Cadmium Cyanide–Ether Clathrates: Crystal Structures of $Cd_8(CN)_{16}(H_2O)_6{\cdot}6G$ (G = Et_2O or $Pr^i{}_2O$) and $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^n{}_2O$†

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The cadmium cyanide host clathrates $Cd_8(CN)_{16}(H_2O)_6{\cdot}6G$ (G = Et_2O **1a** or $Pr^i{}_2O$ **1b**) and $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^n{}_2O$ **2** have been prepared and their structures determined by X-ray crystallography: **1a**, cubic, space group $P\bar{4}3n$, a = 15.661(5) Å, Z = 2, R = 0.045 for 565 reflections; **1b**, cubic, space group $P\bar{4}3n$, a = 15.762(9) Å, Z = 2, R = 0.035 for 653; **2**, monoclinic, space group $C2/c$, a = 14.044(6), b = 18.034(6), c = 12.931(4) Å, β = 111.47(2)°, Z = 4, R = 0.040 for 2003. The novel hosts in **1a** and **1b** contain tetrahedral and octahedral Cd atoms in a 5:3 ratio. The host in **2** is isostructural to that of the previously reported $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^iOH$ **3**, containing tetrahedral and octahedral cadmium atoms in a ratio of 2:1. The guest ether molecules are accommodated in cage-like cavities, and participate in hydrogen bonding between their O atoms and those of the co-ordinated water molecules.

It has been found that $Cd(CN)_2$ behaves as a three-dimensional host for various organic guests. The first example reported, $Cd(CN)_2{\cdot}CCl_4$ in 1988,[1] was complemented by the series of hydrophobic guest (G) clathrates $Cd(CN)_2{\cdot}G$ in which the cage-like host is isostructural with the high-temperature phase of cristobalite,[2,3] *i.e.* all the Cd atoms have a tetrahedral (t) geometry. Another type of cadmium cyanide clathrates are those with alcohol guests, in which the cadmium exists in tetrahedral but also octahedral (oc)[4,5] or trigonal-bipyramidal (tbpy)[6] geometries in a CN-bridged three-dimensional framework. A co-ordination number of greater than four is attained by co-ordination of water molecule(s) to the cadmium, and the hydrophilic guest in the cavity forms hydrogen bonds with the water. The alcohol clathrates, of composition $u\mathrm{Cd(CN)_2}{\cdot}v\text{-}(\mathrm{H_2O}){\cdot}w\mathrm{G}$, vary in their host structures. For example, the hosts in both $3Cd(CN)_2{\cdot}2H_2O{\cdot}3Bu^tOH$[4a] and $3Cd(CN)_2{\cdot}2H_2O{\cdot}2Pr^iOH$[5] have a ratio of $Cd_{oc}:Cd_t$ = 1:2 but their structures are different. The host in $5Cd(CN)_2{\cdot}4H_2O{\cdot}4C_6H_{11}OH$[6] has $Cd_{tbpy}:Cd_t$ = 1:4 and that in $5Cd(CN)_2{\cdot}2H_2O{\cdot}6Pr^nOH$[5] has $Cd_{oc}:Cd_t$ = 1:4.

We have now examined the effect on the $Cd(CN)_2$ host structure of using diethyl, diisopropyl and dipropyl ethers as guests, which are less hydrophilic than alcohols but more so than are CCl_4 and CMe_4. The host structures of the clathrates obtained, $Cd_8(CN)_{16}(H_2O)_6{\cdot}6G$ (G = Et_2O **1a** or $Pr^i{}_2O$ **1b**) and $Cd_3(CN)_6(H_2O)_2{\cdot}Pr^n{}_2O$ **2** are different between **1** and **2**. Compounds **1a** and **1b** are isostructural, having the novel $Cd_{oc}:Cd_t$ ratio of 3:5; **2** is isostructural with $3Cd(CN)_2{\cdot}2H_2O{\cdot}2Pr^iOH$, *i.e.* $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^iOH$ **3** previously reported by Kim *et al.*[5] The hydrophilic character of the ether O is so enhanced in these host structures that the guest molecules are linked to the host framework through hydrogen bonds between the aqua ligands and the ether O atoms.

