Clathrate Compounds of Cadmium Cyanide and Related Hosts with Cristobalite-like Lattice Structures†

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The crystal structures of three series of clathrate compounds with organic guest molecules G have been determined, $Cd(CN)_2{\cdot}G$, $[CdM(CN)_4]{\cdot}2G$ (M = Hg or Zn) and $[NMe_4{\cdot}G][CuM(CN)_4]$ (M = Cd or Zn). The cubic $Fd\bar{3}m$ unit-cell parameter for the first series ($Z = 8$) ranges from 12.647(6) Å for G = $CHCl_3$ to 12.767(2) Å for CCl_3CF_3, depending on the molecular size and orientation of the guest in the cavity. In the second series the space group $Fd\bar{3}m$ is unchanged upon 50% substitution of Cd in the first with Hg or Zn owing to the random distribution of the tetrahedral centres; the lattice parameter varies little when M = Hg, but when M = Zn a = 12.243(2) Å, a decrease of 0.5 Å from the value for $Cd(CN)_2{\cdot}CCl_4$. The anionic host in the third series accommodates the NMe_4^+ guest together with neutral CCl_4; the lattice parameter of the cubic $F\bar{4}3m$ unit cell decreases by *ca.* 0.6 Å in comparison with the values in the first two series. The X-ray data for 24 single crystals are discussed in terms of the crystallographic discrimination between C and N of the linking CN groups and the orientation of the guest molecules, in particular of the tetrahedral and pseudo-tetrahedral guest molecules, in the cavity approximating to a tetrahedron.

A number of polycyanopolycadmate $[Cd_x(CN)_y]^{2x-y}$ structures have been reported as novel host materials of inclusion systems,[1,2] among which the simplest in composition and structure is the single framework of $Cd(CN)_2$. As reported previously,[1c] this host gives a series of clathrate compounds $Cd(CN)_2{\cdot}G$ with various oligoatomic guest molecules G. The host, comprising tetrahedral Cd atoms linked by CN groups, is isostructural with the high-temperature phase of cristobalite and cubic ice I_c, giving a tetrahedral symmetry to the cavity framed by an adamantane-like skeleton. Tetrahedral centres such as Cu^I, Hg^{II} and Zn^{II} may give isostructural hosts; Hoskins and Robson[2a] reported an anionic mixed-metal host $[Cu^IZn(CN)_4]^-$ accommodating NMe_4^+ as a cationic guest.

This paper describes the crystal structures of $Cd(CN)_2{\cdot}G$ clathrates in detail for series of tetrahedral, pseudo-tetrahedral and other guest molecules; those of the isostructural clathrates of the neutral mixed-metal $[CdM(CN)_4]{\cdot}2G$ (M = Hg or Zn) and negatively charged hosts $[NMe_4{\cdot}G][CuM(CN)_4]$ (M = Cd or Zn) are also described. The anticuprate-type single-crystal structures of $Cd(CN)_2$ and $Zn(CN)_2$ have been redetermined by adopting the space group $Pn\bar{3}m$ in which it is impossible to discriminate between the C and N atoms of a CN group spanning the tetrahedral centres. The results are consistent with those of solid-state ^{113}Cd NMR spectroscopy,[3] although Hoskins and Robson[2a] applied the space group $P\bar{4}3m$ to discriminate between C and N.

Experimental

Preparation of Single Crystals.—(*a*) $Cd(CN)_2{\cdot}G$ *clathrates.* In water (100 cm^3), were dissolved 7.75 mmol each of $CdCl_2{\cdot}2.5H_2O$ (1.77 g) and $K_2[Cd(CN)_4]$ (2.26 g). After the solution had been filtered through a plastic membrane (pore size 0.45 μm), it was covered with, or placed on, a layer of the guest organic compound and allowed to stand in a refrigerator or at room temperature for a few days. Colourless crystals of the clathrates were formed at the interface between the organic and the aqueous phases or at the bottom of the aqueous phase. Single crystals of the neopentane(=2,2-dimethylpropane) clathrate $Cd(CN)_2{\cdot}CMe_4$ were obtained as follows: an aqueous solution (100 cm^3) containing equimolar amounts of $CdCl_2$ and $K_2[Cd(CN)_4]$ with a final cadmium concentration of 0.1 mol dm^{-3} was placed in a Schlenk tube connected to a vacuum line. Gaseous neopentane (b.p. = 9.5 °C) was introduced at 20 °C. The tube was removed from the vacuum line and kept in a refrigerator at 6 °C for a few days; colourless octahedral crystals grew on the surface of the aqueous solution. Crystals were also obtained by leaving the aqueous solution of the host moieties bubbled with the neopentane gas in a refrigerator for a few weeks.

