Topologically Different Infinite Co-ordination Structures of $[CdNi(CN)_4]\cdot 2H_2N(CH_2)_nNH_2\cdot mH_2O$ Complexes (n = 2–7 and 9, m = 0–2) caused by the Catenation Behaviour of the Diamine and the $-NC-Ni(CN)_2-CN-$ Moieties†

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The single-crystal structures have been determined for a tris(en)-chelated complex $[Cd(en)_3][Ni(CN)_4]$ **2a** and a series of $[CdNi(CN)_4]\cdot 2H_2N(CH_2)_nNH_2\cdot mH_2O$ complexes with n = 2–7 and 9 and m = 0–2: $[Cd(en)_2Ni(CN)_4]$ **2b** (monoclinic) and **2c** (orthorhombic) (n = 2), $[Cd(tn)_2Ni(CN)_4]$ (n = 3) **3**, $[Cd(dabtn)_2Ni(CN)_4]\cdot 2H_2O$ **4** (n = 4), $[Cd(daptn)_2Ni(CN)_4]\cdot H_2O$ **5** (n = 5), $[Cd(H_2O)_2(dahxn)_2]$-$[Ni(CN)_4]$ **6** (n = 6), $[Cd(dahpn)_2Ni(CN)_4]\cdot H_2O$ **7** (n = 7) and $[Cd(danon)_2Ni(CN)_4]$ **9** (n = 9). Only **2a** comprises discrete $[Cd(en)_3]^{2+}$ and $[Ni(CN)_4]^{2-}$; the other structures are constructed by the catenation of either $H_2N(CH_2)_nNH_2$ or $[Ni(CN)_4]^{2-}$, or both, linking octahedral Cd atoms successively. In **2b** and **2c** the bis(en)-chelated Cd atoms are spanned by *cis*-[–NC–Ni(CN)$_2$–CN–] moieties to form a one-dimensional chain (*cis*-one-dimensional). Each single span of the tn and danon in **3** and **9** links Cd atoms to form a two-dimensional network as a single two-dimensional network builder; a *cis*-one-dimensional $Ni(CN)_4$ moiety reinforces one of the single tn spans in **3**, whereas it bridges the single two-dimensional networks in **9** to build up a three-dimensional framework. Two diamine ligands span the Cd atoms in **4**–**6** to form a doubly bridged one-dimensional chain. The chains are spanned by *trans*-[–NC–Ni(CN)$_2$–CN–] moieties to form a two-dimensional network in **4**, whereas the double one-dimensional chain in **5** is additionally reinforced by a *cis*-one-dimensional $Ni(CN)_4$ moiety to form a triple-span chain. The Cd atom in the double one-dimensional dahxn chain in **6** is co-ordinated by two *trans* related H_2O molecules, among whose chains discrete $[Ni(CN)_4]^{2-}$ anions are accommodated. Complex **7** shows a complicated structure constructed of a four-fold interpenetrating diamondoid three-dimensional sub-lattice framed by Cd–dahpn–Cd spans which has interconnections through the catenation of *cis*-one-dimensional $Ni(CN)_4$ at every Cd. The H_2O molecules in **4**, **5** and **7** are accommodated in the void spaces formed in the respective multidimensional structures. These crystal structures are additionally stabilised by hydrogen bonds involving the NH_2 group of the diamine, the nitrogen end of the $Ni(CN)_4$ moiety and H_2O molecules. The variations of the multidimensional structures are discussed in terms of the number of methylene units n in the diamines.

A common topology of the three-dimensional framework constructed by a two-dimensional network spanned successively by one-dimensional chains in parallel has been observed for the host structures of the Hofmann diamine-type clathrates $[Cd\{H_2N(CH_2)_nNH_2\}_2Ni(CN)_4]\cdot xG$ (n = 2–9, x = 0.5–2, G = aromatic guest),[1,2] where the network is square-meshed $[CdNi(CN)_4]_\infty$ and the chain is the *catena*-μ-diamine-cadmium linkage sharing the Cd atoms with the networks. Although distortions of the three-dimensional framework and cavity structure occur more or less depending on the number of methylene units in the diamine skeleton n, diamines with even n are more favourable than those with odd n in giving well developed crystals of the clathrates suitable for single-crystal X-ray experiments. In the course of our investigations related to the Hofmann diamine-type, in particular attempts to prepare clathrates with odd-n diamine hosts,[3] a number of complexes with general composition $CdNi(CN)_4\cdot 2H_2N(CH_2)_nNH_2\cdot mH_2O$ (n = 2–9, m = 0–2) in which no aromatic guests are involved were obtained from aqueous solutions of the host moieties. The single-crystal structures of these complexes revealed a variety of multidimensional infinite co-ordination structures with different topologies such as one-dimensional chain, two-dimensional network and three-dimensional framework, upon change of n, the structural variations of which are due to the various catenation modes of the diamine and $[Ni(CN)_4]^{2-}$ moieties linking the octahedral Cd atoms. Except for the chelating en (1,2-diaminoethane, n = 2), the diamine bridges the Cd atoms in either single or double spans; the resulting catenation gives the three topologies mentioned above. Except for the case of a discrete anion, the $[Ni(CN)_4]^{2-}$ plays the role of *catena*-μ-linkage builder providing a couple of CN groups at either *cis* or *trans* positions of the Cd atoms; the catenation increases the order of the lattice dimension by bridging the en-chelated Cd atoms, the cadmium–diamine chains or the cadmium–diamine networks, or reinforces the cadmium–diamine chain in parallel. Water molecules behave as guests in the resulting lattice or as ligands to the Cd atom.

This paper describes the topologically different multidimensional structures of these complexes with n = 2–7 and 9, and a tris(en)-chelated complex $[Cd(en)_3][Ni(CN)_4]$ comprising discrete complex cations and anions. As for the complex involving 1,8-diaminooctane (n = 8), crystals suitable for X-ray diffraction were unavailable.

Experimental

Preparation of the Complexes.—The complexes listed in Table 1 were obtained as single crystals from aqueous solutions left to stand at *ca.* 5 °C. Their numbering is in accord with the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical data for the complexes

	Analysis (%)*		
Complex	C	H	N
2a $[Cd(en)_3][Ni(CN)_4]$	26.0 (26.4)	5.15 (5.30)	30.1 (30.8)
2b $[Cd(en)_2Ni(CN)_4]$	24.4 (24.3)	4.05 (4.10)	28.3 (28.3)
2c $[Cd(en)_2Ni(CN)_4]$	24.0 (24.3)	4.30 (4.10)	27.9 (28.3)
3 $[Cd(tn)_2Ni(CN)_4]$	28.3 (28.4)	4.70 (4.75)	26.2 (26.5)
4 $[Cd(dabtn)_2Ni(CN)_4]\cdot 2H_2O$	29.4 (29.6)	5.60 (5.80)	23.1 (23.0)
5 $[Cd(daptn)_2Ni(CN)_4]\cdot H_2O$	33.5 (33.8)	5.85 (6.10)	22.5 (22.5)
6 $[Cd(H_2O)_2(dahxn)_2][Ni(CN)_4]$	35.2 (35.4)	6.55 (6.65)	20.8 (20.6)
7 $[Cd(dahpn)_2Ni(CN)_4]\cdot H_2O$	36.4 (39.0)	6.85 (6.90)	19.6 (20.2)
9 $[Cd(danon)_2Ni(CN)_4]$	44.1 (44.7)	7.20 (7.50)	19.2 (18.9)

* Calculated values in parentheses.

number of methylene units *n* in the diamine skeleton. The compositions were determined based on the results of the chemical analyses, density measurements and refined crystal structures.

(*a*) $[Cd(en)_3][Ni(CN)_4]$ **2a** *and* $[Cd(en)_2Ni(CN)_4]$ **2b** *and* **2c**. From aqueous solutions (100 cm^3) containing $CdCl_2\cdot 2.5H_2O$ (1.14 g, 50 mmol), $K_2[Ni(CN)_4]\cdot H_2O$ (1.30 g, 50 mmol) and 10 molar equivalents of $H_2N(CH_2)_2NH_2$ (en) with respect to Cd, the complexes $[Cd(en)_3][Ni(CN)_4]$ and $[Cd(en)_2Ni(CN)_4]$ crystallised respectively depending on the pH adjusted with citric acid. When the solution at pH > 11 was allowed to stand in a refrigerator at *ca.* 5 °C for a few weeks, yellow tetragonally shaped plate-like crystals of $[Cd(en)_3][Ni(CN)_4]$ **2a** were obtained. From the solution adjusted to pH *ca.* 10, $[Cd(en)_2Ni(CN)_4]$ crystallised as yellow plates of the monoclinic system **2b** or as yellow needles of the orthorhombic system **2c**; either of the crystal types were obtained by chance, even from aliquots prepared and manipulated under conditions adjusted to be as same as possible. From the solution kept at room temperature, or from the solution at pH < 9, crystals of $[Cd(en)Ni(CN)_4]$ **2d**[4,5] were obtained.

(*b*) $[Cd(tn)_2Ni(CN)_4]$ **3**. By using $H_2N(CH_2)_3NH_2$ (1,3-diaminopropane, tn) in place of en, yellow plate-like crystals of **3** were obtained by a procedure similar to that for **2b**.

(*c*) $[Cd(dabtn)_2Ni(CN)_4]\cdot 2H_2O$ **4**, $[Cd(daptn)_2Ni(CN)_4]\cdot H_2O$ **5**, $[Cd(H_2O)_2(dahxn)_2][Ni(CN)_4]$ **6**, $[Cd(dahpn)_2Ni(CN)_4]\cdot H_2O$ **7** *and* $[Cd(danon)_2Ni(CN)_4]$ **9**. Single crystals were obtained for each of these complexes from aqueous solutions of the host moieties used in the preparation of the Hofmann diamine-type clathrates[2,3] by keeping the solution in a refrigerator at *ca.* 5 °C for a few weeks: as yellow plates for **4** (dabtn = 1,4-diaminobutane) and **9** (danon = 1,9-diaminononane), prisms for **5** (daptn = 1,5-diaminopentane) and **6** (dahxn = 1,6-diaminohexane), and needles for **7** (dahpn = 1,7-diaminoheptane). These crystals were also obtained from the solutions containing Cd^{2+}, $[Ni(CN)_4]^{2-}$ and diamine in the molar ratio of 1 : 1 : 1–2. Attempts to obtain single crystals of analogous complexes ligated by $H_2N(CH_2)_8NH_2$ (1,8-diaminooctane, daotn) were unsuccessful.