Results

General.—The crystal structures determined for compounds **1a**, **1b** and **2** are illustrated in Figs. 1 and 2. Atomic coordinates are listed in Table 1, selected bond distances and angles in Table 2.

The present ether clathrates prefer host structures which are favourable to hydrophilic guests rather than the cristobalite-like one for hydrophobic guests such as CCl_4 and CMe_4.[3] Each of the hosts, type 1 for compounds **1a** and **1b** and type 2 for **2**, is built up from CN linkages between Cd_t and Cd_{oc} atoms, the latter being co-ordinated to two water molecules. In type 1 the aqua co-ordination is *trans* similar to that in the Bu^tOH[4a] and Pr^nOH[5] clathrate, whereas it is *cis* in type 2 similar to that in the Pr^iOH[5] clathrate. A characteristic structural feature is a rhombus of O atoms formed by hydrogen bonding among the ether and water oxygens in the respective cavities.

Structures of Compounds **1a** *and* **1b**.—Three crystallographically independent Cd atoms, octahedral Cd(1) and tetrahedral Cd(2) and Cd(3), in a ratio of 3:1:4, are interconnected by CN groups leading to a three-dimensional host framework [Fig. 1(*a*)]. The $Cd_{oc}:Cd_t$ ratio of 3:5 is the first example among cyanide and polycyanopolycadmate systems which give multidimensional structures such as clays (1:2), zeolites (1:2, 1:3), and so-called honeycombs (1:2). Atom Cd(1), on a crystallographic $\bar{4}$ symmetry site, is co-ordinated equatorially by four N atoms from cyanides bonded to four Cd(3) atoms on a crystallographic symmetry site 3, and apically to two water molecules. Atom Cd(2), on a 23 symmetry site, is linked tetrahedrally to four Cd(3) atoms, Cd(3) being connected to three Cd(1) and one Cd(2). Eventually, an approximately hexagonal ring Cd(2)⟨[Cd(3)–Cd(1)–Cd(3)]$_2$⟩Cd(2) is formed [Fig. 1(*b*)] in the cavity of which is trapped a pair of the guest ether molecules, giving a rhombus O(1)⟨[O(2)]$_2$⟩O(1) with O(1)···O(2) 2.799(7) and 2.749(9) Å and O(2)–O(1)–O(2) 110.2(4) and 105.1(3)° for **1a** and **1b**, respectively. According to the symmetry requirements of the space group $P\bar{4}3n$, there are six cavities centred at $0,\frac{1}{2},\frac{1}{2}$ and equivalent positions in the unit cell. The environment around the alkyl groups of the ether guests is similar to that observed for $Cd(CN)_2{\cdot}G$ clathrates with hydrophobic guests. The thermal parameters for the guest atoms of **1b** are smaller than those of **1a** due to the bulkier nature of $Pr^i{}_2O$ than that of Et_2O, the cavities in the two clathrates having similar dimensions.

Structure of Compound **2**.—The host structure of compound **2** [Fig. 2(*a*)] has the same topology as that of $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^iOH$ **3** described by Kim *et al.*[5] with little change in the unit-cell parameters. The remarkable difference in the host