(*b*) *Mixed-metal host series.* (*i*) $[CdHg(CN)_4]{\cdot}2CCl_4$ *and* $[CdHg(CN)_4]{\cdot}2C_6H_{12}$. Two routes, one using $CdCl_2$ and $K_2[Hg(CN)_4]$ and the other $HgCl_2$ and $K_2[Cd(CN)_4]$, gave the same product: 7.75 mmol each of the respective salts were used in procedures similar to that above.

(*ii*) $[CdZn(CN)_4]{\cdot}2CCl_4$. To water (100 cm^3) were added 7.75 mmol each of $K_2[Cd(CN)_4]$ (2.26 g) and $ZnCl_2$ (1.06 g). The white precipitate formed instantaneously was dissolved by adding 2-hydroxyethylamine and citric acid. After the solution had been filtered through a plastic membrane, it was placed on a layer of CCl_4 and allowed to stand in a refrigerator for a few days to obtain colourless crystals.

(*iii*) $[NMe_4{\cdot}CCl_4][CdCu(CN)_4]$. In water (100 cm^3) were dissolved with stirring KCN (3.0 mmol, 1.95 g) and CuCN (1.0 mmol, 0.90 g). A fine white precipitate, formed by addition of $CdCl_2{\cdot}2.5H_2O$ (1.0 mmol, 2.28 g) and NMe_4I (2.8 mmol, 0.57 g) to the aqueous solution, was dissolved by raising the pH to 12.0 with 2-hydroxyethylamine. After the pH had been adjusted to 10 with citric acid, the solution was allowed to stand on a layer of CCl_4 in a refrigerator for a few days. Colourless crystals were obtained (Found: C, 20.9; H, 2.40; Cl, 27.5; N, 13.6. $C_9H_{12}CdCl_4CuN_5$ requires C, 21.3; H, 2.40; Cl, 27.9; N, 13.8%).

(*iv*) $[NMe_4{\cdot}xCCl_4][CuZn(CN)_4]$. Colourless crystals were obtained by a procedure similar to that above using $ZnCl_2$ in place of $CdCl_2$ [Found: C, 24.0; H, 2.90; Cl, 28.6; N, 16.1. $C_{5.9}H_{12}Cl_{3.6}CuN_5Zn$ (x = 0.9) requires C, 24.4; H, 2.70; Cl, 28.9; N, 15.7%].

(*v*) $[NMe_4][CuZn(CN)_4]$. Crystals of this known compound were obtained from an aqueous solution as above without

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

contact with the CCl_4 layer; the procedure is different from that reported.[2a] A remarkably different value of the lattice parameter a, 11.671(2) *vs.* 11.609(3) Å,[2a] was found for the cubic unit cell.

(*c*) *Cadmium and zinc cyanides.* (*i*) $Cd(CN)_2$. In water (60 cm^3) were dissolved 7.75 mmol each of $CdCl_2 \cdot 2.5H_2O$ (1.77 g) and $K_2[Cd(CN)_4]$ (2.26 g), with stirring for 1 h. The solution was filtered through a plastic membrane and allowed to stand in a refrigerator for a few weeks. Colourless truncated octahedral crystals were obtained (Found: C, 14.9; N, 17.1. Calc. for C_2CdN_2: C, 14.6; N, 17.0%).