Crystallography.—The crystallographic and selected experimental data are listed in Table 4. The cell dimensions were refined using 25 reflections in the range 14 ⩽ θ ⩽ 20°. During the intensity-data collection three standard reflections were monitored after every 200 for **2a**, **2b**, **2c**, **5** and **6**, and after every 150 for **3**, **4**, **7** and **9**: no significant decay was observed. Lorentz polarisation corrections were applied, empirical absorption corrections[6] for **2a**–**2c**, **3**, **4** and **9** and extinction corrections for **2a**, **3**, **5** and **7**. The positions of Cd and Ni atoms were located by the Patterson method using SHELXS 86.[7] The structures were solved by the heavy-atom method; successive Fourier and Fourier-difference syntheses and full-matrix least-squares procedures were applied using SHELX 76.[8] All the non-H atoms were refined anisotropically; H atoms except for those of H_2O were located at calculated positions and included in the final structure-factor calculations. The calculations were carried out on a HITAC M-680H computer at the Institute for Molecular Science, Okazaki; atomic scattering factors including those for real and imaginary anomalous dispersion corrections were taken from ref. 9 for Cd and Ni, and SHELX 76 for O, N, C and H.

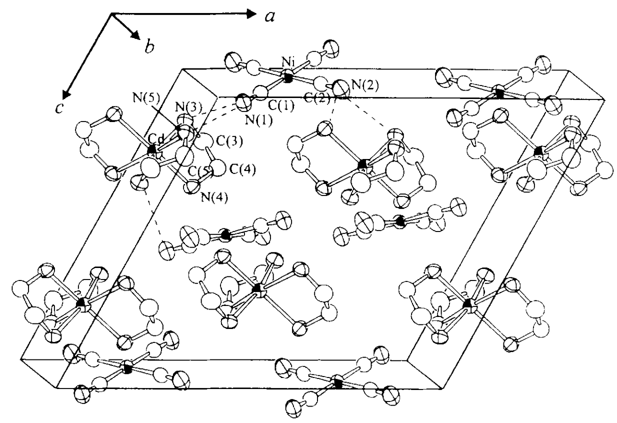

Fig. 1 Perspective view of $[Cd(en)_3][Ni(CN)_4]$ **2a** showing 50% probability thermal ellipsoids; interionic hydrogen bonds are shown with broken lines

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

Results and Discussion

The refined atomic coordinates are listed in Table 5 for all the complexes. The solved structures are shown in Fig. 1 for **2a**, Fig. 2 for **2b** and **2c**, and Fig. 3–8 for **3**–**9**, respectively. Selected interatomic distances and angles are summarised in Table 2.

Description of the Structures.—General. For all the solved structures the bond distances and angles in the diamine skeletons are in expected ranges (1.46–1.51 Å for N–C bonds, 1.47–1.56 Å for C–C and 106–125° for Cd–N–C, N–C–C and C–C–C angles). The distortion of the co-ordination environment is generally less in the square-planar $Ni(CN)_4$ moieties than in the octahedral CdN_6 and CdN_4O_2. The Ni–C distances (1.85–1.89 Å) and C–Ni–C angles (88.9–91.1°) are almost constant except those angles for complexes **2b**, **2c** and **3** (86–95°). In **2b** and **2c** the angle between the bridging CN groups is greater than that between the unidentate ones by *ca.* 9° to lessen the repulsion between the en chelate rings on the bridged Cd atoms. The distortion of the C(1)–Ni–C(4) angle in **3**, that

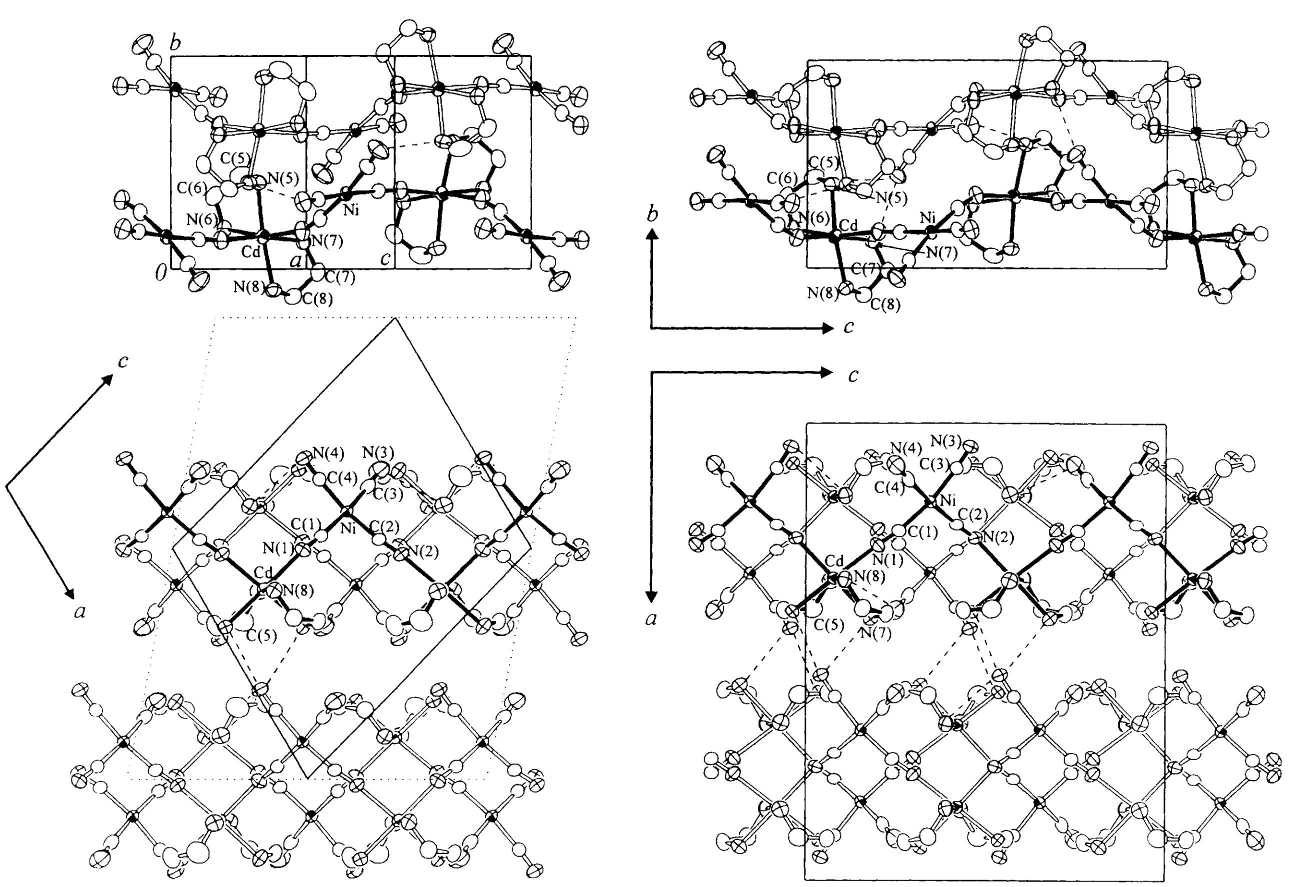

Fig. 2 Structures of the monoclinic **2b** (left) and orthorhombic **2c** (right) modifications of [Cd(en)$_2$Ni(CN)$_4$] showing 50% probability thermal ellipsoids. Top: projection along the [10$\bar{1}$] direction for a couple of the infinite chains in **2b** and that along the *a* axis for those in **2c**. Bottom: the respective views along the *b* axis. Dotted line for left bottom shows the doubled unit cell (Z = 8; see text); broken lines show hydrogen bonds

between the bridging and unidentate CN, may be due to hydrogen-bond formation between the nitrogen end of the unidentate CN and the NH$_2$ group of the tn.

The Cd–N and Cd–O distances are distributed in the range 2.31–2.44 Å as usual in six-co-ordinated CdN$_6$ and CdN$_4$O$_2$. The distortions in the angles are greater in the chelate complexes **2a**–**2c** (75–110°) than in the others (80–100°). As for the linearity of the Ni–C–N–Cd span, more distortions are seen in the Cd–N–C than in the Ni–C–N angles; the greatest distortion being for the former [144.2(7)°] in **9** and for the latter [172.4(4)°] in **2b**. Bending at the N atom of Cd–N–C linkages often occurs to a considerable extent in multidimensional structures comprised of CdNi(CN)$_4$ moieties.[2]

In all the present self-assembled structures, formation of hydrogen bonds was observed among the relevant entities, *i.e.* the NH$_2$ group of the diamine, unbridged nitrogen end of the Ni(CN)$_4$, and the H$_2$O ligated and accommodated, which may contribute to stabilisation of the respective crystal packings.

Complex **2a**. As is illustrated in Fig. 1, the crystal structure is comprised of the packing of discrete [Cd(en)$_3$]$^{2+}$ cations and [Ni(CN)$_4$]$^{2-}$ anions; the cations are located on the two-fold axes at $z = \frac{1}{4}$ and $\frac{3}{4}$, and the anions on the inversion centres at $z = 0$ and $\frac{1}{2}$. The [Cd(en)$_3$]$^{2+}$ cations adopt the pair of absolute configurations Δδδδ and Λλλλ in contrast with Δλλλ and Λδδδ for the [Zn(en)$_3$]$^{2+}$ in [Zn(en)$_3$][Ni(CN)$_4$] **2a′**.[10]

The structures of complexes **2a** (*C*2/*c*) and **2a′** (*P*2$_1$/*n*) differ not only in the absolute configuration of [M(en)$_3$]$^{2+}$ and the space group but also in the orientation of the [Ni(CN)$_4$]$^{2-}$ anions. In **2a** the square-planar anions at $z = 0$ and $\frac{1}{2}$ are arranged with an inclination of 30.9° between their molecular planes, the corresponding angle between those at $y = 0$ and $\frac{1}{2}$ in **2a′** being 82.8°. Those in **2a** are arranged nearly in parallel on each plane at $z = 0$ and $\frac{1}{2}$, whereas the two crystallographically independent anions in **2a′** are almost perpendicular to each other with a dihedral angle of 88.3° (calculated from the data in ref. 10) between the molecular planes at $y = 0$ or $\frac{1}{2}$. The remarkable difference in the inclination angle between **2a** and **2a′** is due to the difference in size of the octahedral co-ordination sphere: the Zn–N(en) distances 2.22–2.24 Å are shorter than those of Cd–N(en) 2.38–2.39 Å. The smaller co-ordination sphere decreases the distance between the neighbouring anions and increases the repulsion between them; the Ni ··· Ni distances between the neighbouring anions in the same layer are 8.89 and 9.46 Å in **2a** and 7.96 and 8.06 Å in **2a′**. The hydrogen bonds between the NH$_2$ groups and the nitrogen ends of [Ni(CN)$_4$]$^{2-}$ stabilise the crystal packings.

Complexes **2b** *and* **2c**. The respective space groups *P*2$_1$/*n* and *Pbca* for the monoclinic and orthorhombic modifications were uniquely determined from the observed systematic absences. As shown in Fig. 2, there are infinite chains of *cis*-[Cd(en)$_2$–*cis*-NC–Ni(CN)$_2$–CN–]$_\infty$ catenation in both structures. The bis(en)-chelated Cd is linked successively with [Ni(CN)$_4$]$^{2-}$ which provides two N atoms of the CN groups at *cis* positions for the catenation; this mode of catenation may be called *cis*-one-dimensional for the Ni(CN)$_4$ moiety as a *catena*-μ-linkage builder. The Ni(CN)$_4$ moieties are arranged at *cis* positions with regard to the Cd atom so that the one-dimensional chain is that of *cis*-(*cis*-one-dimensional). The zigzag chain of the *cis*-one-dimensional catenation is remarkably different from the straight chains in [M(en)$_2$M′(CN)$_4$] (M = Ni, Cu or Zn, M′ = Ni;[11] M = Ni, M′ = Pd[12]) and in the hosts of the aniline clathrates [M(en)$_2$Ni(CN)$_4$]·2PhNH$_2$ (M = Ni, Cu, Zn or Cd),[13] where *trans*-[–NC–M′(CN)$_2$–CN–] links M at *trans* positions in the mode of *trans*-one-dimensional catenation.

