Cyano-linked Structures in Polymeric Cadmium Cyanide–Pyridine (py) and –Isoquinoline (iquin) Complexes: Crystal Structures of [Cd(py)$_2$][Cd(CN)$_4$], [{Cd(CN)(py)$_2$}$_3$][Cd$_2$(CN)$_7$] and [Cd(iquin)$_2$][Cd(CN)$_3$(iquin)$_2$]$_2$†

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Crystal structures of two pyridine (py)- and one isoquinoline (iquin)-ligated cadmium(II) poly(cyano)-cadmate(II) complexes, [Cd(py)$_2$][Cd(CN)$_4$] **1**, [{Cd(CN)(py)$_2$}$_3$][Cd$_2$(CN)$_7$] **2** and [Cd(iquin)$_2$][Cd-(CN)$_3$(iquin)$_2$]$_2$ **3** have been determined from single-crystal X-ray diffraction data; **1**: orthorhombic *Cccm*, $a = 9.386(2)$, $b = 14.358(2)$, $c = 14.439(2)$ Å, $Z = 4$; **2**: trigonal $R\bar{3}c$, $a = b = 13.987(2)$ and $c = 43.769(8)$ Å (hexagonal setting), $Z = 6$; and **3**: (L) monoclinic $P2_1/c$, $a = 8.178(2)$, $b = 20.557(2)$, $c = 16.244(3)$ Å, $\beta = 97.20(2)°$, $Z = 2$. Although they all have the composition of a base adduct of Cd(CN)$_2$, the structures are completely different from one another. Complex **1** [*i.e.* Cd(CN)$_2$·L] has a three-dimensional framework built of an alternate array of tetrahedral [Cd(CN)$_4$]$^{2-}$ and octahedral Cd^{2+} to which a pair of pyridine ligands ligate at the *trans* positions. The three-dimensional structure of complex **2** [*i.e.* 5Cd(CN)$_2$·6L] is comprised of a trimeric assembly [{Cd(CN)(py)$_2$}$_3$]$^{3+}$ and a dimeric condensate [(NC)$_3$Cd(CN)Cd(CN)$_3$]$^{3-}$ linked alternately by cyano bridges extending from the latter. A one-dimensional extension of the meshed chain is seen in the structure of complex **3** [*i.e.* Cd(CN)$_2$·2L], where two kinds of *trans*-[Cd(iquin)$_2$] moieties, one in an octahedral (Cd$_{\text{oct}}$) and the other in a trigonal-bipyramidal (Cd$_{\text{tbpy}}$) co-ordination, are combined with the equatorial CN groups in a 1:2 ratio Cd$_{\text{oct}}$:Cd$_{\text{tbpy}}$. The bulkiness of the aromatic base appears to affect the mode of cyanide linkage in these structures.

We have been developing a number of infinite co-ordination structures which behave as hosts in inclusion compounds built of cyano linkages between cadmium(II) atoms with the additional participation of ammine or amine ligands.[1] In our previous paper,[1e] together with those of the Hofmann-Td-type and analogous clathrates [Cd(R)Cd(CN)$_4$]·2G [R = (NH$_3$)$_2$ or NH$_2$CH$_2$CH$_2$NH$_2$, G = C$_6$H$_6$ or C$_6$H$_5$NH$_2$], the structure of an aniline clathrate, [Cd(C$_6$H$_5$NH$_2$)$_2$Cd(CN)$_4$]·0.5C$_6$H$_5$NH$_2$, was determined. The composition of this clathrate is the same as that of 4Cd(CN)$_2$·5C$_6$H$_5$NH$_2$ reported as an aniline adduct of cadmium cyanide by Mesnard and Gode[2] without any mention of its inclusion structure. They reported the pyridine (py), Cd(CN)$_2$·py, and isoquinoline (iquin), 2Cd(CN)$_2$·3iquin, adducts too. With regard to the pyridine complex, Ülkü[3] reported the crystal structure of [Cd(py)$_2$Ni(CN)$_4$] [*i.e.* CdNi(CN)$_4$·2py] which has a layer structure like the Hofmann-type host [Cd(NH$_3$)$_2$Ni(CN)$_4$] [*i.e.* CdNi(CN)$_4$·2NH$_3$],[1a,b] but no room is left for guest accommodation in the interlayer space due to the bulkiness of the pyridine ligand. Hence, we examined the preparation of so-called adducts formed between cadmium cyanide and organic bases, and analysed their crystal structures to determine whether or not they are clathrates. What we have obtained are not clathrates but infinite co-ordination complexes built of octahedral and tetrahedral or trigonal-bipyramidal cadmium atoms linked by the cyano ligands; the unidentate organic bases ligate to the octahedral and the trigonal-bipyramidal cadmium atoms.

Experimental

Preparation of the Complexes.—[Cd(py)$_2$][Cd(CN)$_4$] **1** *and* [{Cd(CN)(py)$_2$}$_3$][Cd$_2$(CN)$_7$] **2**. To an aqueous solution (100 cm^3) of CdCl$_2$·2.5H$_2$O (1.14 g), K$_2$[Cd(CN)$_4$] (1.47 g) and sodium citrate (5 g), pyridine (*ca.* 2 cm^3) was added dropwise. The white precipitate obtained was filtered off and recrystallised from hot water according to ref. 2 to give colourless prismatic crystals of [Cd(py)$_2$][Cd(CN)$_4$] **1** (Found: C, 34.20; H, 2.10; N, 17.25. C$_{14}$H$_{10}$Cd$_2$N$_6$ requires C, 34.50; H, 2.05; N, 17.25%). After removal of the white precipitate, the filtrate was kept standing in a refrigerator at 5 °C for a few weeks. Colourless, hexagonal plate-like crystals were obtained. From the analytical results and the determined structure, they were concluded to be [{Cd(CN)(py)$_2$}$_3$][Cd$_2$(CN)$_7$] **2** (Found: C, 36.85; H, 2.55; N, 16.75. C$_{40}$H$_{30}$Cd$_5$N$_{16}$ requires C, 37.05; H, 2.35; N, 17.30%).