(*ii*) $Zn(CN)_2$. Single crystals of $Zn(CN)_2$ were prepared by the following two methods. First, the white powder of $Zn(CN)_2$ (0.7 g) suspended in water (100 cm^3) was dissolved by adding 2-hydroxyethylamine (7.5 cm^3). After the pH had been adjusted to 9.5 with citric acid, the aqueous solution was allowed to stand at 7 °C for a few days. Colourless cubes were obtained (Found: C, 20.3; N, 23.8. Calc. for C_2N_2Zn: C, 20.5; N, 23.9%). Secondly, $Zn(CN)_2$ powder (2.6 g) was suspended in water (100 cm^3) with stirring for 2 d. After filtration through a plastic membrane, the filtrate was covered with a layer of $CMeCl_3$ and allowed to stand in a refrigerator for a few months. Although this procedure had been designed to prepare a clathrate of $CMeCl_3$ in a $Zn(CN)_2$ host, the colourless cubes obtained at the interface between the aqueous and the organic phases and the bottom of the former phase were of $Zn(CN)_2$ (Found: C, 20.3; N, 23.8%).

Table 1 lists the compounds prepared with the values of lattice parameter a and the space groups determined from the single-crystal X-ray diffraction.

(*d*) *Properties of the clathrates.* The $Cd(CN)_2 \cdot G$ and $[CdM(CN)_4] \cdot 2G$ (M = Hg or Zn) clathrates are unstable under ambient conditions: it was difficult to determine the chemical composition precisely by conventional chemical analyses. However, the formation and decomposition of the clathrates were ascertained by IR spectroscopy, GC, thermal gravimetry (TG) and powder X-ray diffractometry. On TG each clathrate liberated G in proportions supporting the composition $Cd(CN)_2 \cdot G$ or $[CdM(CN)_4] \cdot 2G$ and leaving a white powder of $Cd(CN)_2$ or $[CdM(CN)_4]$; the former gave an X-ray powder diffraction pattern identical with that observed for neat $Cd(CN)_2$ having the anticuprite structure.

The occupancy of the guest atoms was refined in the X-ray analysis for some of the $Cd(CN)_2 \cdot G$ and $[CdM(CN)_4] \cdot 2G$ clathrates; no significant deviations from the stoichiometric value were obtained.

In comparison with those of the neutral hosts, the clathrates of the anionic hosts are stable enough to give analytical results within an acceptable range. However, in $[NMe_4 \cdot xCCl_4][CuZn(CN)_4]$ the analyses supported $x = 0.9$.

Structure Determinations.—(*a*) *The clathrates.* All the crystals subjected to diffraction analysis were coated with epoxy resin in order to prevent spontaneous decomposition under the ambient atmosphere. Three representative reflections were monitored after every 100; no significant decay was observed. The crystal and experimental data are summarised in Table 2.

The face-centred cubic unit cell and the Laue class $m\bar{3}m$ were confirmed for all the $Cd(CN)_2 \cdot G$ and $[CdM(CN)_4] \cdot 2G$ series from the diffraction data; the observed systematic absences supported the space group $Fd\bar{3}m$ uniquely. According to the second choice of the origin setting in ref. 5, the Cd atom was placed on 1/8, 1/8, 1/8 with site symmetry $\bar{4}3m$–T_d. Since the space group $Fd\bar{3}m$ predicts that discrimination between the N and C atoms of the CN group linking the tetrahedral centres collinearly on ⟨111⟩ is impossible, the atom on x, x, x with site symmetry $3m$ was assumed to have 50% probability for each of the C and N, designated as C·N, in the structure refinement. Additionally, it is also impossible to discriminate Cd and M in the $[CdM(CN)_4]$ hosts, for which the heavy atom at 1/8, 1/8, 1/8 was seen to have 50% probability of each of Cd and M (Cd·Hg or Cd·Zn). The guest molecule was found in the cavity centred at 3/8, 3/8, 3/8 with site symmetry $\bar{4}3m$–T_d. When the guest has real T_d or pseudo-tetrahedral symmetry, the central atom CG(1), or CG(2) when the cationic NMe_4^+ guest is co-accommodated, was found at the centre of the cavity. Other guest atoms except hydrogens were located by means of Fourier and Fourier-difference syntheses.