For the sake of comparison the monoclinic unit cell of complex **2b** (Z = 4) may be doubled to Z = 8 to be the same as

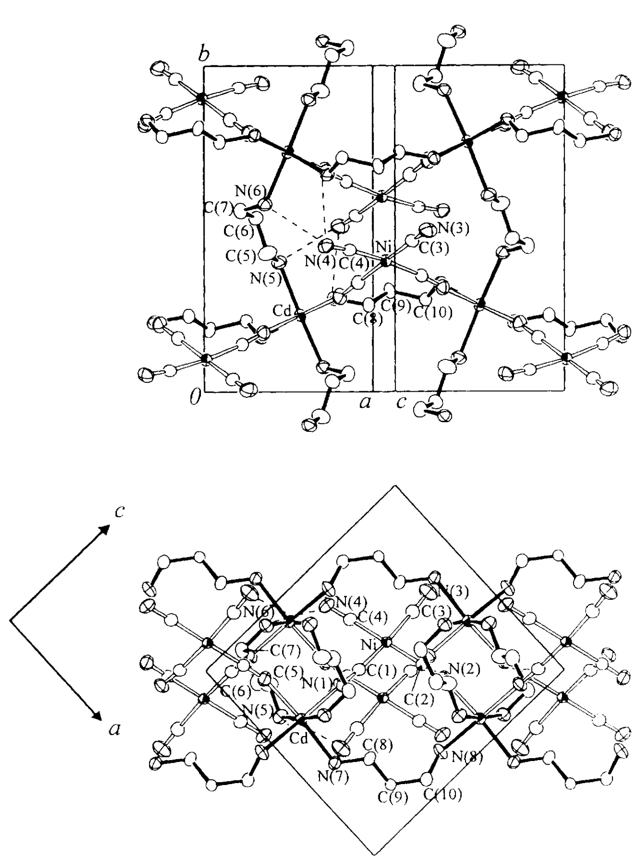

Fig. 3 Structure of $[Cd(tn)_2Ni(CN)_4]$ **3** showing 50% probability thermal ellipsoids. Top: projection along the $[10\bar{1}]$ direction. Bottom: projection along the *b* axis for a two-dimensional network. A single two-dimensional network is shown with solid bonds, hydrogen bonds with broken lines

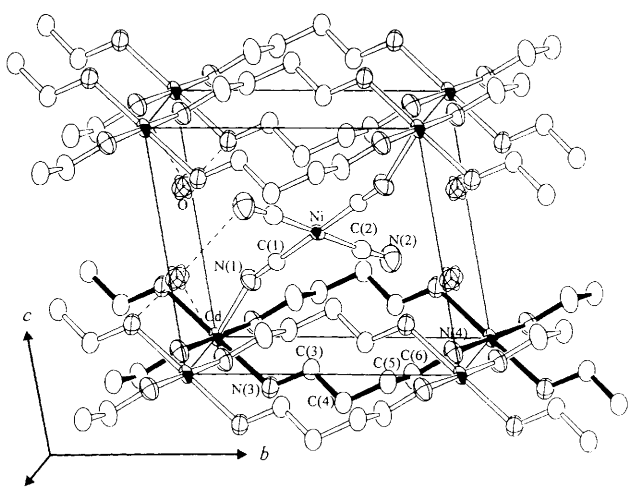

Fig. 4 A perspective view of $[Cd(dabtn)_2Ni(CN)_4]\cdot 2H_2O$ **4** showing 50% probability thermal ellipsoids. A double one-dimensional chain is shown with solid bonds, hydrogen bonds with broken lines

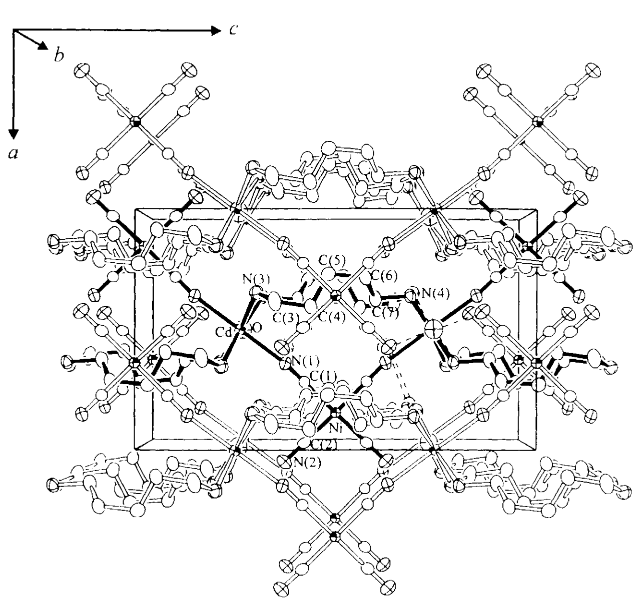

Fig. 5 A perspective view of $[Cd(daptn)_2Ni(CN)_4]\cdot H_2O$ **5** along the *b* axis showing 50% probability thermal ellipsoids. A triple-span chain is shown with solid bonds, hydrogen bonds with broken lines

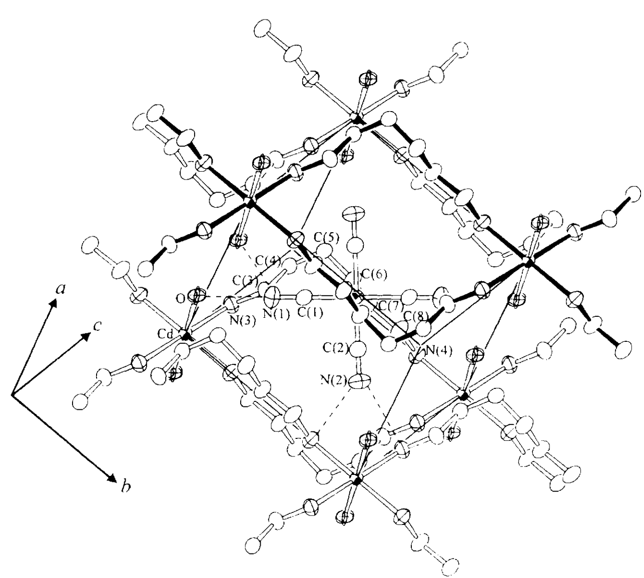

Fig. 6 A perspective view of $[Cd(H_2O)_2(dahxn)_2][Ni(CN)_4]$ **6** showing 50% probability thermal ellipsoids. A double one-dimensional chain is shown with solid bonds, hydrogen bonds with broken lines

that in **2c**, with the corresponding parameters $a' = a - c = 20.493(2)$, $b' = b = 9.257(1)$, $c' = a + c = 15.438(2)$ Å and $\beta' = 100.696(7)°$; the axial parameters are similar to those of **2c** but with a distortion in β' of *ca.* 10.7° from the rectangle in **2c**. The cis-(*cis*-one-dimensional) chains run along the [101] direction in **2b** and parallel to the *c* axis in **2c**. The absolute configurations of the $Cd(en)_2$ moieties are $-\{[\Delta\lambda\lambda\text{-}Cd(en)_2]\text{-}NC\text{-}Ni(CN)_2\text{-}CN\text{-}[\Lambda\delta\delta\text{-}Cd(en)_2]\text{-}NC\text{-}Ni(CN)_2\text{-}CN\text{-}\}_\infty$ along the chain in both structures, the array of both configurations being correlated by the glide planes normal to the *b* axes. The two modifications differ in the method of chain stacking along the *b* axis in relation to the array of the two $Cd(en)_2$ moieties differing in absolute configuration. The chains are stacked with the same phase in **2b** correlated by the 2_1 screw axis at $\frac{1}{4}$, *y*, $\frac{1}{4}$, but those in **2c** with a shift of a half period correlated by the 2_1 screw axis at $\frac{1}{4}$, $\frac{1}{2}$, *z*. In consequence the arrangement of the chains in **2b** along the $[10\bar{1}]$ direction is slightly shifted owing to the monoclinic distortion in comparison with that in orthorhombic **2c**.

Hydrogen-bond networks are formed between the N atoms of unidentate CN and the NH_2 of en in both **2b** and **2c**, but the modes of linkage are different. The interchain hydrogen bonds along the *b* axis are N(3)···N(5) 3.207(6) and N(4)···N(8) 3.246(7) Å in **2b**, and N(3)···N(8) 3.299(7), N(4)···N(5) 3.140(8) and N(4)···N(7) 3.119(8) Å in **2c**. Those along the

