.869(5) 2.414(4) 2.313(4) 2.371(4) 2.339(4) 2.351(4) 2.325(4)	$\begin{array}{c} C(1)-N(1)\\ C(2)-N(2)\\ C(3)-N(3)\\ C(4)-N(4)\\ N(5)-C(5)\\ C(5)-C(6)\\ N(6)-C(6)\\ N(6)-C(6)\\ N(7)-C(7)\\ C(7)-C(7^n)\\ O(11)-C(11) \end{array}$	$\begin{array}{c} 1.136(5) \\ 1.136(5) \\ 1.131(6) \\ 1.124(6) \\ 1.508(8) \\ 1.42(1) \\ 1.418(8) \\ 1.460(6) \\ 1.505(7) \\ 1.353(6) \end{array}$	$\begin{array}{c} C(11)-C(12)\\ C(12)-C(13)\\ C(13)-C(14)\\ C(14)-C(15)\\ C(15)-C(16)\\ C(16)-C(11)\\ O(21)-C(21)\\ C(21)-C(22)\\ C(22)-C(23)\\ C(23)-C(21^{111}) \end{array}$	1.405(7) 1.380(8) 1.369(9) 1.393(9) 1.394(8) 1.373(7) 1.32(1) 1.36(1) 1.377(9) 1.41(1)	$\begin{array}{c} O(31)-C(31)\\ O(32)-C(32)\\ C(31)-C(32)\\ C(32)-C(33)\\ C(33)-C(31^{IV})\\ N(4)\cdots O(11)\\ N(4)\cdots N(6^V)\\ N(6)\cdots O(32)\\ O(1)\cdots O(21)\\ O(11)\cdots O(31^{V1}) \end{array}$	1.05(3) 1.05(2) 1.39(1) 1.37(1) 1.36(2) 2.711(7) 3.275(7) 3.19(2) 2.86(1) 2.97(3)
$\begin{array}{c} C(1)-Ni(1)-C(2)\\ C(3)-Ni(2)-C(4)\\ N(1)-Cd-N(2^{1})\\ N(1)-Cd-N(3)\\ N(1)-Cd-N(5)\\ N(1)-Cd-N(5)\\ N(1)-Cd-N(6)\\ N(2^{1})-Cd-N(3)\\ N(2^{1})-Cd-N(5)\\ N(2^{1})-Cd-N(6)\\ N(2^{1})-Cd-N(6)\\ N(3)-Cd-N(7)\\ N(3)-Cd-N(6)\\ N(3)-Cd-N(6)\\ N(5)-Cd-N(7)\\ N(5)-Cd-N(7)\\ N(6)-Cd-N(7)\\ N(6)-Cd-N(7)\\ \end{array}$	$\begin{array}{c} 90.6(2)\\ 89.2(2)\\ 95.0(1)\\ 172.3(1)\\ 85.2(1)\\ 87.7(2)\\ 84.8(2)\\ 92.6(1)\\ 93.0(2)\\ 168.7(2)\\ 86.5(2)\\ 95.4(2)\\ 85.0(2)\\ 94.7(2)\\ 76.2(2)\\ 169.9(2)\\ 104.7(2)\\ \end{array}$		$\begin{array}{l} Ni(1)-C(1)-N(1)\\ Ni(1)-C(2)-N(2)\\ Ni(2)-C(3)-N(3)\\ Ni(2)-C(4)-N(4)\\ Cd-N(1)-C(1)\\ Cd-N(2^{1})-C(2^{1})\\ Cd-N(3)-C(3)\\ Cd-N(5)-C(5)\\ Cd-N(6)-C(6)\\ Cd-N(7)-C(7)\\ N(5)-C(5)-C(6)\\ N(6)-C(6)-C(5)\\ N(7)-C(7)-C(7^{11})\\ O(11)-C(11)-C(12)\\ O(11)-C(11)-C(16)\\ C(12)-C(11)-C(16)\\ C(11)-C(12)-C(13)\\ \end{array}$	178.4(4) $177.5(4)$ $177.6(4)$ $178.0(5)$ $169.1(4)$ $170.6(4)$ $155.9(4)$ $107.5(4)$ $109.5(4)$ $121.2(3)$ $115.5(6)$ $116.0(6)$ $113.2(4)$ $116.8(5)$ $121.0(5)$ $122.2(5)$ $118.6(6)$		$\begin{array}{c} C(12)-C(13)-C(14)\\ C(13)-C(14)-C(15)\\ C(14)-C(15)-C(16)\\ C(11)-C(16)-C(15)\\ O(21)-C(21)-C(22)\\ O(21)-C(21)-C(23^{II})\\ C(21)-C(22)-C(23)\\ C(22)-C(23)-C(21^{III})\\ C(22)-C(23)-C(21^{III})\\ O(31)-C(31)-C(32)\\ O(31)-C(31)-C(33^{IV})\\ O(32)-C(32)-C(31)\\ O(32)-C(32)-C(33)\\ C(32)-C(33)-C(33)^{V}\\ C(31)-C(32)-C(33)\\ C(32)-C(33)-C(33)\\ C(32)-C(33)-C(31)^{V}\\ \end{array}$	120.8(6) 119.4(6) 121.7(6) 117.2(6) 117.2(6) 119.9(7) 120.4(6) 119.7(7) 108(3) 127(2) 126(2) 116(1) 124(1) 118(1)
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 NH₂ group of en, N(6), and the terminal N of the $Ni(2)(CN)_4$, N(4), have $O(11) \cdots O(21)$, $O(11) \cdots O(31)$, $N(4) \cdots O(11)$, $N(6) \cdots O(32)$ and $N(4) \cdots N(6)$ distances ranging from 2.7 to 3.3 Å.

Comparison of the Structures among the Aniline Clathrates and the Host Complexes.—Isostructural series of $[M(en)_2-M'(CN)_4]_n$ 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*-onedimensional 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 NH₂ group of the chelating en. Each of the octahedral MN₆ co-ordination spheres is elongated along the chain, in particular for 2' due to the Jahn–Teller effect on the Cu²⁺. 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 Å³ in comparison with

342 and 345 Å³ 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 $N \cdots N$ 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]. 2PhNH₂ 4, [{Cd(en)}₂(en){Ni(CN)₄}₂]·4PhOH 5 and [Cd(en)-Ni(CN)₄]-2C₆H₆ 6.—The inclusion compounds 4, 5 and the known² Hofmann-en-type $[Cd(en)Ni(CN)_4] \cdot 2C_6H_6$ 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-onedimensional linkage builder in 4, catena-doubly-one-dimensional and trans-bridging ligand in 5, and catena-tetraclose-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 [$>Ni\langle$ $(CN-Cd-NC-)_2$ at one side, whereas the C₆H₆ in 6 is clipped with a couple of bridging en ligands and capped with the closetwo-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. $NH_3 \cdot G = Ni(NH_3)_2Ni(CN)_4 \cdot 2G$ where $G = C_6H_6$, $PhNH_2$ or PhOH·H₂O 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 $[Cd(NH_3)_2Ni(CN)_4]$ -2G are replaced by one en for C₆H₆, 1.5 en for PhOH and 2 en for PhNH₂.

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