It appears that the formation of either complex **1** or **2** depends on the concentration of pyridine in the starting solution. Complex **2**, unlike complex **1**, has never been obtained by recrystallisation from hot water. When the pyridine concentration was higher or lower than *ca.* 0.1 mol dm^{-3}, crystals of **2** or **1** were respectively given at room temperature from the solution in which the total concentration of Cd$^{\text{II}}$ including both Cd^{2+} and [Cd(CN)$_4$]$^{2-}$ was 0.02–0.2 mol dm^{-3} at pH 7–9.

[Cd(iquin)$_2$][Cd(CN)$_3$(iquin)$_2$]$_2$ **3**. To an aqueous solution (100 cm^3) of CdCl$_2$·2.5H$_2$O (1.14 g), K$_2$[Cd(CN)$_4$] (1.47 g) and sodium citrate (5 g), isoquinoline (*ca.* 2 cm^3) was added dropwise. Both procedures, recrystallisation of the precipitate from hot water and leaving the filtrate in a refrigerator at 5 °C, gave colourless needle-like crystals of the same compound, [Cd(iquin)$_2$][Cd(CN)$_3$(iquin)$_2$]$_2$ **3** (Found: C, 54.00; H, 3.35;

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

Table 1 Crystallographic and selected experimental data[a]

Compound	**1**	**2**	**3**
Formula	$C_{14}H_{10}Cd_2N_6$	$C_{40}H_{30}Cd_5N_{16}$	$C_{60}H_{42}Cd_3N_{12}$
M	487.10	1296.84	1268.31
Crystal system	Orthorhombic	Trigonal	Monoclinic
Space group	*Cccm* (no. 66)	$R\bar{3}c$ (no. 167)	$P2_1/c$ (no.
a/Å	9.386(2)	13.987(2)	14)
b/Å	14.358(2)	13.987(2)	8.178(2)
c/Å	14.439(2)	43.769(8)	20.557(2)
α/°	90	90	16.244(3)
β/°	90	90	90
γ/°	90	120	97.20(2)
U/Å^3	1945.9(5)	7415(2)	90
Z	4	6	2709.4(7)
D_m, D_c/g cm^{-3}	1.67(1), 1.66	1.74(1), 1.74	2
F(000)	928	3732	1.58(1), 1.55
Crystal size/mm	0.30 × 0.08 × 0.08	0.20 × 0.20 × 0.08	1260
μ(Mo-Kα)/cm^{-1}	21.82	21.54	0.30 × 0.10 × 0.10
Scan range/°	$5 < 20 < 55$	$5 < 2\theta < 60$	12.11
h,k,l	0–12, 0–18, 0–18	−17–17, 0–19, 0–61	$5 < 2\theta < 60$
Scan width/°	$1.000 + 0.3 \tan\theta$	$0.840 + 0.3 \tan\theta$	0–11, 0–28, −22–22
Reflections observed	1321	5263	$1.000 + 0.3 \tan\theta$
N_r[b]	712	1169	8810
N_p[b]	67	93	3114
R_{int}	0.007	0.014	361
g[b]	5.0×10^{-4}	3.0×10^{-4}	0.004
R[b], R'[b]	0.0387, 0.0409	0.0796, 0.0699	4.0×10^{-4}
Goodness of fit[b]	0.987	1.720	0.0769, 0.0483
Maximum Δ/σ	0.005	0.058	1.437
Maximum, minimum $\Delta\rho$/e Å^{-3}	+0.60, −0.61	+1.19, −0.91	0.062
			+1.09, −1.31

[a] Conditions in common: Rigaku AFC-5R diffractometer, rotating Mo anode (Mo-Kα_1, $\lambda = 0.709\,26$ Å), graphite monochromator; 2θ–ω scan. The densities were measured by the flotation method in bromoform–chloroform for complexes **1** and **2**, and in bromoform–mesitylene for complex **3**. [b] N_r = Number of reflections used with $|F_o| > 4\sigma(F_o)$, N_p = number of refined parameters, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(\Delta_r - N_p)]^{\frac{1}{2}}$.

N, 13.45. $C_{60}H_{42}Cd_3N_{12}$ requires C, 56.80; H, 3.35; N, 13.25%).

Crystallography.—Table 1 summarises the crystallographic and selected experimental data for complexes **1**, **2** and **3**. The unit-cell parameters were refined using 25 reflections in the 2θ ranges 31.02–34.50° for **1**, 25.76–31.09° for **2** and 25.01–32.34° for **3**. During the intensity data collection for each crystal three representative reflections were monitored after every 200 reflections: no significant decay was observed. A correction was made for Lorentz polarisation but not for extinction. An absorption correction based on psi scans was applied for complexes **1** and **2** using the program ADC80 in UNICSIII[4] but not for complex **3**.

The cadmium atoms were located by the Patterson method using SHELXS 86.[5] 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.[6] Atomic scattering factors including those for real and imaginary anomalous dispersion corrections were taken from ref. 7 for Cd and SHELX 76[6] for N, C and H. Since the $R\bar{3}c$ space group applied for complex **2** predicts that the N and C atoms of the cyanide between the octahedral Cd atoms and those between the tetrahedral Cd atoms are crystallographically equivalent to each other, atomic scattering factors were defined for a CN atom with a 50% probability each for C and N according to Cromer and Larson.[8] All the calculations were carried out on a HITAC M-680H computer at the Institute for Molecular Science, Okazaki. All the non-hydrogen atoms were refined anisotropically for complexes **1**, **2** and **3**. Hydrogen atoms were refined isotropically for **1**, located at calculated positions with fixed $B_{iso} = 15$ Å^2 for **2** and refined isotropically at calculated positions for **3**. The parameters for the hydrogen atoms were included in the structure factor calculations.