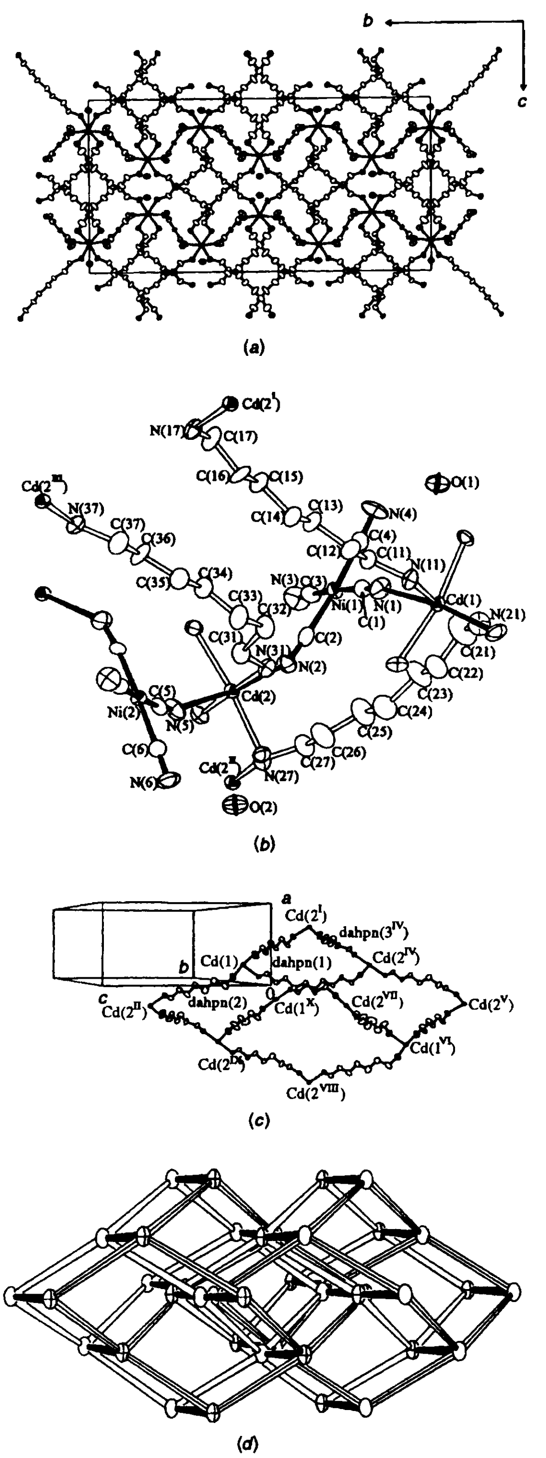

Fig. 7 Structure of $[Cd(dahpn)_2Ni(CN)_4]\cdot H_2O$ 7. (*a*) Projection along the *a* axis, (*b*) the asymmetric unit, (*c*) the diamondoid three-dimensional Cd-dahpn sub-lattice [with 50% probability thermal ellipsoids for (*a*)–(*c*)] and (*d*) a ball-and-stick illustration of the four-fold interpenetrating diamondoid three-dimensional sub-lattices interconnected by the *trans*-(*cis*-one-dimensional) catenation of $Ni(CN)_4$: a couple of the two-fold interpenetrating sub-lattices are given with triple-linked dahpn spans, one connecting open and the other crossed cadmium ellipsoids, which doublet generates the doublet with open dahpn spans with open and crossed Cd, respectively, from the symmetry requirements of the *Pnna* space group; each Cd is spanned by the *trans*-(*cis*-one-dimensional) catenation of $Ni(CN)_4$ with solid bonds to the nearest neighbours. Symmetry operations: I $x + \frac{1}{2}, y, -z$; II $x - \frac{1}{2}, y, 1 - z$; III $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$, IV $x, \frac{1}{2} - y, -\frac{1}{2} - z$; V $x - \frac{1}{2}, y, -z - 1$; VI $x - 1, y, z - 1$; VII $-x, -y, -z$; VIII $x - \frac{3}{2}, y, -z$; IX $x - 1, \frac{1}{2} - y, \frac{1}{2} - z$; X $-x, y + \frac{1}{2}, z - \frac{1}{2}$

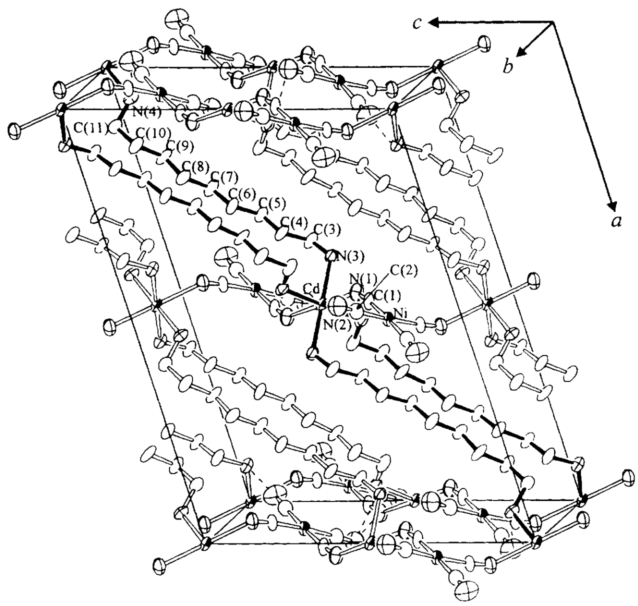

Fig. 8 A perspective view of $[Cd(danon)_2Ni(CN)_4]$ 9 showing 50% probability thermal ellipsoids. The single two-dimensional network along the (101) plane is shown with solid bonds, hydrogen bonds with broken lines

[10$\bar{1}$] direction for **2b** and along the *a* axis for **2c** are N(3) ··· N(7) 3.028(7), N(4) ··· N(6) 3.066(6) and N(4) ··· N(7) of 3.367(7), and N(3) ··· N(6) 3.054(7) and N(3) ··· N(7) 3.348(7) Å respectively.

Complex **3**. The space group $P2_1/n$ was uniquely determined from the systematic absences. As shown in Fig. 3, complex **3** has a two-dimensional network structure: each tn spans a couple of Cd atoms, and each of the Cd atoms is linked by four tn ligands to four other Cd atoms. The catenation behaviour of the tn may be regarded as single two-dimensional network building. In addition, the Cd–tn–Cd span along the [101] direction is reinforced with *cis*-(*cis*-one-dimensional) catenation of the $Ni(CN)_4$ moieties. In the tn–$Ni(CN)_4$ double span the tn skeleton adopts a *trans-gauche-trans-trans* (tgt_2) conformation to adjust the span length to the rigid *cis*-one-dimensional $Ni(CN)_4$ moiety. The t_2g_2 conformation of the tn in the single span between the double spans along the *b* axis is appropriate for making the crystal packing dense. Hydrogen-bond formation is suggested in the double span, N(3) ··· N(5) 3.229(8), N(3) ··· N(7) 3.106(8), N(4) ··· N(6) 3.190(7) and N(4) ··· N(8^{III}) 3.087(8) Å, and between both chains, N(4) ··· N(6^{IV}) 3.225(7) and N(4) ··· N(8^{V}) 3.201(7) Å.

Complex **4**. As shown in Fig. 4, the Cd atoms of the origin and equivalent positions in the triclinic $P\bar{1}$ unit cell are doubly spanned along the *b* axis by a couple of dabtn ligands adopting the skeletal conformation t_2gt_2, the catenation mode being double one-dimensional. The chains are bridged by the *trans*-one-dimensional $Ni(CN)_4$ moiety located at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ between Cd atoms at 0, 0, 0 and 1, 1, 1 so that the *trans*-[Cd–*trans*-NC–$Ni(CN)_2$–CN–$]_\infty$ chain runs along the [111] direction. Eventually a two-dimensional network is extended along the (10$\bar{1}$) plane. Such a network also occurs in the host structures of $[Cd(diamine)_2Ni(CN)_4]\cdot 2G$ inclusion compounds [diamine = danon, G = $3,5-Me_2C_6H_3NH_2$; 1,10-diaminodecane (dadcn), G = $PhNH_2$, *o*-, *m*- or *p*-$MeC_6H_4NH_2$ or 2,3-, 3,4- or 2,6-$Me_2C_6H_3NH_2$].[14] The H_2O molecules are accommodated between the double one-dimensional chains as the guests; hydrogen bonds are suggested to the N atom of the unidentate CN group with distances of 3.049(6) Å and to the N atoms of the dabtn, 3.197(6) and 3.298(6) Å.

Complex **5**. The space group $C222_1$ was uniquely determined from the observed systematic absences. The absolute structure was confirmed by comparing the two enantiomorphs having *R'*

Table 2 Selected interatomic distances (Å) and angles (°)

(*a*) $[Cd(en)_3][Ni(CN)_4]$ **2a** [a]

Ni–C(1)	1.852(7)	Cd–N(4)	2.375(6)	C(2)–N(2)	1.125(9)	N(1) ··· N(5^{II})	3.303(8)
Ni–C(2)	1.865(7)	Cd–N(5)	2.387(6)	N(1) ··· N(3)	3.291(11)	N(2) ··· N(3^{III})	3.252(9)
Cd–N(3)	2.389(6)	C(1)–N(1)	1.141(9)	N(1) ··· N(5)	3.112(12)	N(2) ··· N(4^{IV})	3.252(11)

C(1)–Ni–C(2)	89.3(3)	N(3)–Cd–N(5)	90.5(2)	Ni–C(1)–N(1)	177.9(7)	Ni–C(2)–N(2)	178.4(7)
N(3)–Cd–N(4)	74.9(2)	N(4)–Cd–N(5)	99.3(2)				

(*b*) $[Cd(en)_2Ni(CN)_4]$ **2b** and **2c** [b]

	2b	**2c**		**2b**	**2c**
Ni–C(1)	1.878(5)	1.870(6)	C(3)–N(3)	1.140(6)	1.133(7)
Ni–C(2)	1.863(4)	1.873(6)	C(4)–N(4)	1.134(6)	1.144(7)
Ni–C(3)	1.851(5)	1.862(6)	N(3) ··· N(5^{II})	3.207(6)	
Ni–C(4)	1.858(4)	1.856(6)	N(3) ··· N(7^{II})	3.028(7)	
Cd–N(1)	2.414(4)	2.391(5)	N(4) ··· N(6^{III})	3.066(6)	
Cd–N(2^{I,V})	2.359(4)	2.441(5)	N(4) ··· N(7^{III})	3.367(7)	
Cd–N(5)	2.352(4)	2.323(5)	N(4) ··· N(8^{IV})	3.246(7)	
Cd–N(6)	2.350(4)	2.337(5)	N(3) ··· N(6^{VI})		3.054(7)
Cd–N(7)	2.372(4)	2.384(5)	N(3) ··· N(7^{VI})		3.348(7)
Cd–N(8)	2.343(4)	2.322(5)	N(4) ··· N(5^{VIII})		3.140(8)
C(1)–N(1)	1.140(6)	1.138(7)	N(4) ··· N(7^{VIII})		3.119(8)
C(2)–N(2)	1.158(6)	1.156(7)	N(3) ··· N(8^{VII})		3.299(7)
C(1)–Ni–C(2)	95.1(2)	94.6(2)	N(2^{I,V})–Cd–N(8)	95.5(2)	97.8(2)
C(1)–Ni–C(3)	173.1(2)	170.0(2)	N(5)–Cd–N(6)	76.6(1)	77.6(2)
C(1)–Ni–C(4)	90.1(2)	89.1(3)	N(5)–Cd–N(7)	97.2(1)	95.5(2)
C(2)–Ni–C(3)	89.6(2)	91.0(2)	N(5)–Cd–N(8)	173.0(1)	171.2(2)
C(2)–Ni–C(4)	171.2(2)	172.4(3)	N(6)–Cd–N(7)	93.2(1)	94.7(2)
C(3)–Ni–C(4)	85.9(2)	86.3(2)	N(6)–Cd–N(8)	104.5(1)	106.3(2)
N(1)–Cd–N(2^{I,V})	94.9(2)	95.7(2)	N(7)–Cd–N(8)	75.9(1)	76.5(2)
N(1)–Cd–N(5)	90.1(2)	89.4(2)	Ni–C(1)–N(1)	172.4(4)	172.6(6)
N(1)–Cd–N(6)	166.7(2)	166.9(2)	Ni–C(2)–N(2)	172.4(4)	174.9(5)
N(1)–Cd–N(7)	88.5(2)	85.3(2)	Ni–C(3)–N(3)	175.4(5)	174.9(5)
N(1)–Cd–N(8)	88.7(2)	86.5(2)	Ni–C(4)–N(4)	176.9(4)	176.5(6)
N(2^{I,V})–Cd–N(5)	91.5(2)	90.4(2)	Cd–N(1)–C(1)	156.1(4)	173.4(5)
N(2^{I,V})–Cd–N(6)	85.5(1)	85.7(2)	Cd–N(2^{I,V})–C(2^{I,V})	172.0(4)	148.1(5)
N(2^{I,V})–Cd–N(7)	170.7(2)	174.1(2)			