Table 1 Lattice parameters and the space groups of $Cd(CN)_2 \cdot G$ and analogous clathrates, and related cyanides

$Cd(CN)_2 \cdot G$: space group $Fd\bar{3}m$ (no. 227), $Z = 8$

G	a/Å	G	a/Å
$CHCl_3$	12.647(6)	$CHMe_2Cl$	12.668(3)
$CHMeClCH_2Cl$	12.691(2)	$CHMe_2CH_2Cl$	12.692(2)
CCl_4	12.714(1)	$CMeCl_3$	12.717(1)
cyclo-$C_6H_{11}Me$	12.729(2)	CMe_2Cl_2	12.731(1)
$CHMeCl_2$	12.732(2)	*cyclo*-C_6H_{12}	12.735(1)
$CFCl_2CF_2Cl$	12.742(1)	$CHCl_2CHCl_2$	12.743(1)
CMe_3Cl	12.743(2)	CMe_3Et	12.744(1)
CMe_4	12.757(2)	CCl_3CF_3	12.767(2)

$[CdM(CN)_4] \cdot 2G$: space group $Fd\bar{3}m$ (no. 227), $Z = 4$

M	G	a/Å	G	a/Å
Hg	CCl_4	12.7138(5)	*cyclo*-C_6H_{12}	12.734(1)
Zn	CCl_4	12.243(2)		

$[NMe_4 \cdot G][CuM(CN)_4]$: space group $F\bar{4}3m$ (no. 216), $Z = 4$

M	G	a/Å	G	a/Å
Zn	CCl_4	11.771(2)	None	11.671(2)
Cd	CCl_4	12.189(2)		

$Cd(CN)_2$ and $Zn(CN)_2$: space group $Pn\bar{3}m$ (no. 224), $Z = 2$

	a/Å		a/Å
$Cd(CN)_2$	6.300(1)	$Zn(CN)_2$	5.9086(7)

The anisotropically refined atomic parameters are listed in Table 3, for disorders enforced by the symmetry operations in the applied space group, the occupancies are noted.

The systematic absences observed for the series of anionic hosts, $[NMe_4 \cdot G][CuM(CN)_4]$ (M = Cd or Zn), were consistent with the space group $F\bar{4}3m$ which had been applied previously for $[NMe_4][CuZn(CN)_4]$.[2a] According to this space group the Cu atom was located at 0, 0, 0 and M (Cd or Zn) at 1/4, 1/4, 1/4; the x, x, x positions of the C and N atoms of the CN group were refined independently. The anisotropically refined atomic parameters are included in Table 3.

(*b*) *The cadmium and zinc cyanides.* The crystal data and details of the experimental conditions are included in Table 2; the refined parameters are listed in Table 3. The primitive cubic unit cell and the Laue class $m\bar{3}m$ were confirmed from the diffraction data. The space group $Pn\bar{3}m$ was selected from systematic absences $hk0$ for $h + k = 2n + 1$ and $h00$ for $h = 2n + 1$; among these reflections, nine for $Cd(CN)_2$ and 11 for $Zn(CN)_2$ of the non-zero intensities were all smaller than three times their estimated standard deviation (e.s.d.). According to the second choice of the origin setting in ref. 5, the Cd atom was placed at 1/4, 1/4, 1/4 with site symmetry $\bar{4}3m$. Since the space group $Pn\bar{3}m$ predicts that discrimination is impossible between the N and C of CN, the atom on x, x, x with site symmetry $3m$ was treated in the same manner as that in (*a*) above. All the diffraction data observed for $Zn(CN)_2$ supported it being isomorphous with $Cd(CN)_2$.