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

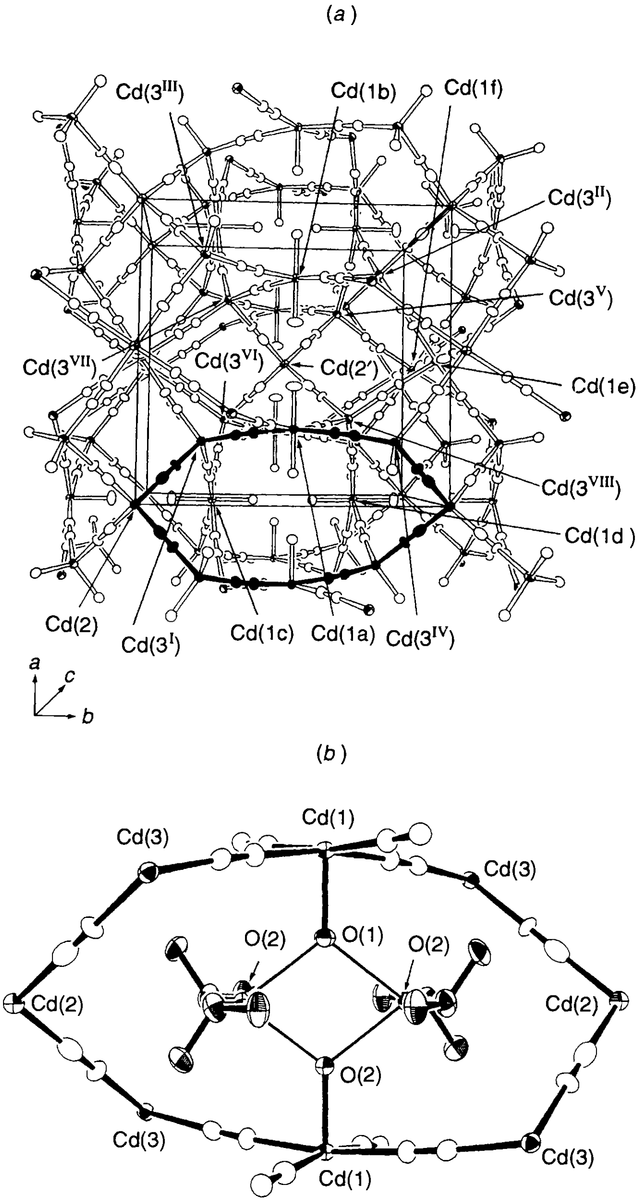

Fig. 1 (*a*) Perspective view of the host framework $Cd_8(CN)_{16}(H_2O)_6$ of compounds **1a** and **1b**. Hydrogen atoms and ether molecules are omitted; thermal ellipsoids with 50% probability. Atom Cd(1) has octahedral co-ordination, with two *trans* water molecules and four N atoms from cyanide bound to Cd(3); Cd(2) and Cd(3) have tetrahedral co-ordination; Cd(2) has four links to Cd(3), Cd(3) three links to Cd(1) and one to Cd(2). Atom Cd(1a) is at $\frac{1}{4}, \frac{1}{2}, 0$, Cd(1b) at $\frac{3}{4}, \frac{1}{2}, 0$, Cd(1c) at $0, \frac{1}{4}, \frac{1}{2}$, Cd(1d) at $0, \frac{3}{4}, \frac{1}{2}$, Cd(1e) at $\frac{1}{2}, 1, \frac{1}{4}$, Cd(1f) at $\frac{1}{2}, 1, \frac{3}{4}$, Cd(2) at 0, 0, 0 and Cd(2′) at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Symmetry operations: I x, x, x; II, $1 - x, 1 - x, x$; III $1 - x, x, -x$; IV $x, 1 - x, -x$; V $x + \frac{1}{2}, x + \frac{1}{2}, x + \frac{1}{2}$; VI $-x + \frac{1}{2}, -x + \frac{1}{2}, x + \frac{1}{2}$; VII $x + \frac{1}{2}, -x + \frac{1}{2}, -x + \frac{1}{2}$; VIII $-x + \frac{1}{2}, x + \frac{1}{2}, -x + \frac{1}{2}$. The bold lines represent one of the hexagonal rings. (*b*) Structure of the hexagonal ring and the guest $Pr^i{}_2O$ molecules. Hydrogen atoms are omitted; thermal ellipsoids with 50% probability. The hexagonal ring has a twist-boat conformation. Two co-ordinated water molecules and two ether O(2) atoms form a rhombic hydrogen-bonding network (thin lines)