(*c*) $[Cd(tn)_2Ni(CN)_4]$ **3** [c]

Ni–C(1)	1.854(6)	Cd–N(2^{I})	2.413(5)	C(1)–N(1)	1.154(7)	N(3) ··· N(7^{III})	3.106(8)
Ni–C(2)	1.864(5)	Cd–N(5)	2.384(5)	C(2)–N(2)	1.152(7)	N(4) ··· N(6)	3.190(7)
Ni–C(3)	1.867(6)	Cd–N(6^{II})	2.398(5)	C(3)–N(3)	1.143(8)	N(4) ··· N(6^{IV})	3.225(7)
Ni–C(4)	1.851(5)	Cd–N(7)	2.401(5)	C(4)–N(4)	1.151(7)	N(4) ··· N(8^{III})	3.087(8)
Cd–N(1)	2.312(5)	Cd–N(8^{I})	2.350(5)	N(3) ··· N(5^{III})	3.229(8)	N(4) ··· N(8^{V})	3.201(7)

C(1)–Ni–C(2)	91.1(2)	N(1)–Cd–N(5)	85.1(2)	N(2^{I})–Cd–N(8^{I})	81.0(2)	Ni–C(3)–N(3)	176.1(6)
C(1)–Ni–C(3)	174.6(3)	N(1)–Cd–N(6^{II})	89.2(2)	N(5)–Cd–N(6^{II})	173.1(2)	Ni–C(4)–N(4)	174.6(5)
C(2)–Ni–C(3)	91.9(2)	N(1)–Cd–N(7)	88.3(2)	N(5)–Cd–N(7)	89.0(2)	Cd–N(1)–C(1)	169.3(5)
C(1)–Ni–C(4)	86.1(2)	N(1)–Cd–N(8^{I})	175.8(2)	N(6^{II})–Cd–N(8^{I})	87.2(2)	Cd–N(2^{I})–C(2^{I})	164.7(5)
C(2)–Ni–C(4)	174.3(2)	N(2^{I})–Cd–N(5)	91.1(2)	N(7)–Cd–N(8^{I})	94.1(2)	N(5)–Cd–N(8^{I})	98.3(2)
C(3)–Ni–C(4)	90.5(2)	N(2^{I})–Cd–N(6^{II})	85.7(2)	Ni–C(1)–N(1)	176.0(6)	N(6^{II})–Cd–N(7)	94.7(2)
N(1)–Cd–N(2^{I})	96.6(2)	N(2^{I})–Cd–N(7)	175.0(2)	Ni–C(2)–N(2)	174.9(5)		

(*d*) $[Cd(dabtn)_2Ni(CN)_4]\cdot 2H_2O$ **4** [d]

Ni–C(1)	1.860(3)	Cd–N(3)	2.387(3)	C(2)–N(2)	1.154(4)	N(3) ··· O^{III}	3.298(6)
Ni–C(2)	1.861(3)	Cd–N(4^{I})	2.365(3)	N(2) ··· N(3^{I})	3.253(5)	N(4) ··· O^{IV}	3.197(6)
Cd–N(1)	2.347(3)	C(1)–N(1)	1.137(4)	N(2) ··· O^{II}	3.049(6)		

C(1)–Ni–C(2)	91.1(1)	N(1)–Cd–N(4^{I})	92.9(1)	Ni–C(1)–N(1)	178.9(3)	Cd–N(1)–C(1)	160.0(3)
N(1)–Cd–N(3)	92.1(1)	N(3)–Cd–N(4^{I})	92.0(1)	Ni–C(2)–N(2)	175.4(3)		

(*e*) $[Cd(daptn)_2Ni(CN)_4]\cdot H_2O$ **5** [e]

Ni–C(1)	1.871(4)	Cd–N(3)	2.383(4)	C(2)–N(2)	1.155(7)	N(2) ··· O^{IV}	3.004(7)
Ni–C(2)	1.851(5)	Cd–N(4^{I})	2.353(5)	N(2) ··· N(3^{II})	3.373(7)	N(4) ··· O^{I}	3.192(7)
Cd–N(1)	2.383(4)	C(1)–N(1)	1.137(6)	N(2) ··· N(4^{III})	3.309(7)		

C(1)–Ni–C(2)	88.9(2)	Ni–C(1)–N(1)	178.4(4)	N(3)–Cd–N(4^{I})	89.2(2)	Cd–N(1)–C(1)	169.4(4)
N(1)–Cd–N(4^{I})	91.3(2)	N(1)–Cd–N(3)	100.1(2)	Ni–C(2)–N(2)	179.6(4)		

(*f*) $[Cd(H_2O)_2(dahxn)_2][Ni(CN)_4]$ **6** [f]

Ni–C(1)	1.867(5)	Cd–N(4^{I})	2.354(5)	C(2)–N(2)	1.146(7)	N(2) ··· N(3^{III})	3.192(8)
Ni–C(2)	1.867(5)	Cd–O	2.395(4)	N(1) ··· O	2.824(7)	N(2) ··· N(4^{IV})	3.236(8)
Cd–N(3)	2.355(4)	C(1)–N(1)	1.135(6)	N(1) ··· O^{II}	3.015(7)		

C(1)–Ni–C(2)	91.0(2)	N(3)–Cd–O	94.7(2)	Ni–C(1)–N(1)	178.3(6)	Ni–C(2)–N(2)	177.4(6)
N(3)–Cd–N(4^{I})	88.4(2)	N(4^{I})–Cd–O	96.8(2)				

Table 2 (*Continued*)

(*g*) [Cd(dahpn)$_2$Ni(CN)$_4$]·H$_2$O **7**[g]

Ni(1)–C(1)	1.846(10)	Cd(2)–N(2)	2.330(8)	C(3)–N(3)	1.136(13)	N(4) ··· N(21^{IV})	3.246(12)
Ni(1)–C(2)	1.868(11)	Cd(2)–N(5)	2.387(8)	C(4)–N(4)	1.151(13)	N(4) ··· O(1^{V})	3.008(13)
Ni(1)–C(3)	1.887(10)	Cd(2)–N(17^{I})	2.420(8)	C(5)–N(5)	1.142(12)	N(6) ··· N(17^{VI})	3.281(13)
Ni(1)–C(4)	1.872(10)	Cd(2)–N(27^{II})	2.339(9)	C(6)–N(6)	1.154(12)	N(6) ··· N(37^{VII})	3.173(12)
Ni(2)–C(5)	1.845(9)	Cd(2)–N(31)	2.371(8)	N(3) ··· N(27^{VIII})	3.374(13)	N(6) ··· O(2^{II})	3.022(14)
Ni(2)–C(6)	1.862(9)	Cd(2)–N(37^{III})	2.369(8)	N(3) ··· N(31^{IX})	3.123(12)	N(11) ··· O(1)	3.260(13)
Cd(1)–N(1)	2.370(8)	C(1)–N(1)	1.155(12)	N(3) ··· O(2^{VIII})	3.049(14)	N(27) ··· O(2^{VIII})	3.188(13)
Cd(1)–N(11)	2.351(7)	C(2)–N(2)	1.154(12)	N(4) ··· N(11^{IX})	3.175(12)	N(37) ··· O(2^{X})	3.188(12)
Cd(1)–N(21)	2.413(9)						
C(1)–Ni(1)–C(2)	90.3(4)	N(11)–Cd(1)–N(21)	168.8(3)	N(5)–Cd(2)–N(37^{III})	92.7(3)	Ni(1)–C(2)–N(2)	176.4(9)
C(1)–Ni(1)–C(3)	175.4(5)	N(2)–Cd(2)–N(5)	171.7(3)	N(31)–Cd(2)–N(17^{I})	93.0(3)	Ni(1)–C(3)–N(3)	177.0(10)
C(1)–Ni(1)–C(4)	89.9(4)	N(2)–Cd(2)–N(31)	85.2(3)	N(31)–Cd(2)–N(27^{II})	87.7(3)	Ni(1)–C(4)–N(4)	177.3(10)
C(2)–Ni(1)–C(3)	90.3(4)	N(5)–Cd(2)–N(31)	89.6(3)	N(31)–Cd(2)–N(37^{III})	177.2(3)	Ni(2)–C(5)–N(5)	173.4(9)
C(2)–Ni(1)–C(4)	175.4(4)	N(2)–Cd(2)–N(17^{I})	91.2(3)	N(17^{I})–Cd(2)–N(27^{II})	173.5(3)	Ni(2)–C(6)–N(6)	178.6(9)
C(3)–Ni(1)–C(4)	89.8(4)	N(2)–Cd(2)–N(27^{II})	95.3(3)	N(17^{I})–Cd(2)–N(37^{III})	88.8(3)	Cd(1)–N(1)–C(1)	153.6(9)
C(5)–Ni(2)–C(6)	90.3(4)	N(2)–Cd(2)–N(37^{III})	92.7(3)	N(27^{II})–Cd(2)–N(37^{III})	90.7(3)	Cd(2)–N(2)–C(2)	151.4(8)
N(1)–Cd(1)–N(11)	97.7(3)	N(5)–Cd(2)–N(17^{I})	82.6(3)	Ni(1)–C(1)–N(1)	178.0(9)	Cd(2)–N(5)–C(5)	146.9(8)
N(1)–Cd(1)–N(21)	91.2(3)	N(5)–Cd(2)–N(27^{II})	90.9(3)				

(*h*) [Cd(danon)$_2$Ni(CN)$_4$] **9**[h]

Ni–C(1)	1.863(10)	Cd–N(3)	2.399(7)	C(1)–N(1)	1.113(13)	N(2) ··· N(3^{II})	3.066(14)
Ni–C(2)	1.849(11)	Cd–N(4^{I})	2.383(8)	C(2)–N(2)	1.175(16)	N(2) ··· N(4^{III})	3.092(12)
Cd–N(1)	2.353(8)						
C(1)–Ni–C(2)	91.0(5)	N(1)–Cd–N(4^{I})	89.2(3)	Ni–C(1)–N(1)	174.4(8)	Cd–N(1)–C(1)	144.2(7)
N(1)–Cd–N(3)	85.6(3)	N(3)–Cd–N(4^{I})	86.9(3)	Ni–C(2)–N(2)	175.2(10)		