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

Results and Discussion

Disorder of the CN *Group in* $Cd(CN)_2$ *and* $Zn(CN)_2$.—The crystal structures revealing disorder between the C and N atoms of the CN group are supported by the solid-state ^{113}Cd NMR spectra observed for $Cd(CN)_2$ and its cyclohexane clathrate

Table 2 The crystal and experimental data[a]

Host	$Cd(CN)_2$	$Cd(CN)_2$	$Cd(CN)_2$	$Cd(CN)_2$	$Cd(CN)_2$	$[CdHg(CN)_4]$
Guest	CMe_4	CMe_3Cl	CMe_2Cl_2	$CMeCl_3$	CCl_4	$2CCl_4$
Formula	$C_7H_{12}CdN_2$	$C_6H_9CdClN_2$	$C_5H_6CdCl_2N_2$	$C_4H_3CdCl_3N_2$	$C_3CdCl_4N_2$	$C_6CdCl_8HgN_4$
M	236.60	257.02	277.43	297.85	318.27	724.72
Cubic space group	$Fd\bar{3}m$ (no. 227)	$Fd\bar{3}m$ (no. 227)	$Fd\bar{3}m$ (no. 227)	$Fd\bar{3}m$ (no. 227)	$Fd\bar{3}m$ (no. 227)	$Fd\bar{3}m$ (no. 227)
a/Å	12.757(2)	12.743(2)	12.731(1)	12.717(1)	12.714(1)	12.7138(5)
U/Å^3, Z	2076(1), 8	2069(1), 8	2063(1), 8	2057(1), 8	2055(1), 8	2055(1), 4
D_m/g cm^{-3}	1.53(2)	1.64(1)	1.78(2)	1.92(1)	2.09(2)	2.37(2)
D_c/g cm^{-3}	1.51	1.65	1.79	1.92	2.06	2.34
μ(Mo-Kα)/cm^{-1}	20.2	22.9	25.5	28.2	30.74	94.59
F(000)	928	992	1080	1120	1184	1312
Crystal size/mm	0.21 × 0.21 × 0.23	0.12 × 0.12 × 0.07	0.15 × 0.12 × 0.09	0.20 × 0.20 × 0.15	0.20 × 0.20 × 0.17	0.10 × 0.10 × 0.10
Peak scan width/°	1.30 + 0.3 tan θ	1.10 + tan θ	1.05 + 0.3 tan θ	1.42 + 0.3 tan θ	1.26 + 0.3 tan θ	1.30 + 0.3 tan θ
Reflections						
observed	196	206	206	206	206	191
used	134	81	89	92	114	75
No. of parameters	9	9	12	14	12	12
R, R'[b]	0.028, 0.027	0.068, 0.083	0.065, 0.093	0.047, 0.032	0.035, 0.048	0.055, 0.078
Goodness of fit[b]	1.184	1.024	0.9763	1.821	0.878	2.012
g	0.000 130	0.004	0.007	0.000 04	0.002	0.001
Maximum Δ/σ						
host	0.032	0.052	0.012	0.03	0.023	0.065
guest	0.074	0.275	0.195	0.208	0.107	0.078
Maximum, minimum residual electron density/e Å^{-3}	0.35, −0.77	0.89, −0.85	0.66, −0.98	0.74, −0.70	0.455, −0.65	0.82, −0.82