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

Results and Discussion

The refined atomic parameters for complexes **1**, **2** and **3** are listed in Tables 2, 3 and 4, respectively. Selected bond distances and angles for all three complexes are summarised in Table 5; no unusual bond distances and angles have been observed.

Structure of $[Cd(py)_2][Cd(CN)_4]$ **1**.—The centrosymmetric space group *Cccm* was chosen for complex **1** because it gave a better convergence than *Ccc*2 which was also possible from the observed systematic absences. The three-dimensional framework structure revealed is topologically the same as the host framework of the Hofmann-Td type $[Cd(NH_3)_2M(CN)_4]\cdot 2G$ clathrates (M = Cd, G = C_6H_6 or $C_6H_5NH_2$;[1e] M = Hg, G = C_6H_6[9]), compared in Fig. 1. The framework consists of an alternate array of tetrahedral Cd_{tet} [from $Cd(CN)_4$] and octahedral Cd_{oct} atoms, a pair of pyridine ligands co-ordinating to the latter at the *trans* positions.

The three-dimensional framework of both complex **1** and the Hofmann-Td type host $[Cd(NH_3)_2Cd(CN)_4]$ **4** is built up of alternate crossings of one-dimensional meshed $\{Cd_{oct}\langle[NC\text{–}Cd_{tet}(CN)_2\text{–}CN]_2\rangle\}_\infty$ chains sharing every Cd_{tet} atom as the joint. In complex **4**, two kinds of cavities, α and β, are formed: α between the chains running parallel to each other and β between those running orthogonally. The ammine ligands, being less bulky than the pyridine ligands in complex **1**, can

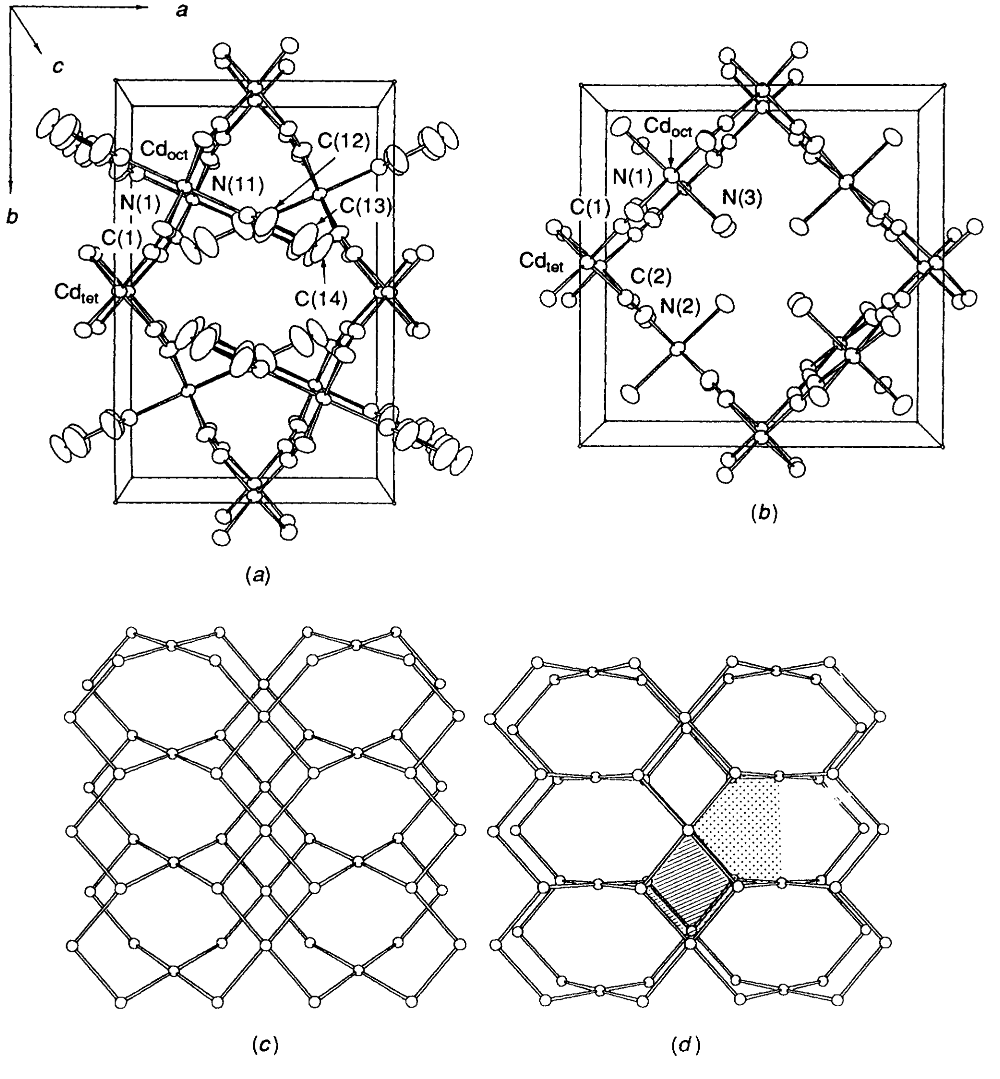

Fig. 1 Structures of $[Cd(py)_2][Cd(CN)_4]$ **1** and the host complex, **4**, of the clathrate $[(NH_3)_2Cd(CN)_4Cd]\cdot 2C_6H_6$. (*a*) Projection along the *c* axis for complex **1**, (*b*) projection along the *c* axis for complex **4**: Cd_{oct} at $\frac{1}{4}, \frac{1}{4}, 0$, Cd_{tet} at 0, *ca.* $\frac{1}{2}, \frac{1}{4}$, the centre of the α cavity at $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$ and that of the β cavity at $\frac{1}{2}, \frac{1}{2}$, (*c*) ball(Cd)-and-stick(CN) sketch of structure **1** and (*d*) ball(Cd)-and-stick(CN) sketch of structure **4**; α cavity is hatched and β cavity is dotted