[a] Symmetry operations: I $-x, y, \frac{1}{2} - z$; II $-x, -y, -z$; III $x + \frac{1}{2}, y + \frac{1}{2}, z$; IV $-x + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2} - z$. [b] Symmetry operations: for complex **2b**, I $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; II $1 - x, 1 - y, 1 - z$; III $x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; IV $\frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$ for **2c**, V $x, \frac{1}{2} - y, z - \frac{1}{2}$; VI $x - \frac{1}{2}, y, \frac{1}{2} - z$; VII $\frac{1}{2} - x, -y, z + \frac{1}{2}$; VIII $\frac{1}{2} - x, y - \frac{1}{2}, z$. [c] Symmetry operations: I $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; II $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; III $1 - x, 1 - y, 1 - z$; IV $-x, 1 - y, 1 - z$; V $x - 1, y, z$. [d] Symmetry operations: I $-x, 1 - y, -z$; II $x, y + 1, z$; III $x, y, z - 1$; IV $x, y + 1, z - 1$. [e] Symmetry operations: I $x, 1 - y, 1 - z$; II $x + 1, y, z$; III $x + 1, 1 - y, 1 - z$; IV $x + \frac{1}{2}, y - \frac{1}{2}, z$. [f] Symmetry operations: I $x, y - 1, z - 1$; II $1 - x, -y, -z$; III $x, y + 1, z$; IV $x, y, z - 1$. [g] Symmetry operations: I $x - \frac{1}{2}, y, -z$; II $x + \frac{1}{2}, y, 1 - z$; III $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; IV $-x - \frac{1}{2}, -y, z$; V $-x, -y, -z$; VI $x + \frac{1}{2}, y, -z$; VII $x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; VIII $x - \frac{1}{2}, y, 1 - z$; IX $x - 1, y, z$; X $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$. [h] Symmetry operations: I $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; II $x, y + 1, z$; III $x + \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.

values 0.0454 and 0.0492 for non-H atoms. Similarly to complex **4**, the Cd atoms are spanned by the daptn ligands with a g$_2$tgt$_2$ conformation in double one-dimensional mode. The chain running along the *c* axis is reinforced with the *cis*-one-dimensional Ni(CN)$_4$ moiety to form a triple-span chain structure. The *cis*-one-dimensional moieties are arranged in *trans* positions with regard to the Cd atoms, extending their unco-ordinated N atoms to within distances of hydrogen-bond formation with the NH$_2$ groups of the daptn in the adjacent chain. Including these hydrogen bonds, the triple-span chains are connected by hydrogen bonds to form a two-dimensional layer parallel to the *ac* plane. The H$_2$O molecule located at $\frac{1}{2}$, 0.8014(4), $\frac{1}{4}$, being on the indentical two-fold axis with that of the Cd, appears to be linked to N(4) of the daptn and to the free nitrogen end of the *cis*-one-dimensional moiety in the adjacent layer. Eventually the H$_2$O molecule behaves as an additional hydrogen-bond connector between the hydrogen-bonded two-dimensional arrays.

Complex **6**. The remarkable feature of this structure is the presence of the discrete [Ni(CN)$_4$]$^{2-}$ sandwiched between the double one-dimensional $>$[Cd$\langle$(dahxn)$_2$$\rangle$]$_\infty$ chains. The dahxn skeleton adopts a t$_2$g$_2$t$_3$ conformation between the Cd atoms, to which two H$_2$O molecules co-ordinate at *trans* positions. The [Ni(CN)$_4$]$^{2-}$ sandwiched parallel to the *bc* plane directs a couple of N atoms, N(1) and its equivalent, toward the aqua ligands with hydrogen-bond distances of 2.824(7) and 3.015(7) Å, and N(2) and its equivalent toward the NH$_2$ groups of the adjacent double one-dimensional chains with distances of 3.192(8) and 3.236(8) Å.

Complex **7**. The space group *Pnna* was uniquely determined from the observed systematic absences. As shown in Fig. 7(*a*) the three-dimensional structure has a complicated topology. The unit cell contains two crystallographically independent octahedral Cd and square-planar Ni atoms, Cd(1) and Cd(2) and Ni(1) and Ni(2), and three kinds of dahpn ligands, dahpn(1) in a t$_7$g, dahpn(2) in a gt$_7$ and dahpn(3) in a t$_2$gt$_5$ conformation [Fig. 7(*b*)]. Atoms Cd(1) and Cd(2), and their equivalents, are arranged with the Ni(CN)$_4$ moieties of Ni(1) and Ni(2) along the 2$_1$ screw axes at $\frac{1}{4}$, *y*, $\frac{1}{4}$ and $\frac{3}{4}$, *y*, $\frac{3}{4}$ to give the *trans*-(*cis*-one-dimensional) *trans*-[Cd–*cis*-NC–Ni(CN)$_2$–CN–]$_\infty$ chains (abbreviated to Cd–Ni chain) parallel to the *b* axis of crystal. The dahpn ligands span the Cd–Ni chains at every Cd atom to form a four-fold interpenetrating sub-framework structure as follows: by the dahpn bridges connecting the equivalents of Cd(1) ($x = \frac{1}{4}$ or $\frac{3}{4}$) and Cd(2) ($x = 0.75 \pm 0.02$ or 0.25 ± 0.02) alternately, giving six one-dimensional zigzag chains (Cd–dahpn chain) running approximately parallel to the (031) and (0$\bar{3}$1) planes of the unit cell; with respect to each cadmium octahedron the four dahpn spans extend in pseudo-tetrahedral directions owing to the twisted [N(21) and its equivalent at Cd(1), N(17) and the N(31) equivalent at Cd(2)] and untwisted ends [N(11) and its equivalent at Cd(1), each of the N(27) and N(37) equivalents at Cd(2)]; the (031) and (0$\bar{3}$1) Cd-dahpn chains are cross-linked to adjacent chains parallel to one another in the neighbouring unit cells up-and-up and down-and-down the *a* axis to make an extremely distorted diamondoid three-dimensional sub-framework [Cd-dahpn sub-framework: Fig. 7(*c*)]; one diamondoid Cd-dahpn sub-framework and another sub-framework interpenetrate each other without direct connections; according to the

Table 3 Structural features of the complexes

Compound	Diamine	$Ni(CN)_4$	H_2O	Dimension
2a	Tris(chelate)	Discrete	None	None
2b	Bis(chelate)	*cis*-(*cis*-one-dimensional)	None	One
2c	Bis(chelate)	*cis*-(*cis*-one-dimensional)	None	One
3	Single two-dimensional [double span of tn and $Ni(CN)_4$]	*cis*-(*cis*-one-dimensional)	None	Two
4	Double one-dimensional	*trans*-one-dimensional	Guest	Two
5	Double one-dimensional [triple span of daptn and $Ni(CN)_4$]	*trans*-(*cis*-one-dimensional)	Guest	One
6	Double one-dimensional	Discrete	Ligand	One
7	Single three-dimensional	*trans*-(*cis*-one-dimensional)	Guest	Three
9	Single three-dimensional	*trans*-(*cis*-one-dimensional)	None	Three

symmetry requirements of the *Pnna* space group, another set of doubly interpenetrating sub-frameworks is added to build up the four-fold interpenetrating lattice structure [Fig. 7(*d*)]; each of the single diamondoids is successively interconnected to adjacent ones by the Cd–Ni chains.

Both H_2O molecules at the general positions and the special positions on the two-fold axis parallel to the *c* axis are captured in the cavities formed between the dahpn chains by the hydrogen bonding to the NH_2 groups at the untwisted end of the dahpn ligands and to the terminal CN groups.

Complex **9**. The centrosymmetric space group *C*2/*c* was applied. The danon ligand extends the single two-dimensional network on the (101) plane with the skeletal gt_7gt conformation, and is spanned by *trans*-(*cis*-one-dimensional) $Ni(CN)_4$ moieties along the *c* axis to build up the three-dimensional framework. This structure is topologically the same as that of the host of the $[Cd(danon)_2Ni(CN)_4]\cdot 2G$ clathrates (G = *m*-, *p*-$Me_2C_6H_4$, *o*-$MeC_6H_4NH_2$, or 2,4- and 2,5-$Me_2C_6H_3NH_2$).[14] The Cd–N(1)–C(1) angle of 144.2(7)° makes the interlayer space so narrow that any guests are not allowed therein; no H_2O molecules were found.

The Structural Features.—The structural features of these complexes are summarised in Table 3 based on the mode of ligation for the diamine and $Ni(CN)_4$ moieties, the role of H_2O and the dimensions of the integrated structure.

As for the structural variations upon the change in methylene chain length of the bridging ligands, the series $[Cu\{NC(CH_2)_nCN\}_2]NO_3$ (n = 2–4) forms a precedent.[15] The succinonitrile (n = 2) behaves as a double one-dimensional *catena*-μ-linkage builder with the tetrahedral Cu^I;[15a] a single two-dimensional network is formed in the glutaronitrile (n = 3) compound;[15b] and a six-fold interpenetrating three-dimensional structure is given by the single span of the adiponitrile (n = 4).[15c] The present system of octahedral Cd, square-planar $Ni(CN)_4$ and α,ω-diaminoalkane is more complicated in the way the multi-dimensional structures are built up.

The chelating behaviour for en to Cd^{2+} is reasonable in aqueous solution: the stability constants, log *K* are *ca.* 5.5, 10.0 and 12.0 for Cd(en), $Cd(en)_2$ and $Cd(en)_3$ species respectively.[16] The mono- (**2d**), bis- (**2b** and **2c**) and tris-en (**2a**) complexes crystallise out in a stepwise manner from solution of pH <9 to >11. However, the formation of the two bis(en) modifications, monoclinic **2b** and orthorhombic **2c**, by chance at pH 10 is subtle; no significant differences between **2b** and **2c** in the bond distances and angles have been observed to justify one being more stable than the other. The *cis*-(*cis*-one-dimensional) array of $Ni(CN)_4$ moieties in the present complexes appears to be favourable for stabilising the crystal packings without guests, in comparison with the *trans*-one-dimensional catenation in the aniline-guest inclusion compound $[Cd(en)_2Ni(CN)_4]\cdot 2PhNH_2$[13] and with that in $[M(en)_2Ni(CN)_4]$ (M = Ni, Cu or Zn) complexes[11] owing to the bulkier $Cd(en)_2$ moiety.

Increasing *n* from 2 to 3, the tn does not behave as a chelating ligand in the solid state but as a bridging one to give complex **3**. The stability constants for the Cd–tn chelates are somewhat lower than those for the corresponding Cd–en chelates: log *K* *ca.* 4.5, 7.2 and 8.0 for Cd(tn), $Cd(tn)_2$ and $Cd(tn)_3$.[16] The six-membered chelate ring of tn may be too bulky to give a chain structure like that in **2a** or **2b** in the solid state. Crystals of tn-chelated complexes might be obtained using counter anions bulkier than $[Ni(CN)_4]^{2-}$

The double one-dimensional span of $Cd\langle(dabtn)_2\rangle Cd$ in complex **4** becomes too long for the additional spanning of *cis*-one-dimensional $Ni(CN)_4$ as in **3**. Instead the *trans*-one-dimensional $Ni(CN)_4$ spans the double one-dimensional $>[Cd\langle(dabtn)_2\rangle]_\infty$ chains to produce void space for guest H_2O molecules between the chains bridged by *trans*-one-dimensional $Ni(CN)_4$. The double one-dimensional $Cd\langle(daptn)_2\rangle Cd$ span in **5** is again short enough for the *trans*-(*cis*-one-dimensional) $Ni(CN)_4$ spanning owing to the increase in flexibility of the daptn skeleton.

However, the double one-dimensional dahxn bridge in **6** appears to be too long even for *trans*-one-dimensional interchain span of $Ni(CN)_4$, which moiety is not located in the catenation structure but left as a discrete anion in the interchain cavity. The void space between the double one-dimensional chains is filled up by the two co-ordinated H_2O molecules protruding from the octahedral Cd atoms.