Host	$[CdZn(CN)_4]$	$[CuZn(CN)_4]^-$	$[CuZn(CN)_4]^-$	$[CdCu(CN)_4]^-$	$Cd(CN)_2$	$Zn(CN)_2$
Guest	$2CCl_4$	NMe_4^+, $x$$CCl_4$[c]	NMe_4^+	NMe_4^+, CCl_4	None	None
Formula	$C_6CdCl_8N_4Zn$	$C_9H_{12}Cl_4CuN_5Zn$	$C_8H_{12}CuN_5Zn$	$C_9H_{12}CdCl_4CuN_5$	C_2CdN_2	C_2N_2Zn
M	589.50	460.96	307.14	508.00	164.45	117.43
Cubic space group	$Fd\bar{3}m$ (no. 227)	$F\bar{4}3m$ (no. 216)	$F\bar{4}3m$ (no. 216)	$F\bar{4}3m$ (no. 216)	$Pn\bar{3}m$ (no. 224)	$Pn\bar{3}m$ (no. 224)
a/Å	12.243(1)	11.771(2)	11.671(2)	12.189(2)	6.300(1)	5.9086(7)
U/Å^3, Z	1834.9(6), 4	1628(1), 4	1583(1), 4	1815(1), 4	250.1(1), 2	206.27(7), 2
D_m/g cm^{-3}	2.07(2)	1.75–1.87[c]	1.27(2)	1.87(2)	2.19(1)	1.91(1)
D_c/g cm^{-3}	2.13	1.88	1.29	1.86	2.18	1.89
μ(Mo-Kα)/cm^{-1}	35.69	34.11	29.01	25.25	41.71	58.7
F(000)	1152	942	616	984	148	112
Crystal size/mm	0.12 × 0.12 × 0.16	0.20 × 0.10 × 0.08	0.40 × 0.35 × 0.35	0.30 × 0.30 × 0.30	0.15 × 0.15 × 0.10	0.10 × 0.07 × 0.07
Peak scan width/°	1.15 + 0.35 tan θ	1.30 + 0.35 tan θ	1.20 + 0.30 tan θ	1.20 + 0.35 tan θ	1.302 + 0.3 tan θ	1.30 + 0.35 tan θ
Reflections						
observed	862[d]	675[d]	155	187	699[d]	365
used	96	133	105	167	49[e]	53
No. of parameters	12	23	13	38	5	5
R, R'[b]	0.073, 0.091	0.064, 0.072	0.048, 0.057	0.044, 0.065	0.066, 0.052	0.045, 0.044
Goodness of fit[b]	1.064	5.4896[c]	0.7450	0.4896	3.467	1.464
g	0.007	0.000 04	0.002	0.0002	0.0001	0.000 381
Maximum Δ/σ						
host	0.030	0.030	0.017	0.130	0.005	0.007
guest	0.207	0.577	0.299	0.677		
Maximum, minimum residual electron density/e Å^{-3}	1.36 (near Cd, Zn), −0.70	0.97, −1.24	0.49, −0.47	0.44, −1.35	1.00 (near Cd), −0.86	0.40, −0.45

[a] Details in common: Rigaku AFC 5 diffractometer, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), 293 K, 2θ–ω scan in the 2θ range 4–60°, reflections used $|F_o| > 3\sigma(F_o)$, SHELX 76,[4] weighting scheme $w^{-1} = (\sigma^2 + gF^2)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$, goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(\text{number of reflections used} - \text{number of parameters})]^{\frac{1}{2}}$. [c] The composition is for the full occupancy ($x = 1$) by the CCl_4 guest, although $x = 0.9$ was suggested by the analytical results; owing to the instability of the product, values of the measured densities varied from sample to sample; the considerably large goodness of fit may be due to the poor quality of the crystal. [d] Including two or four sets of equivalent reflections which were compared to establish the assigned space group. [e] Those reflections with $|F_o| > 4\sigma(F_o)$ were used.

$Cd(CN)_2 \cdot C_6H_{12}$ prepared in this work.[3a] Five peaks were observed with the intensity ratio 1:11.5:25:11.5:1, assigned to CdC_4, CdC_3N, CdC_2N_2, $CdCN_3$ and CdN_4 respectively as the co-ordination environments distributed in the three-dimensional framework. Although the CdC_2N_2 band was relatively stronger and those of CdC_4 and CdN_4 much weaker than the predicted ratio of 1:4:6:4:1 for an entirely random distribution, the ordered structure predicts that only two equal-intensity bands should be observed for CdC_4 and CdN_4.

The earlier powder data[6] did not contain any reflections with intensities significant enough to break the rule of systematic absences for the space group $Pn\bar{3}m$ we have applied; no attention appeared to be paid to the possibility of disorder in the orientation of the CN group in previous studies.[2a,6] The recent single-crystal work[2a] reported shorter bond lengths for M–C than for M–N (M = Cd or Zn) from full-matrix least-squares calculations using SHELX 76[4] with large values of the final k parameters, 15.1 and 26.1, in the weighting scheme.