Table 2 Final atomic coordinates for $[Cd(py)_2][Cd(CN)_4]$ **1**

Atom	G*	X/a	Y/b	Z/c
Cd_{oct}	0.25	$\frac{1}{4}$	$\frac{1}{4}$	0
Cd_{tet}	0.25	0	$\frac{1}{2}$	$\frac{1}{4}$
N(1)	1.00	0.1799(8)	0.3544(4)	0.1141(5)
C(1)	1.00	0.1257(8)	0.4057(6)	0.1611(6)
N(12)	0.50	0.4769(11)	0.3177(7)	0
C(12)	1.00	0.5431(13)	0.3348(11)	0.0772(10)
C(13)	1.00	0.6796(23)	0.3774(17)	0.0797(17)
C(14)	0.50	0.7419(28)	0.3972(20)	0
H(12)	1.00	0.495(17)	0.318(8)	0.151(10)
H(13)	1.00	0.685(22)	0.418(12)	0.114(16)
H(14)	0.50	0.845(17)	0.420(11)	0

* Multiplicity.

confront each other between the Cd_{oct} atoms bridged with $Cd_{tet}(CN)_4$ moieties so as to make the α and β cavities large enough to accommodate the aromatic guest molecules. These cavities, however, are lost in complex **1**, where the framework is distorted from that in complex **4** collapsing the β cavity, and the α cavity is invaded by the aromatic ring of the bulkier pyridine ligand.

Structure of $[\{Cd(CN)(py)_2\}_3][Cd_2(CN)_7]$ **2**.—The $R\bar{3}c$ space group was applied because the $|E^2 - 1|$ values, 0.940 for 0*kl* and *h*0*l*, 0.974 for *hk*0 and 0.979 for *hkl*, supported the centrosymmetric structure rather than the non-centrosymmetric space group *R*3*c*. The three-dimensional framework of complex **2** is a structure built of columns and layers (Fig. 2). The three Cd_{oct} atoms, co-ordinated at the *trans* positions, by a pair of pyridine ligands are equatorially bound to three CN groups to make up the trimeric cation $[\{Cd(CN)(py)_2\}_3]^{3+}$ in D_3 symmetry. The equatorial plane of the trimer is approximated to a triangle cornered with the Cd_{oct} atoms, each of which leaves two co-ordination sites outside the equatorial triangle. A pair of Cd_{tet} atoms are linked to a CN group to compose a dimeric $[(NC)_3Cd(CN)Cd(CN)_3]^{3-}$ anion with a staggered configuration of C_{3i} symmetry. A puckered two-dimensional network is formed by linking the equatorial plane of the D_3 trimeric cation with three each of the tops and the bottoms of the C_{3i}-twisted octahedral prisms alternately. In other words, the puckered layer consists of the equatorial triangles of $[Cd_{oct}(CN)]_3$ and the basal triangles of $[Cd_{tet}(CN)_3]$ tetrahedra which are the upper and the lower halves of the $[(NC)_3Cd(CN)Cd(CN)_3]^{3-}$ dimeric units. Thus the puckered layers along the *ab* plane are columned with the dimeric twisted prisms along the *c* axis.

A topological feature of edge-sharing hexagons is seen in the puckered layer, although there is no direct chemical bond on the edge. The hexagon cornered with the six Cd_{tet} atoms

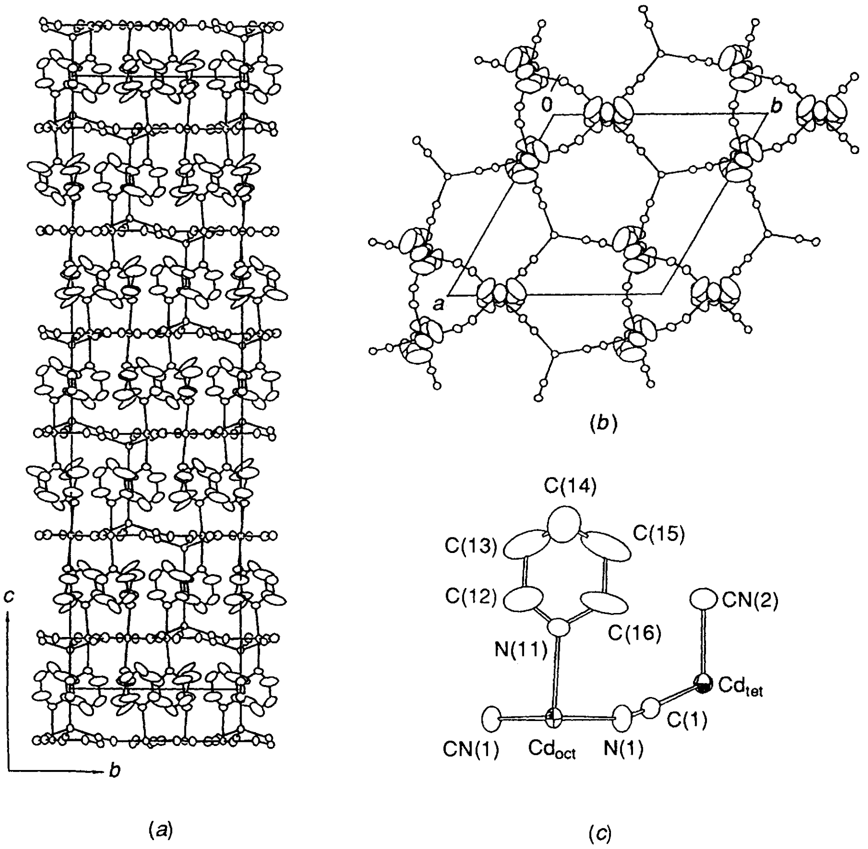

Fig. 2 Structure of complex 2. (*a*) Projection along the 2*a* + *b* direction, (*b*) projection along the *c* axis at *c* = *ca.* $\frac{1}{4}$ and (*c*) the asymmetric unit