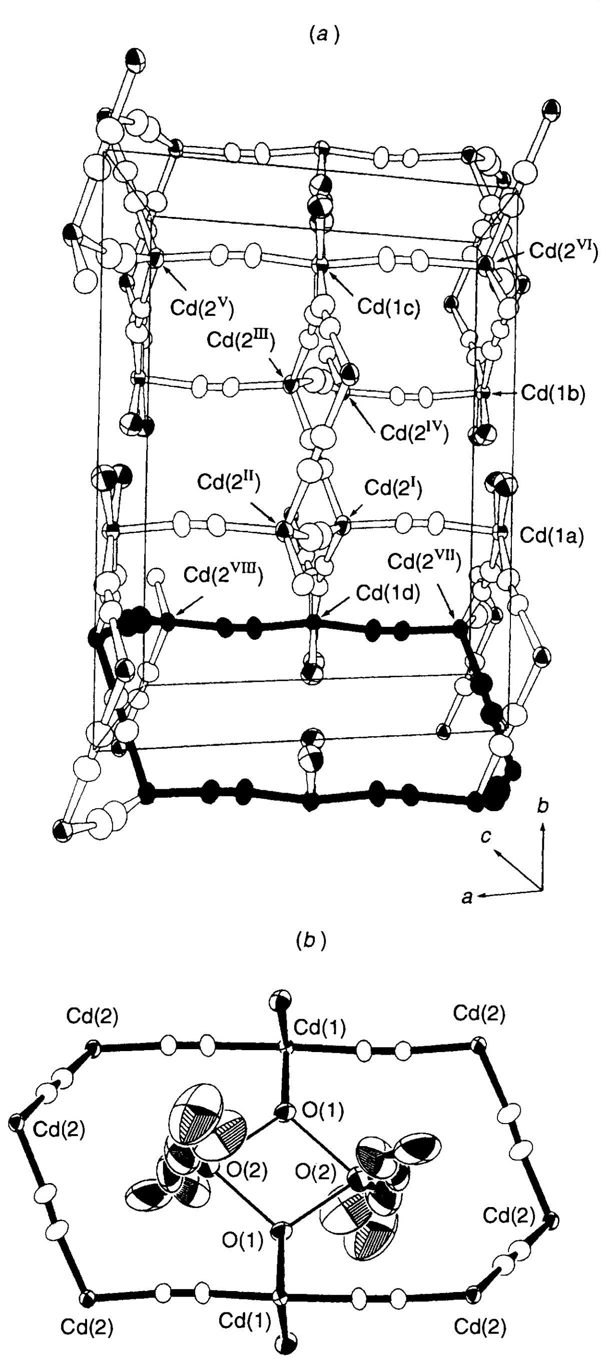

Fig. 2 (*a*) Structure of $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^n{}_2O$ **2**. Hydrogen atoms and ether molecules are omitted; thermal ellipsoids with 50% probability. View approximately along the *c* axis. Atom Cd(1) has octahedral and Cd(2) tetrahedral geometry. Atom Cd(1a) is at $0, y, \frac{1}{4}$, Cd(1b) at $0, 1 - y, \frac{3}{4}$, Cd(1c) at $\frac{1}{2}, y + \frac{1}{2}, \frac{1}{4}$ and Cd(1d) at $\frac{1}{2}, -y + \frac{1}{2}, \frac{3}{4}$. Symmetry operations: I x, y, z; II, $1 - x, y, -z + \frac{1}{2}$; III $1 - x, 1 - y, 1 - z$; IV $x, 1 - y, z + \frac{1}{2}$; V, $x + \frac{1}{2}, y + \frac{1}{2}, z$; VI $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; VII $-x + \frac{1}{2}, -y + \frac{1}{2}, 1 - z$; VIII $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$. Bold lines represent one of the hexagonal rings. (*b*) Structure of the hexagonal ring and the guest $Pr^n{}_2O$ molecules. Hydrogen atoms are omitted; thermal ellipsoids with 30% probability. The hexagonal ring has a chair conformation. Two co-ordinated water molecules and two ether O(2) atoms form a rhombic hydrogen-bonding network (thin lines)

structure between types 1 and 2 is the cis co-ordination of aqua ligands at the octahedral Cd atom. Although the disordered arrangement of the guest Pr^iOH molecules was not reported,[5] the $Pr^n{}_2O$ molecules in **2** are trapped in the cavity by hydrogen bonds between the aqua and ether O atoms. A hexagonal ring is formed, *viz*. Cd(2)⟨[Cd(2)–Cd(1)–Cd(2)]$_2$⟩ Cd(2), where Cd(1) is octahedral and Cd(2) tetrahedral [Fig. 2(*b*)]. It has a chair conformation whereas that of the type 1 structure is a twist-boat. A rhombus, though a little distorted, of the O atoms is also formed with O(1) (aqua)···O(2)(ether) distances of 2.860(8) and 2.876(9) Å and O(2)–O(1)–O(2) 100.4(2)°.