The four-fold interpenetrating three-dimensional structure of complex **7** was not foreseen, although examples of manifold interpenetration have been found for the infinite co-ordination structures involving long bridges such as those of –NC–Ag–CN–, –NC–Ag–(CN)–Ag–CN– in our laboratory[17] besides the case of adiponitrile.[15c] From the observations that no well defined structures are yet available for analogous daotn (n = 8) complexes and that **9** gives a well ordered structure, a methylene chain length of 8 appears to be critical.

Two- and three-dimensional host clathrate structures with composition $[Cd\{H_2N(CH_2)_nNH_2\}_2Ni(CN)_4]\cdot 2G$ have been found only for n = 9 and 10.[14] The diamine skeletons with n < 9 in double-one- or single-two-dimensional catenation mode are too short to build up a two- or three-dimensional host together with *cis*- or *trans*-one-dimensional $Ni(CN)_4$ moieties for aromatic guest molecules. Without a guest or with the less bulky H_2O molecule, the multidimensional structures **3**–**7** are obtained; missing **8**, **9** gives the guest-free host structure of $[Cd(diamine)_2Ni(CN)_4]$. The present crystals were grown spontaneously from aqueous solutions containing the respective constituents; no special procedures have been applied. It is well known that the process of crystal growth under ambient conditions is self-assembling; of importance is what self-assemblies are allowed under the specified conditions.

Table 4 Crystallographic and experimental data[a]

Compound	**2a**	**2b**	**2c**	**3**	**4**	**5**	**6**	**7**	**9**
Formula	$C_{10}H_{24}CdN_{10}Ni$	$C_8H_{16}CdN_8Ni$	$C_8H_{16}CdN_8Ni$	$C_{10}H_{20}CdN_8Ni$	$C_{12}H_{28}CdN_8NiO_2$	$C_{14}H_{30}CdN_8NiO$	$C_{16}H_{36}CdN_8NiO_2$	$C_{18}H_{38}CdN_8NiO$	$C_{22}H_{44}CdN_8Ni$
M	455.47	395.37	395.37	423.43	487.51	497.55	543.62	553.66	591.75
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	C_2/c (no. 15)	$P2_1/n$ (no. 14)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$C222_1$ (no. 20)	$P\bar{1}$ (no. 2)	*Pnna* (no. 52)	$C2/c$ (no. 15)
a/Å	16.699(2)	11.628(1)	20.078(2)	10.474(2)	8.253(2)	9.794(2)	8.470(2)	9.621(4)	20.839(6)
b/Å	8.894(2)	9.257(1)	9.140(2)	13.696(4)	8.527(1)	12.961(3)	9.750(3)	38.925(6)	9.141(4)
c/Å	14.320(2)	13.926(1)	15.655(2)	11.107(2)	7.921(2)	16.049(3)	8.114(3)	19.953(4)	15.206(4)
α/°					97.84(2)		111.59(2)		
β/°	117.351(9)	106.285(7)		92.90(2)	107.48(2)		106.68(2)		105.58(2)
γ/°					104.39(1)		71.53(2)		
U/Å^3	1889.1(6)	1439.0(2)	2872.9(6)	1591.2(6)	501.4(2)	2037.3(5)	579.6(3)	7472(3)	2790(1)
Z	4	4	8	4	1	4	1	12	4
D_m,[b] D_c/g cm^{-3}	1.57(1), 1.60	1.82(1), 1.82	1.79(1), 1.83	1.76(1), 1.77	1.61(1), 1.61	1.61(1), 1.62	1.55(1), 1.56	1.47(1), 1.48	1.41(1), 1.41
F(000)	920	784	1568	848	248	1016	280	3432	1232
Diffractometer[c]	AFC5R	AFC5R	AFC5R	AFC5S	AFC5S	AFC5R	AFC5R	AFC6A	AFC5S
μ(Mo-Kα)/cm^{-1}	21.35	27.86	27.91	25.25	20.21	19.88	17.56	81.44[d]	14.61
Crystal size/mm	0.30 × 0.28 × 0.20	0.32 × 0.32 × 0.20	0.28 × 0.22 × 0.20	0.25 × 0.25 × 0.17	0.37 × 0.37 × 0.13	0.32 × 0.32 × 0.26	0.25 × 0.25 × 0.25	0.23 × 0.23 × 0.23	0.25 × 0.25 × 0.08
θ_{max}/°	30	30	30	30	30	30	30	60	30
hkl ranges	0–23, 0–12, −20 to 17	0–16, 0–13 −19 to 18	0–28, 0–12, 0–22	0–14, 0–19, −15 to 15	0–11, −12 to 11, −11 to 10	0–13, 0–18, 0–22	0–11, −13 to 13, −11 to 10	0–10, 0–43, 0–22	0–29, −12 to 12, −21 to 20
Scan width/°	0.997 + 0.3 tan θ	1.155 + 0.3 tan θ	1.207 + 0.3 tan θ	0.945 + 0.3 tan θ	1.628 + 0.3 tan θ	1.207 + 0.3 tan θ	0.945 + 0.3 tan θ	0.638 + 0.3 tan θ	0.892 + 0.3 tan θ
Transmission factors	0.85–1.00	0.83–0.99	0.88–1.00	0.89–1.00	0.86–1.00		—	—	0.88–1.00
x[e]	7.6(11) × 10^{-8}	—	—	1.30(19) × 10^{-7}	—	1.58(12) × 10^{-7}	—	9.3(5) × 10^{-8}	—
Reflections measured	3307	4748	4797	5192	3207	3441	3672	6370	8553
Unique reflections	2438	3844	3738	3254	2816	1658	3163	4983	3276
Reflections used, N_r	1780	3150	2827	3253	2559	1601	2652	4051	2054
Parameters, N_p	103	163	163	182	112	116	130	395	147
g	1.0 × 10^{-3}	5.0 × 10^{-4}	1.0 × 10^{-4}	1.0 × 10^{-3}	8.0 × 10^{-4}	5.0 × 10^{-4}	4.0 × 10^{-4}	2.5 × 10^{-3}	5.0 × 10^{-4}
R, R'	0.0502, 0.0596	0.0328, 0.0446	0.0404, 0.0355	0.0395, 0.0507	0.0237, 0.0387	0.0263, 0.0367	0.0424, 0.0519	0.0599, 0.0768	0.0571, 0.0583
Goodness of fit	1.133	1.292	1.402	1.011	1.069	1.195	1.478	1.171	1.190
$(\Delta/\sigma)_{max}$	0.002	0.017	0.021	0.014	0.001	0.000	0.007	0.013	0.002
Maximum, minimum $\Delta\rho$/e Å^{-3}	+0.82, −0.82	+0.92, −0.58	+0.75, −0.50	+0.62, −0.64	+0.48, −0.34	+0.75, −0.33	+0.94, −1.12	+1.83, −1.98	+0.67, −1.34

[a] Details in common: ambient temperature, graphite monochromator, 2θ–ω scan, reflections with $|F_o| > 4\sigma(F_o)$ were used, $\omega^{-1} = \sigma^2(F_o) + g(F_o)^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}}$, goodness of fit $= [\Sigma\omega(|F_o| - |F_c|)^2/(N_r - N_p)]^{\frac{1}{2}}$. [b] Measured by the flotation method in a bromoform–mesitylene mixture. [c] Rigaku AFC-5R: Mo-Kα radiation (λ = 0.709 26 Å) from a rotating anticathode. Rigaku AFC5S: Mo-Kα radiation (λ = 0.709 26 Å) from a fine-focus sealed tube. Rigaku AFC6A: Cu-Kα radiation (λ = 1.541 84 Å) from a fine-focus sealed tube. [d] μ(Cu-Kα)/cm^{-1}. [e] Refined extinction parameter according to the equation $F_{corr} = F_c\{1 - [x(F_c)^2/\sin\theta]\}$.