Table 3 Final atomic coordinates for $[\{Cd(CN)(py)_2\}_3][Cd_2(CN)_7]$ **2**

Atom	G^a	X/a	Y/b	Z/c
Cd$_{oct}$	0.5000	0.229 26(9)	0	$\frac{1}{4}$
Cd$_{tet}$	0.3333	$\frac{2}{3}$	$\frac{1}{3}$	0.269 85(4)
CN(1)^b	1.0000	0.1840(10)	0.1373(10)	0.2494(3)
CN(2)^b	0.3333	$\frac{2}{3}$	$\frac{1}{3}$	0.3206(5)
C(1)	1.0000	0.5051(11)	0.2002(11)	0.2554(3)
N(1)	1.0000	0.4181(9)	0.1312(10)	0.2493(3)
N(11)	1.0000	0.2467(11)	0.0160(11)	0.3040(3)
C(12)	1.0000	0.1792(23)	0.0101(30)	0.3210(6)
C(13)	1.0000	0.1989(41)	0.0385(40)	0.3535(7)
C(14)	1.0000	0.2531(29)	0.0132(32)	0.3654(7)
C(15)	1.0000	0.3397(30)	0.0337(41)	0.3520(8)
C(16)	1.0000	0.3221 (32)	0.0035(28)	0.3185(5)

^{a} Multiplicity. ^{b} Refined with 50% occupancy each of C and N atoms at this position.

enclosing a $[Cd_{oct}(CN)]_3$ triangle gives the skeletal topology of the framework that the six-cornered planar unit has upward and downward extensions alternately at every corner the same as that of the single host framework of the quinol-host clathrates.[10] Each of the interlayer spaces between the puckered layers is filled with the pyridine ligands co-ordinating to the Cd$_{oct}$ atoms. The $R\bar{3}c$ unit cell in the hexagonal setting contains six layers along the *c* axis.

As for the $[Cd_{oct}(CN)]_3$ triangle unit, a very similar structure of a discrete triangle is known for the $Pd(CN)_3$ unit in the trimeric complex $[Pd_3(Ph_2PCH_2CH_2PPh_2)_3(\mu\text{-}CN)_3][ClO_4]_3$,[11] in which the Pd takes a distorted square-planar co-ordination with two CN ligands and the two P atoms of the chelated diphosphine. The $R\bar{3}$ space group applied made the C and N of the μ-CN distinguishable in the X-ray crystal structure determination, however the NMR spectroscopic results suggest disorder in the orientation of the CN groups.

Structure of $[Cd(iquin)_2][Cd(CN)_3(iquin)_2]_2$ **3**.—The space group $P2_1/c$ was determined uniquely from the systematic absences. In contrast with the three-dimensional structures of complexes **1** and **2**, complex **3** is composed of a CN-linked infinite meshed chain of Cd$_{oct}$ and five-co-ordinated trigonal-bipyramidal Cd$_{tbpy}$ atoms [Cd$_{oct}$:Cd$_{tbpy}$ = 1:2], with both Cd$_{oct}$ and Cd$_{tbpy}$ being *trans* co-ordinated by a pair of iquin ligands. A pair of $[Cd_{tbpy}(CN)_3(iquin)_2]$ moieties share two of their CN groups with two Cd$_{oct}$ atoms to make up the one-dimensional meshed chain $\{Cd_{oct}\langle[NC\text{-}Cd_{tbpy}(CN)\text{-}CN]_2\rangle\}_\infty$ extending along the *a* axis (Fig. 3); the remaining CN at Cd$_{tbpy}$ is unidentate and protrudes from the equatorial plane outside the chain. The chains are arranged parallel to one another along the *a* axis with respect to their running direction. Although the meshed chain is puckered, the approximate equatorial planes of the meshes are parallel to one another along the *c* axis. This puckering causes the iquin ligands to protrude slantwise from the respective Cd$_{oct}$ and Cd$_{tbpy}$ atoms so as to form a triple-decker of aromatic planes, one from Cd$_{oct}$ being sandwiched between those from the two Cd$_{tbpy}$. The intrachain triple-decker is additionally sandwiched between the triple-deckers of adjacent chains shifted by $|b \pm c|/2$. The intra- and inter-chain distances of the fused aromatic planes are *ca.* 3.4 Å of the van der Waals contact.

Comparison of the Structures.—When the Cd$_{tbpy}$ is read as Cd$_{tet}$, the one-dimensional meshed chain in complex **3** is analogous to those in complexes **1** and **4**. The framework structure built of the one-dimensional chains is affected by the bulkiness of the ligand co-ordinating to Cd$_{oct}$ at the *trans* positions. The replacement of NH_3 in complex **4** by pyridine brings about a distortion of the three-dimensional framework composed of cross-connections of the one-dimensional chains. As for the relative positioning of Cd$_{oct}$ and Cd$_{tet}$, the distortion from complex **4** to **1** is accompanied by a shift in the $\{Cd_{oct}\langle[NC\text{-}Cd_{tet}(CN)_2\text{-}CN]_2\rangle\}_\infty$ mesh by a half period

Table 4 Final atomic coordinates for [Cd(iquin)$_2$][Cd(CN)$_3$(iquin)$_2$]$_2$ **3**