Table 1 Final atomic coordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
$Cd_8(CN)_{16}(H_2O)_6 \cdot 6Et_2O$, **1a**							
Cd(1)	$\frac{1}{4}$	$\frac{1}{2}$	0	CN(1)	0.081 4(10)	0.081 4	0.081 4
Cd(2)	0	0	0	CN(2)	0.125 2(8)	0.125 2	0.125 2
Cd(3)	0.207 54(6)	0.207 54	0.207 54	O(2)	0.353 5	0	0
O(1)	0.397 7(8)	$\frac{1}{2}$	0	C(11)	0.304(2)	0.089(3)	−0.024(2)
N(1)	0.240 1(8)	0.378 4(6)	0.084 4(7)	C(12)	0.360(2)	0.149(2)	−0.016(2)
C(1)	0.231 7(9)	0.323 3(9)	0.123 7(8)				
$Cd_8(CN)_{16}(H_2O)_6 \cdot 6Pr^i_2O$ **1b**							
Cd(1)	$\frac{1}{4}$	$\frac{1}{2}$	0	CN(1)	0.082 5(8)	0.082 5	0.082 5
Cd(2)	0	0	0	CN(2)	0.123 8(6)	0.123 8	0.123 8
Cd(3)	0.206 87(5)	0.206 87	0.206 87	O(2)	0.361 5(5)	0	0
O(1)	0.394 0(6)	$\frac{1}{2}$	0	C(11)	0.312 3(7)	0.081 2(7)	−0.003(1)
N(1)	0.238 5(7)	0.375 8(5)	0.082 6(6)	C(12)	0.375 6(7)	0.152 2(7)	−0.001(1)
C(1)	0.230 1(7)	0.319 0(7)	0.123 8(7)	C(13)	0.258 6(7)	0.082(1)	−0.085 4(9)
$Cd_3(CN)_6(H_2O)_2 \cdot 2Pr^n_2O$ **2**							
Cd(1)	0	0.354 48(4)	$\frac{1}{4}$	CN(2)	0.487 9(5)	0.344 7(4)	0.287 1(5)
Cd(2)	0.425 65(4)	0.360 08(3)	0.420 64(4)	O(2)	0.664 1(5)	0.023 1(4)	0.542 9(5)
O(1)	0.002 3(4)	0.450 0(3)	0.124 5(4)	C(11)	0.808(1)	−0.124(1)	0.704(1)
N(1)	0.172 1(4)	0.368 8(4)	0.310 9(5)	C(12)	0.713(1)	−0.077(1)	0.635(1)
C(1)	0.258 7(5)	0.368 1(4)	0.344 7(5)	C(13)	0.751(1)	−0.012(1)	0.603(1)
N(2)	0.008 6(5)	0.269 0(3)	0.384 6(5)	C(14)	0.712(2)	0.087(1)	0.515(2)
C(2)	0.026 3(5)	0.225 7(4)	0.451 2(6)	C(15)	0.628(2)	0.119(1)	0.438(2)
CN(1)	0.484 8(6)	0.470 1(3)	0.484 6(5)	C(16)	0.672(2)	0.195(2)	0.389(2)