Table 5 Refined atomic coordinates for complexes **2a**–**9**

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
(*i*) $[Cd(en)_3][Ni(CN)_4]$ **2a**							
Cd	0	0.362 78(8)	$\frac{1}{4}$	N(5)	0.024 3(4)	0.576 5(7)	0.165 3(5)
Ni	$\frac{1}{4}$	$\frac{1}{4}$	0	C(1)	0.188 0(5)	0.377 6(8)	0.046 3(5)
N(1)	0.147 4(4)	0.454 9(8)	0.072 3(5)	C(2)	0.327 8(5)	0.407 5(8)	0.011 8(5)
N(2)	0.375 1(5)	0.503 1(8)	0.021 2(6)	C(3)	0.140 8(6)	0.134 0(9)	0.236 6(6)
N(3)	0.055 1(4)	0.200 4(7)	0.159 5(4)	C(4)	0.199 2(5)	0.256 2(9)	0.314 9(6)
N(4)	0.151 7(4)	0.310 5(7)	0.373 3(4)	C(5)	0.035 5(6)	0.713 1(9)	0.229 8(7)
(*ii*) $[Cd(en)_2Ni(CN)_4]$ **2b**							
Cd	0.366 48(3)	0.151 26(3)	0.187 83(2)	N(8)	0.399 2(4)	−0.097 1(4)	0.214 5(3)
Ni	0.387 07(4)	0.348 94(6)	0.547 84(4)	C(1)	0.382 2(4)	0.234 5(5)	0.435 4(3)
N(1)	0.370 1(4)	0.175 9(5)	0.361 2(3)	C(2)	0.553 6(4)	0.361 9(5)	0.590 8(3)
N(2)	0.656 0(3)	0.366 0(5)	0.627 9(3)	C(3)	0.377 7(4)	0.475 2(5)	0.648 4(4)
N(3)	0.365 5(4)	0.557 1(6)	0.705 9(4)	C(4)	0.222 9(4)	0.325 5(5)	0.524 8(3)
N(4)	0.123 3(4)	0.312 4(5)	0.515 2(3)	C(5)	0.390 8(7)	0.436 9(7)	0.076 8(6)
N(5)	0.358 8(4)	0.404 0(5)	0.169 9(3)	C(6)	0.329 8(7)	0.339 6(7)	−0.005 6(5)
N(6)	0.361 1(3)	0.186 1(4)	0.019 5(3)	C(7)	0.606 4(4)	−0.013 9(6)	0.289 2(4)
N(7)	0.578 1(3)	0.128 8(4)	0.240 4(3)	C(8)	0.527 4(5)	−0.127 6(6)	0.224 9(4)
(*iii*) $[Cd(en)_2Ni(CN)_4]$ **2c**							
Cd	0.339 79(2)	0.153 25(4)	0.078 30(3)	N(8)	0.342 4(3)	−0.095 4(5)	0.108 5(3)
Ni	0.171 46(3)	0.172 86(8)	0.345 75(4)	C(1)	0.235 0(3)	0.173 8(7)	0.258 4(4)
N(1)	0.267 3(2)	0.176 0(6)	0.198 8(3)	C(2)	0.221 6(3)	0.290 9(7)	0.419 4(4)
N(2)	0.251 3(2)	0.352 4(6)	0.471 4(3)	C(3)	0.098 1(3)	0.184 4(7)	0.418 2(4)
N(3)	0.050 8(2)	0.187 2(6)	0.457 6(3)	C(4)	0.122 4(3)	0.037 1(7)	0.284 0(4)
N(4)	0.091 3(3)	−0.049 7(7)	0.249 8(4)	C(5)	0.406 0(4)	0.439 8(8)	0.019 0(5)
N(5)	0.344 5(3)	0.406 7(5)	0.068 7(3)	C(6)	0.408 9(3)	0.347 1(8)	−0.060 4(4)
N(6)	0.411 9(2)	0.189 2(6)	−0.037 0(3)	C(7)	0.416 6(3)	−0.011 1(8)	0.224 2(4)
N(7)	0.426 6(2)	0.132 1(5)	0.181 4(3)	C(8)	0.404 7(3)	−0.127 5(7)	0.158 1(4)
(*iv*) $[Cd(tn)_2Ni(CN)_4]$ **3**							
Cd	0.406 19(4)	0.235 38(3)	0.143 91(3)	C(1)	0.425 7(5)	0.335 1(4)	0.429 8(5)
Ni	0.426 01(6)	0.400 79(5)	0.575 70(6)	C(2)	0.589 3(5)	0.354 5(4)	0.618 7(5)
N(1)	0.418 3(5)	0.292 4(4)	0.340 1(4)	C(3)	0.412 0(5)	0.460 6(4)	0.725 5(5)
N(2)	0.687 0(5)	0.319 0(4)	0.642 9(5)	C(4)	0.258 6(5)	0.433 9(4)	0.532 4(5)
N(3)	0.399 7(7)	0.492 7(4)	0.819 2(5)	C(5)	0.213 9(7)	0.425 0(5)	0.142 0(6)
N(4)	0.153 2(5)	0.446 9(4)	0.502 5(5)	C(6)	0.176 8(6)	0.532 3(5)	0.114 1(6)
N(5)	0.339 6(5)	0.397 1(4)	0.092 3(5)	C(7)	0.042 5(6)	0.555 1(5)	0.152 3(5)
N(6)	0.040 1(5)	0.575 3(4)	0.282 3(4)	C(8)	0.708 4(5)	0.266 2(5)	0.235 2(5)
N(7)	0.624 1(4)	0.285 7(3)	0.126 8(4)	C(9)	0.841 4(5)	0.309 0(5)	0.228 1(5)
N(8)	0.889 0(5)	0.333 6(4)	0.450 0(4)	C(10)	0.927 4(5)	0.282 3(4)	0.341 0(5)
(*v*) $[Cd(dabtn)_2Ni(CN)_4]\cdot 2H_2O$ **4**							
Cd	0	0	0	C(1)	0.321 6(4)	0.308 3(3)	0.352 1(4)
Ni	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	C(2)	0.361 2(4)	0.632 0(4)	0.409 1(4)
O	0.351 5(6)	0.020 0(4)	0.662 8(5)	C(3)	0.181 2(5)	0.350 4(4)	−0.104 0(5)
N(1)	0.214 5(4)	0.189 7(4)	0.261 8(4)	C(4)	0.236 4(5)	0.454 1(4)	−0.229 9(5)
N(2)	0.284 2(5)	0.723 0(4)	0.360 9(6)	C(5)	0.315 7(4)	0.640 9(4)	−0.133 0(5)
N(3)	0.076 1(4)	0.175 5(3)	−0.192 7(4)	C(6)	0.167 6(5)	0.715 6(4)	−0.132 2(6)
N(4)	0.227 8(4)	0.885 8(3)	−0.023 9(4)				
(*vi*) $[Cd(daptn)_2Ni(CN)_4]\cdot H_2O$ **5**							
Cd	$\frac{1}{2}$	0.463 05(3)	$\frac{1}{4}$	C(1)	0.726 7(4)	0.482 5(3)	0.418 5(3)
Ni	0.861 31(8)	$\frac{1}{2}$	$\frac{1}{2}$	C(2)	0.992 7(6)	0.483 8(3)	0.418 1(3)
O	$\frac{1}{2}$	0.801 4(4)	$\frac{1}{4}$	C(3)	0.380 3(7)	0.243 5(4)	0.343 5(4)
N(1)	0.645 9(5)	0.469 6(4)	0.368 7(3)	C(4)	0.403 1(6)	0.266 7(4)	0.435 8(3)
N(2)	1.074 1(5)	0.473 7(5)	0.366 6(3)	C(5)	0.265 8(5)	0.285 7(4)	0.480 5(4)
N(3)	0.341 1(5)	0.335 4(4)	0.294 8(3)	C(6)	0.280 7(6)	0.295 9(4)	0.575 7(3)
N(4)	0.357 4(5)	0.408 7(3)	0.693 5(2)	C(7)	0.368 5(6)	0.386 2(4)	0.602 2(3)
(*vii*) $[Cd(H_2O)_2(dahxn)_2][Ni(CN)_4]$ **6**							
Cd	0	0	0	C(2)	0.304 4(7)	0.632 1(6)	0.418 4(7)
Ni	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	C(3)	0.198 5(7)	0.132 1(6)	0.419 7(7)
O	0.282 4(5)	−0.022 3(4)	−0.025 8(6)	C(4)	0.255 4(7)	0.127 2(5)	0.615 1(6)
N(1)	0.414 8(7)	0.234 4(5)	0.184 8(7)	C(5)	0.396 9(7)	0.212 7(6)	0.721 8(7)
N(2)	0.188 1(7)	0.716 6(6)	0.368 7(8)	C(6)	0.345 3(7)	0.383 2(6)	0.746 1(8)
N(3)	0.067 1(6)	0.045 2(5)	0.315 0(6)	C(7)	0.197 1(7)	0.473 0(6)	0.844 7(8)
N(4)	0.032 3(6)	0.742 3(5)	0.964 6(6)	C(8)	0.174 4(8)	0.641 6(6)	0.872 1(8)
C(1)	0.446 1(7)	0.336 3(6)	0.302 2(7)				

Table 5 (*Continued*)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
(*viii*) $[Cd(dahpn)_2Ni(CN)_4]\cdot H_2O$ **7**							
Cd(1)	$\frac{1}{4}$	0	0.172 24(4)	C(6)	0.739 2(9)	0.234 4(3)	0.309 7(5)
Cd(2)	0.225 86(6)	0.171 99(2)	0.343 10(3)	C(11)	0.350 2(10)	0.057 5(2)	0.059 6(5)
Ni(1)	−0.134 1(2)	0.085 24(4)	0.252 60(8)	C(12)	0.455 3(10)	0.071 9(3)	0.011 5(5)
Ni(2)	0.604 4(2)	$\frac{1}{4}$	$\frac{1}{4}$	C(13)	0.400 9(10)	0.103 9(3)	−0.025 8(5)
O(1)	$\frac{1}{4}$	0	−0.055 3(6)	C(14)	0.516 9(11)	0.120 5(3)	−0.068 0(5)
O(2)	0.217 9(11)	0.169 5(2)	0.561 7(5)	C(15)	0.454 5(10)	0.148 5(3)	−0.115 6(5)
N(1)	0.098 3(9)	0.047 6(2)	0.184 3(4)	C(16)	0.563 1(11)	0.164 1(3)	−0.161 3(5)
N(2)	0.073 4(9)	0.125 7(2)	0.334 4(4)	C(17)	0.494 2(11)	0.188 2(3)	−0.211 3(5)
N(3)	−0.367 5(10)	0.117 1(3)	0.332 6(5)	C(21)	−0.000 1(15)	−0.020 0(4)	0.291 8(7)
N(4)	−0.339 8(10)	0.051 8(3)	0.158 5(5)	C(22)	0.058 5(14)	0.001 6(3)	0.345 1(6)
N(5)	0.380 1(9)	0.219 9(2)	0.334 7(4)	C(23)	−0.056 2(15)	0.015 9(4)	0.390 7(8)
N(6)	0.824 1(10)	0.225 5(3)	0.346 6(5)	C(24)	−0.000 7(14)	0.044 0(3)	0.437 8(6)
N(11)	0.390 4(8)	0.022 7(2)	0.086 6(4)	C(25)	−0.113 3(13)	0.062 1(3)	0.478 1(7)
N(17)	0.598 2(9)	0.203 5(2)	−0.258 6(4)	C(26)	−0.063 9(11)	0.095 6(3)	0.508 8(6)
N(21)	0.111 2(10)	−0.033 7(3)	0.248 5(5)	C(27)	−0.165 6(11)	0.111 0(3)	0.556 6(5)
N(27)	−0.134 3(8)	0.147 0(2)	0.574 4(4)	C(31)	0.437 8(11)	0.164 0(3)	0.212 3(5)
N(31)	0.360 8(8)	0.142 3(2)	0.262 4(4)	C(32)	0.482 7(12)	0.143 8(3)	0.150 3(5)
N(37)	0.588 9(8)	0.300 9(2)	−0.073 7(4)	C(33)	0.577 0(13)	0.165 9(3)	0.105 3(7)
C(1)	0.008 8(9)	0.062 5(2)	0.209 7(5)	C(34)	0.502 7(11)	0.195 5(3)	0.069 8(5)
C(2)	−0.005 5(10)	0.109 4(3)	0.304 6(5)	C(35)	0.602 3(11)	0.215 7(3)	0.024 5(5)
C(3)	−0.281 6(10)	0.105 4(3)	0.301 0(5)	C(36)	0.539 3(10)	0.247 9(3)	−0.004 3(5)
C(4)	−0.262 7(10)	0.064 0(3)	0.195 6(5)	C(37)	0.637 8(10)	0.266 1(3)	−0.052 9(5)
C(5)	0.466 4(9)	0.233 0(3)	0.304 9(4)				
(*ix*) $[Cd(danon)_2Ni(CN)_4]$ **9**							
Cd	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	C(4)	0.348 2(5)	0.349 2(10)	0.576 6(6)
Ni	$\frac{1}{2}$	0.858 6(2)	$\frac{1}{4}$	C(5)	0.314 7(5)	0.257 9(10)	0.636 3(7)
N(1)	0.460 4(4)	0.623 8(10)	0.360 2(5)	C(6)	0.286 3(5)	0.349 5(10)	0.699 4(6)
N(2)	0.445 6(5)	1.096 9(11)	0.347 4(8)	C(7)	0.253 1(6)	0.260 2(11)	0.759 9(7)
N(3)	0.402 1(4)	0.351 2(9)	0.449 7(5)	C(8)	0.220 1(5)	0.349 3(10)	0.818 0(6)
N(4)	0.054 1(4)	0.171 8(8)	0.926 1(5)	C(9)	0.181 3(5)	0.260 3(11)	0.870 5(7)
C(1)	0.472 2(5)	0.711 2(10)	0.315 9(5)	C(10)	0.146 5(5)	0.351 7(11)	0.927 3(7)
C(2)	0.467 3(5)	1.000 7(13)	0.312 9(6)	C(11)	0.111 5(5)	0.256 0(12)	0.986 4(7)
C(3)	0.374 9(5)	0.255 2(10)	0.512 4(7)				

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