Atom*	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cd$_{oct}$	0	0	0	C(21)	0.8168(13)	0.1760(5)	0.1339(6)
Cd$_{tbpy}$	0.494 55(11)	0.174 88(4)	−0.019 52(5)	N(22)	0.6563(11)	0.1798(5)	0.1205(5)
N(1)	0.1920(13)	0.0818(5)	0.0404(5)	C(23)	0.5768(16)	0.1876(6)	0.1876(7)
N(2)	0.8032(13)	0.0780(5)	−0.0578(5)	C(24)	0.6533(14)	0.1930(6)	0.2667(7)
N(3)	0.4910(18)	0.3350(5)	−0.0146(6)	C(25)	0.9183(16)	0.1931(6)	0.3612(7)
C(1)	0.2943(14)	0.1168(5)	0.0288(6)	C(26)	1.0835(19)	0.1890(7)	0.3694(8)
C(2)	0.6989(15)	0.1126(6)	−0.0542(6)	C(27)	1.1660(15)	0.1805(6)	0.3020(8)
C(3)	0.4926(16)	0.2819(5)	−0.0204(6)	C(28)	1.0869(15)	0.1757(6)	0.2233(7)
C(10)	−0.2022(18)	0.0182(6)	0.2842(8)	C(29)	0.9108(13)	0.1809(5)	0.2132(6)
C(11)	−0.2631(14)	0.0088(6)	0.1355(7)	C(30)	0.1609(14)	0.1501(6)	−0.3194(7)
N(12)	−0.1051(11)	0.0083(5)	0.1272(6)	C(31)	0.1725(14)	0.1552(5)	−0.1703(6)
C(13)	0.0034(16)	0.0126(6)	0.1971(8)	N(32)	0.3342(11)	0.1595(4)	−0.1580(5)
C(14)	−0.0386(18)	0.0175(6)	0.2764(9)	C(33)	0.4108(14)	0.1592(5)	−0.2277(7)
C(15)	−0.2530(21)	0.0259(7)	0.3671(9)	C(34)	0.3330(15)	0.1557(6)	−0.3056(7)
C(16)	−0.4118(24)	0.0262(9)	0.3720(12)	C(35)	0.0671(17)	0.1446(7)	−0.3988(7)
C(17)	−0.5314(24)	0.0227(8)	0.3003(12)	C(36)	−0.0998(17)	0.1415(8)	−0.4066(8)
C(18)	−0.4826(19)	0.0140(8)	0.2193(10)	C(37)	−0.1811(16)	0.1412(6)	−0.3374(8)
C(19)	−0.3191(15)	0.0146(6)	0.2157(6)	C(38)	−0.0962(15)	0.1457(6)	−0.2600(7)
C(20)	0.8284(15)	0.1891(5)	0.2815(6)	C(39)	0.0775(13)	0.1507(5)	−0.2492(6)

* Multiplicity 0.5 for Cd$_{oct}$ and 1.0 for all other atoms.

Table 5 Selected bond distances (Å) and angles (°) for complexes **1–3**

(*a*) [Cd(py)$_2$][Cd(CN)$_4$] **1**

Cd$_{tet}$–C(1)	2.207(8)	C(1)–N(1)	1.12(1)	C(13)–C(14)	1.32(2)	C(13)–H(13)	0.8(2)
Cd$_{oct}$–N(1)	2.323(7)	N(11)–C(12)	1.30(1)	C(12)–H(12)	1.2(1)	C(14)–H(14)	1.0(2)
Cd$_{oct}$–N(11)	2.34(1)	C(12)–C(13)	1.42(2)				
C(1)–Cd$_{tet}$–C(1^{I})	104.3(3)	Cd$_{tet}$–C(1)–N(1)	174.6(8)	C(12)–N(11)–C(12^{III})	118(1)	C(12)–C(13)–C(14)	118(2)
N(1)–Cd$_{oct}$–N(1^{II})	89.7(3)	Cd$_{oct}$–N(1)–C(1)	168.5(8)	N(11)–C(12)–C(13)	122(2)	C(13)–C(14)–C(13^{III})	121(2)
N(1)–Cd$_{oct}$–N(11)	89.4(3)	Cd$_{oct}$–N(11)–C(12)	120.9(7)				

(*b*) [{Cd(CN)(py)$_2$}$_3$][Cd$_2$(CN)$_7$] **2**

Cd$_{tet}$–C(1)	2.18(1)	Cd$_{oct}$–N(11)	2.37(1)	N(11)–C(12)	1.17(3)	C(13)–C(14)	1.11(4)
Cd$_{tet}$–CN(2)	2.22(2)	C(1)–N(1)	1.14(2)	N(11)–C(16)	1.32(3)	C(14)–C(15)	1.24(5)
Cd$_{oct}$–N(1)	2.35(1)	CN(1)–CN(1^{IV})	1.13(2)	C(12)–C(13)	1.46(4)	C(15)–C(16)	1.51(4)
Cd$_{oct}$–CN(1)	2.30(1)	CN(2)–CN(2^{V})	1.11(4)				
C(1)–Cd$_{tet}$–CN(2)	106.8(3)	Cd$_{tet}$–C(1)–N(1)	176(1)	Cd$_{oct}$–N(11)–C(12)	126(2)	C(13)–C(14)–C(15)	116(3)
N(1)–Cd$_{oct}$–CN(1)	91.1(4)	Cd$_{tet}$–CN(2)–CN(2^{V})	180	Cd$_{oct}$–N(11)–C(16)	121(1)	C(14)–C(15)–C(16)	113(3)
N(11)–Cd$_{oct}$–CN(1)	89.5(5)	Cd$_{oct}$–N(1)–C(1)	165(1)	N(11)–C(12)–C(13)	124(3)	C(15)–C(16)–N(11)	117(3)
N(11)–Cd$_{oct}$–N(1)	85.2(4)	Cd$_{oct}$–CN(1)–CN(1^{IV})	163.4(9)	C(12)–C(13)–C(14)	116(4)	C(16)–N(11)–C(12)	111(2)

(*c*) [Cd(iquin)$_2$][Cd(CN)$_3$(iquin)$_2$]$_2$ **3**

Cd$_{oct}$–N(1)	2.34(1)	Cd$_{tbpy}$–C(2)	2.23(1)	Cd$_{tbpy}$–N(22)	2.486(8)	C(2)–N(2)	1.12(1)
Cd$_{oct}$–N(2^{VI})	2.38(1)	Cd$_{tbpy}$–C(3)	2.20(1)	Cd$_{tbpy}$–N(32)	2.478(8)	C(3)–N(3)	1.10(1)
Cd$_{tbpy}$–C(1)	2.25(1)	Cd$_{oct}$–N(12)	2.341(9)	C(1)–N(1)	1.14(1)		