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

(*a*) $Cd_8(CN)_{16}(H_2O)_6 \cdot 6Et_2O$ **1a**[a]							
Cd(1)–O(1)	2.31(1)	Cd(3)–CN(2)	2.23(2)	CN(1)–CN(2)	1.19(3)	O(1)···O(2^{I})	2.799(7)
Cd(1)–N(1)	2.32(1)	Cd(3)–C(1)	2.27(1)	O(2)–C(11)	1.64(4)	Cd(1)···Cd(3)	5.656(2)
Cd(2)–CN(1)	2.21(3)	N(1)–C(1)	1.07(1)	C(11)–C(12)	1.28(5)	Cd(2)···Cd(3)	5.630(2)
O(1)–Cd(1)–O(1^{II})	180	N(1^{II})–Cd(1)–N(1^{III})	172.3(6)	CN(2)–Cd(3)–C(1)	102.9(3)	Cd(3)–C(1)–N(1)	177(1)
O(1)–Cd(1)–N(1)	93.8(3)	CN(1)–Cd(2)–CN(1^{IV})	109.47	Cd(2)–CN(1)–CN(2)	180	C(11)–O(2)–C(11^{VI})	124(2)
O(1)–Cd(1)–N(1^{II})	86.2(3)	C(1)–Cd(3)–C(1^{V})	115.2(2)	Cd(3)–CN(2)–CN(1)	180	O(2)–C(11)–C(12)	106(3)
N(1)–Cd(1)–N(1^{II})	90.26(4)	O(2^{I})–O(1)–O(2^{VII})	110.2(4)	Cd(1)–N(1)–C(1)	177(1)		
(*b*) $Cd_8(CN)_{16}(H_2O)_6 \cdot 6Pr^i_2O$ **1b**[a]							
Cd(1)–O(1)	2.270(9)	Cd(3)–C(1)	2.23(1)	O(2)–C(11)	1.50(1)	O(1)···O(2^{I})	2.749(9)
Cd(1)–N(1)	2.359(9)	N(1)–C(1)	1.11(1)	C(11)–C(12)	1.50(1)	Cd(1)···Cd(3)	5.696(3)
Cd(2)–CN(1)	2.25(2)	CN(1)–CN(2)	1.13(2)	C(11)–C(13)	1.55(2)	Cd(2)···Cd(3)	5.648(4)
Cd(3)–CN(2)	2.27(2)						
O(1)–Cd(1)–O(1^{II})	180	CN(1)–Cd(2)–CN(1^{IV})	109.47	CN(2)–Cd(3)–C(1)	102.3(3)	C(11)–O(2)–C(11^{VI})	118(1)
O(1)–Cd(1)–N(1)	94.4(3)	C(1)–Cd(3)–C(1^{V})	115.6(2)	Cd(3)–CN(2)–CN(1)	180	O(2)–C(11)–C(12)	107.1(8)
O(1)–Cd(1)–N(1^{II})	85.6(3)	Cd(2)–CN(1)–CN(2)	180	Cd(1)–N(1)–C(1)	177(1)	O(2)–C(11)–C(13)	108(1)
N(1)–Cd(1)–N(1^{II})	90.34(4)	O(2^{I})–O(1)–O(2^{VII})	105.1(3)	Cd(3)–C(1)–N(1)	177(1)	C(12)–C(11)–C(13)	112(1)
N(1^{II})–Cd(1)–N(1^{III})	171.2(5)						
(*c*) $Cd_3(CN)_6(H_2O)_2 \cdot 2Pr^n_2O$ **2**[b]							
Cd(1)–O(1)	2.375(5)	Cd(2)–CN(2)	2.219(6)	O(2)–C(14)	1.45(2)	O(1)···O(2^{IV})	2.860(8)
Cd(1)–N(1)	2.266(6)	N(1)–C(1)	1.132(8)	C(11)–C(12)	1.56(2)	O(1)···O(2^{V})	2.876(9)
Cd(2)–N(2)	2.295(6)	N(2)–C(2)	1.120(8)	C(12)–C(13)	1.40(2)	Cd(1)···Cd(2)	5.564(3)
Cd(2)–C(1)	2.191(7)	CN(1)–CN(1^{II})	1.17(1)	C(14)–C(15)	1.37(3)	Cd(2)···Cd(2^{III})	5.530(2)
Cd(2)–C(2^{I})	2.186(7)	CN(2)–CN(2^{III})	1.13(1)	C(15)–C(16)	1.71(3)	Cd(2)···Cd(2^{II})	5.559(2)
Cd(2)–CN(1)	2.193(6)	O(2)–C(13)	1.34(1)				
O(1)–Cd(1)–O(1^{VI})	87.0(3)	N(1)–Cd(1)–N(2^{VI})	95.4(2)	C(2^{I})–Cd(2)–CN(2)	113.7(3)	Cd(2)–CN(2)–CN(2^{III})	171.0(5)
O(1)–Cd(1)–N(1)	82.9(2)	N(2)–Cd(1)–N(2^{VI})	95.6(3)	CN(1)–Cd(2)–CN(2)	101.7(3)	C(13)–O(2)–C(14)	97(1)
O(1)–Cd(1)–N(1^{VI})	87.7(2)	C(1)–Cd(2)–C(2^{I})	111.7(3)	Cd(1)–N(1)–C(1)	172.5(7)	C(11)–C(12)–C(13)	107(2)
O(1)–Cd(1)–N(2)	174.5(2)	C(1)–Cd(2)–CN(1)	107.8(3)	Cd(2)–C(1)–N(1)	175.2(7)	O(2)–C(13)–C(12)	102(1)
O(1)–Cd(1)–N(2^{VI})	88.8(2)	C(1)–Cd(2)–CN(2)	108.7(2)	Cd(1)–N(2)–C(2)	170.4(7)	O(2)–C(14)–C(15)	99(2)
N(1)–Cd(1)–N(1^{VI})	166.9(4)	C(2^{I})–Cd(2)–CN(1)	112.7(3)	C(2^{I})–C(2)–N(2)	174.7(7)	C(14)–C(15)–C(16)	106(2)
N(1)–Cd(1)–N(2)	93.4(2)	O(2^{IV})–O(1)–O(2^{V})	100.4(2)	Cd(2)–CN(1)–CN(1^{II})	177.9(8)		