Isoquinoline rings

Ring 1:	C(10)–C(19)	N–C(average)	1.34	C–C(average)	1.39
Ring 2:	C(20)–C(29)	N–C(average)	1.33	C–C(average)	1.39
Ring 3:	C(30)–C(39)	N–C(average)	1.34	C–C(average)	1.39

N(1)–Cd$_{oct}$–N(2^{VI})	91.3(3)	C(2)–Cd$_{tbpy}$–C(3)	125.2(5)	C(2)–Cd$_{tbpy}$–N(32)	91.5(3)	Cd$_{oct}$–N(2)–C(2)	152.9(9)
N(1)–Cd$_{oct}$–N(12)	90.5(3)	C(1)–Cd$_{tbpy}$–N(22)	91.7(3)	C(3)–Cd$_{tbpy}$–N(32)	96.9(3)	Cd$_{tbpy}$–C(1)–N(1)	168(1)
N(2^{VI})–Cd$_{oct}$–N(12)	89.7(3)	C(2)–Cd$_{tbpy}$–N(22)	85.7(3)	N(22)–Cd$_{tbpy}$–N(32)	175.0(3)	Cd$_{tbpy}$–C(2)–N(2)	168(1)
C(1)–Cd$_{tbpy}$–C(2)	112.7(4)	C(3)–Cd$_{tbpy}$–N(22)	88.2(4)	Cd$_{oct}$–N(1)–C(1)	153.1(9)	Cd$_{tbpy}$–C(3)–N(3)	175(1)
C(1)–Cd$_{tbpy}$–C(3)	121.9(4)	C(1)–Cd$_{tbpy}$–N(32)	85.6(3)				

Symmetry operations: I $-x, y, -z + \frac{1}{2}$; II $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; III $x, y, -z$; IV $y, x, -z + \frac{1}{2}$; V $-x + \frac{4}{3}, -y + \frac{2}{3}, -z + \frac{2}{3}$; VI $x - 1, y, z$.

between the adjacent chains running in parallel so as to collapse the β cavity and to hold the pyridine ligand in the remaining void space which corresponds to an α cavity in complex **4**. When the pyridine in complex **1** is replaced by the bulkier iquin ligand the analogous three-dimensional framework can no longer be maintained and is disjointed into one-dimensional chains at the Cd$_{tet}$ crossings. The disjointed Cd$_{tet}$ keeps one CN group unidentate and is additionally ligated by two iquin ligands to accomplish the Cd$_{tbpy}$ five-co-ordination at the antinode of the meshed chain; the formation of the distinct one-dimensional chain makes the stoichiometry of the compound Cd(CN)$_2$·2iquin. Owing to different preparation conditions from those of Mesnard and Gode,[2] we did not obtain any single crystals of the composition 2Cd(CN)$_2$·3iquin that they had reported.

As for the co-ordination geometries about the cadmium centres, the Cd$_{tet}$–C distance (2.18–2.21 Å) is always shorter than the Cd$_{oct}$–N distance (2.32–2.35 Å) whenever the C and N ends are discriminated in the structure refinement. Distortion from a regular octahedron or tetrahedron for Cd$_{oct}$ or Cd$_{tet}$ is small with bond angles 90 ± 5 or 109.5 ± 5.5°, respectively;