[a] Symmetry operations: I $z + \frac{1}{2}, -y + \frac{1}{2}, -x + \frac{1}{2}$; II $-x + \frac{1}{2}, z + \frac{1}{2}, -y + \frac{1}{2}$; III $x, -y + 1, -z$; IV $-x, y, -z$; V z, x, y; VI, $x, -y, -z$; VII $z + \frac{1}{2}, y + \frac{1}{2}, x - \frac{1}{2}$. [b] Symmetry operations: I $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; II $-x + 1, -y + 1, -z + 1$; III $-x + 1, y, -z + \frac{1}{2}$; IV $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; V $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; VI $-x, y, -z + \frac{1}{2}$.

Table 3 Crystallographic and selected experimental data[a]

	1a	**1b**	**2**
Formula	$C_{40}H_{72}Cd_8N_{16}O_{12}$	$C_{52}H_{96}Cd_8N_{16}O_{12}$	$C_{18}H_{32}Cd_3N_6O_4$
M	1868.39	2036.71	733.72
Crystal system	Cubic	Cubic	Monoclinic
Space group	$P\bar{4}3n$ (no. 218)	$P\bar{4}3n$ (no. 218)	$C2/c$ (no. 15)
a/Å	15.661(5)	15.762(9)	14.044(6)
b/Å			18.034(6)
c/Å			12.931(4)
β/°			111.47(2)
U/Å^3	3841(1)	3916(2)	3048(4)
Z	2	2	4
D_c/g cm^{-3}	1.61	1.72	1.60
D_m[b]/g cm^{-3}	1.59(3)	1.72(1)	1.57(3)
F(000)	1808	2000	1432
μ(Mo-Kα)/cm^{-1}	22.15	21.80	20.96
Crystal dimensions/mm	0.45 × 0.45 × 0.40	0.45 × 0.40 × 0.35	0.30 × 0.20 × 0.20
No. reflections for unit cell determination (2θ range)/°	25 (26.2–29.7)	25 (28.6–30.0)	25 (29.4–30.0)
Scan width/°	1.10 + 0.30 tan θ	1.21 + 0.30 tan θ	1.52 + 0.30 tan θ
h,k,l ranges	0–20, 0–14, 0–10	0–20, 0–14, 0–10	0–18, 0–23, −16 to 15
No. of reflections			
measured	945	966	3778
used [$I > 3.00\sigma(I)$], N_o	565	653	2003
R	0.045	0.035	0.040
R'	0.046	0.036	0.042
Goodness of fit	2.41	2.34	2.40
No. of parameters, N_p	58	68	141
Maximum shift/error in final cycle	0.32	0.15	0.33
Maximum, minimum peaks in final difference map/e Å^{-3}	0.65, −1.33	0.59, −0.53	0.52, −0.86

[a] Details in common: Mo-Kα radiation (λ = 0.710 69 Å), graphite monochromator; ω–2θ scan; scan range 2θ 3–55°; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = 4F_o^2/\sigma^2(F_o^2)$, goodness of fit $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$. [b] Measured by the flotation method in a bromoform–mesitylene mixture immediately after the crystals were removed from the flask.

Discussion

We have found a number of examples where the host structure in cadmium cyanide and polycyanopolycadmate systems is determined by the guest. This is reasonable for the isomers Pr^n_2O and Pr^i_2O, as well as Pr^nOH and Pr^iOH, which have different effective dimensions in a cavity. However, it is difficult to generalise because the determined structures are so variegated from one to the others and the number of well defined structures is still small. For the ether guests, Et_2O is analogous to Pr^i_2O giving a type 1 structure. It is curious that Pr^iOH gives the same type 2 host structure in clathrate **3** as that in **2**, assuming both have the same stoichiometry: the value of $Z = 8$ given in ref. 5 should be 12 according to the formulation of **3** as $Cd(CN)_2{\cdot}\frac{2}{3}H_2O{\cdot}\frac{2}{3}Pr^iOH$. However, in **3** there is a considerable void space corresponding to the volume of one less isopropyl group in the cavity in comparison with the Pr^n_2O in **2**. In this respect the dimensions of the guest cannot be the most influential factor in the selection of the host structure. Other factors to be considered are the hydrophilic and/or hydrophobic character, polarity, shape, size, possible configuration, freedom of thermal motion, *etc.*, of the guest molecules. A combination of such factors may determine the host structure.

Experimental

Preparation.—The compounds $Cd_8(CN)_{16}(H_2O)_6{\cdot}6Et_2O$ **1a**, $Cd_8(CN)_{16}(H_2O)_6{\cdot}6Pr^i_2O$ **1b** and $Cd_3(CN)_6(H_2O)_2{\cdot}2Pr^n_2O$ **2** were obtained by procedures similar to those applied for the cristobalite-like host clathrates $Cd(CN)_2{\cdot}G$.[1,3] An aqueous solution of the host components was treated with the neat liquid ether. Colourless single crystals of **1a** and **2** were obtained within a few days at room temperature; those for **1b** were after a few weeks at 6 °C in a refrigerator. The products lose the guest and water molecules so readily upon exposure to air that the above compositions have been based on the results of the X-ray analyses. The residual white powder had the composition $Cd(CN)_2$ and a powder X-ray diffraction pattern identical to that of authentic $Cd(CN)_2$.[3b]

Structure Determination.—The crystallographic and experimental data are listed in Table 3. Each of the single crystals was coated with epoxy resin, and three representative reflections were monitored after every 150 during the intensity data collection on a Rigaku AFC-5S diffractometer at 295 K; no significant decay was observed.

The non-centrosymmetric space group $P\bar{4}3n$ to $Pm\bar{3}n$ was preferred for compounds **1a** and **1b**, both being possible from the systematic absences, because the latter did not give convergence. That for **2**, $C2/c$, was determined from the systematic absences. The structures were solved using the TEXSAN[7] software package installed on the diffractometer system, with ψ-scan absorption correction. Crystallographic diagrams were obtained using the ORTEP[8] program. The heavy-atom method with successive Fourier and Fourier-difference syntheses and full-matrix least-squares procedures were applied. All the non-H atoms were refined anisotropically. Hydrogen atoms were not located. The C and N atoms of the CN group linking two Cd_t atoms were seen as CN(1) and CN(2) each having 50% probability of being C or N. The order–disorder problem about CN bridges has been discussed for related structures.[6,9]

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

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