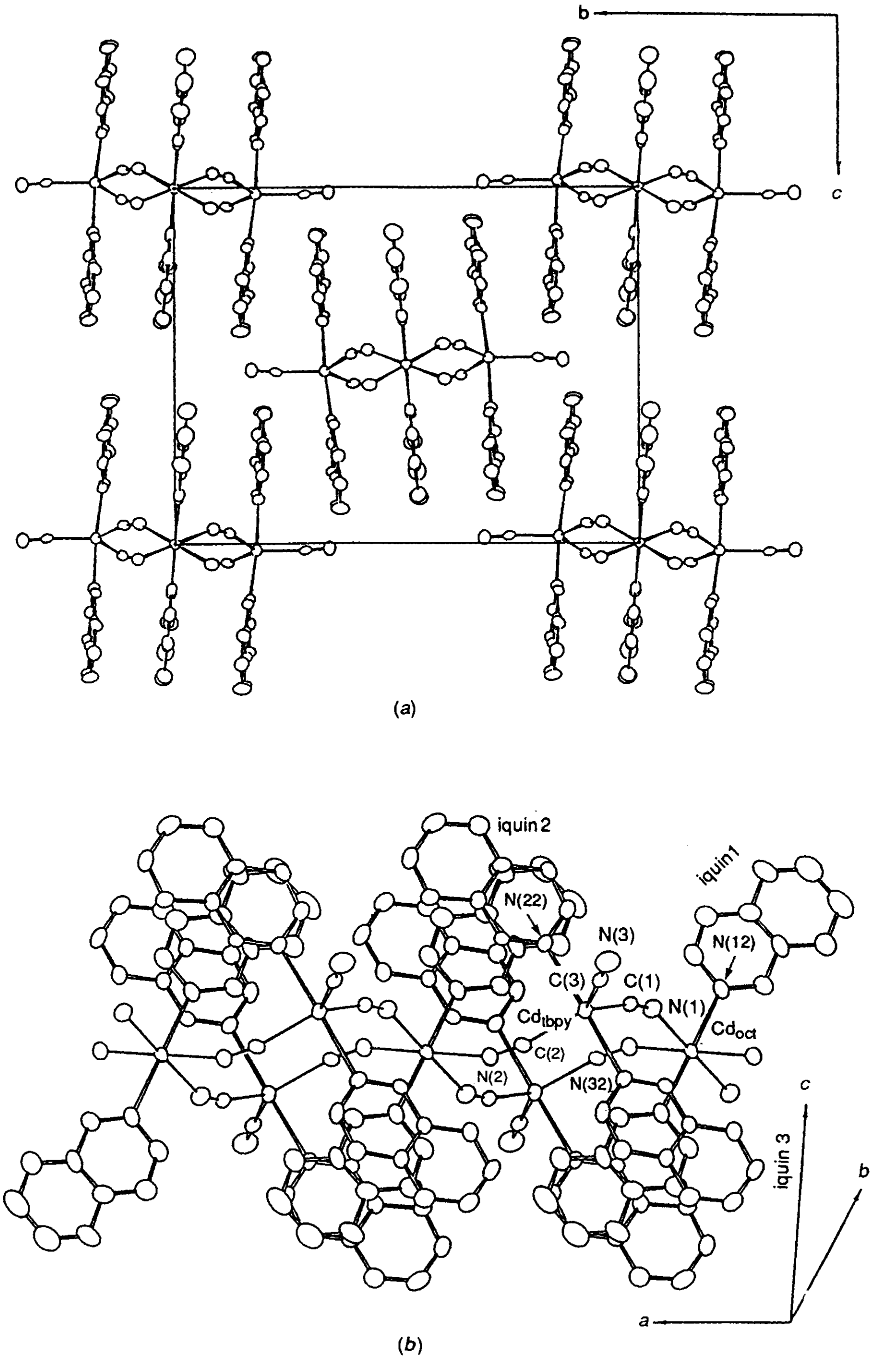

Fig. 3 Structure of complex **3**. (*a*) Projection along the *a* axis and (*b*) perspective view of the one-dimensional meshed chain

the deviation from linearity in Cd$_{tet}$–C–N–Cd$_{oct}$ is larger for C–N–Cd$_{oct}$ (11.5–27.1°) than for Cd$_{tet}$–C–N (4.0–5.4°). Little distortion is observed for the trigonal-bipyramidal geometry about the Cd$_{tbpy}$ in complex **3**. The bonding of the bending of the Cd$_{tbpy}$–C–N–Cd$_{oct}$ sequence, Cd$_{tbpy}$–C–N (12°) and C–N–Cd$_{oct}$ (27°), is greater than that in Cd$_{tet}$–C–N–Cd$_{oct}$ with longer Cd$_{oct}$–N (2.34–2.38 Å) and Cd$_{tbpy}$–C (2.20–2.25 Å) distances than Cd$_{oct}$–N and Cd$_{tet}$–C in complexes **1** and **2**.

When the number of pyridine ligands available in the preparation conditions exceeds that required for complex **1**, [Cd(py)$_2$][Cd(CN)$_4$] {*i.e.* 2[Cd(CN)$_2$·py]}, crystals of complex **2**, [{Cd(CN)(py)$_2$}$_3$][Cd$_2$(CN)$_7$] {*i.e.* 5[Cd(CN)$_2$·1.2py]}, are obtained. The 20% increase in pyridine content causes a 50% increase in the pyridine-ligated Cd$_{oct}$ in the crystal structure. This is due to the condensation of the cationic species into the trimer which leaves only two co-ordination sites per Cd$_{oct}$ for the framework formation. The condensed dimer unit of the anionic Cd$_{tet}$(CN)$_7$ is seen in the clay- and zeolite-like mineralomimetic structures built of Cd$_3$(CN)$_7$ moieties, in which the Cd$_{oct}$:Cd$_{tet}$ ratio is 1:2.[1c,d] A discrete anion analogous to pyrosilicate $Si_2O_7^{2-}$ has recently been found in the crystal structure of [PPh$_4$]$_3$[Cd$_2$(CN)$_7$].[12]

In contrast with the cadmium and cyanide moieties, the skeletal atoms of the aromatic ligands gave considerably larger estimated standard deviations for the atomic parameters. In particular, extremely large thermal amplitudes were given to the pyridine ring in complexes **1** and **2** and the *x* coordinates were determined with less precision for complex **3**. The relatively large *R* values for complexes **2** and **3** are attributable to the high degree of thermal displacement and/or disorder of these atoms. The pyridine ligand in the pseudocavity begins to dissociate at 140 °C from complex **2** and at 155 °C from complex **1** under similar thermogravimetric conditions (*ca.* 10 mg specimen with a heating rate of 10° min^{-1} under ambient atmosphere). These observations and the fact that complex **2** has never been obtained from hot solutions suggest the lower stability of the condensed species at high temperature both in the solution and solid state.

References

1 (*a*) T. Iwamoto, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London, 1984, vol. 1, ch. 2, pp. 29–57; (*b*) T. Iwamoto, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, Oxford, 1991, vol. 5, ch. 6, pp. 172–212; (*c*) T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *Chem. Lett.*, 1988, 459, 1729; (*d*) T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1992, 413; (*e*) H. Yuge and T. Iwamoto, *J. Inclusion Phenom.*, 1992, **14**, 217.

2 P. Mesnard and D. Gode, *C. R. Hebd. Seances Acad. Sci.*, 1961, **253**, 870.

3 D. Ülkü, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1975, **142**, 271.

4 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.* (*Jpn.*), 1979, **55**, 69.

5 G. M. Sheldrick, SHELXS 86, Program for crystal structure determination, University of Göttingen, 1986.

6 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.

7 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 72.

8 D. T. Cromer and A. C. Larson, *Acta Crystallogr., Sect. B*, 1973, **29**, 251.

9 R. Kuroda, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 13.

10 E. E. Palin and H. M. Powell, *J. Chem. Soc.*, 1947, 208.

11 J. A. Davies, F. R. Hartley, S. G. Murray and M. A. Pierce-Butler, *J. Chem. Soc., Dalton Trans.*, 1983, 1305.

12 T. Kitazawa and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 1993, 309.

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