The Host Structures.—The $Cd(CN)_2$ host structure is compared with the anticuprite-type double framework of $Cd(CN)_2$ in Fig. 1. The clathrate structure is obtained by replacing one framework in the anticuprite $Cd(CN)_2$ by guest molecules; the guest CMe_4 is shown in Fig. 1. The cage-like cavity is framed by the other $Cd(CN)_2$ framework, the Cd–(CN)–Cd linkage, like the skeleton of an adamantane molecule. Although the ten Cd atoms involved in the cage are crystallographically equivalent, there are apparently two kinds in the cavity skeleton: four are located on the tripod vertices of $Cd[-(CN)-Cd]_3$, the remaining six on the expanded edges of –(CN)–Cd–(CN)–, respectively. Hence, to the first approximation, the cavity can be regarded as a tetrahedron with the four tripod Cd atoms at the corners, an edge length of $a/2^{\frac{1}{2}}$ (*ca.* 9 Å) and height $a/3^{\frac{1}{2}}$ (*ca.* 7.3 Å). The centre of the cavity at 3/8, 3/8, 3/8 has site symmetry $\bar{4}3m$ as does each cadmium position. Each

Table 3 Atomic parameters and selected bond distances (Å)[a]

(1) $Cd(CN)_2 \cdot G$

G	Atom[b]	Occupancy[c]	*x*	*y*	*z*	$B_{eq}/Å^2$
CMe_4	Cd	1	0.125	*x*	*x*	4.03(2)
	C·N	1	0.0257(2)	*x*	*x*	4.3(1)
	CG(1)	1	0.375	*x*	*x*	5.6(3)
	CG(2)	1	0.3068(5)	*x*	*x*	14.6(4)
	Cd–C·N 2.195(5), C·N–C·N 1.134(11), CG(1)–CG(2) 1.508(11)					
CMe_3Cl	Cd	1	0.125	*x*	*x*	4.2(1)
	C·N	1	0.0257(10)	*x*	*x*	4.7(5)
	CG(1)	1	0.375	*x*	*x*	11(2)
	3C/Cl	1	0.3058(13)	*x*	*x*	26(2)
	Cd–C·N 2.19(2), C·N–C·N 1.13(5), CG(1)–3C/Cl 1.53(5)					
CMe_2Cl_2	Cd	1	0.125	*x*	*x*	4.9(1)
	C·N	1	0.0249(11)	*x*	*x*	5.1(4)
	CG(1)	1	0.375	*x*	*x*	12(1)
	C/Cl	*1/3*	0.2892(16)	*x*	0.3356(25)	25(1)
	Cd–C·N 2.21(2), C·N–C·N 1.10(5), CG(1)–C/Cl 1.62(3)					
$CMeCl_3$	Cd	1	0.125	*x*	*x*	5.37(7)
	C·N	1	0.0257(4)	*x*	*x*	5.4(3)
	CG(1)	1	0.375	*x*	*x*	8.3(6)
	CG(2)	*1/4*	0.3039(42)	*x*	*x*	6.4(9)
	Cl	*1/4*	0.3335(6)	*x*	0.2519(10)	13.9(6)
	Cd–C·N 2.195(10), C·N–C·N 1.13(2), CG(1)–CG(2) 1.57(9), CG(1)–Cl 1.74(1)					
CCl_4	Cd	1	0.125	*x*	*x*	6.06(3)
	C·N	1	0.0260(3)	*x*	*x*	5.7(1)
	CG(1)	1	0.375	*x*	*x*	8.7(4)
	Cl	*1/3*	0.3341(4)	*x*	0.2495(7)	15.6(4)
	Cd–C·N 2.187(7), C·N–C·N 1.15(2), CG(1)–Cl 1.756(9)					

(2) $[CdM(CN)_4] \cdot 2CCl_4$

M	Atom[b]	Occupancy[c]	*x*	*y*	*z*	$B_{eq}/Å^2$
Hg	Cd·Hg	1	0.125	*x*	*x*	5.5(1)
	C·N	1	0.0245(9)	*x*	*x*	3.1(3)
	CG(1)	1	0.375	*x*	*x*	4.9(9)
	Cl	*1/3*	0.3340(9)	*x*	0.253(2)	13.7(9)
	Cd·Hg–C·N 2.22(2), C·N–C·N 1.08(4), CG(1)–Cl 1.71(2)					
Zn	Cd·Zn	1	0.125	*x*	*x*	3.6(2)
	C·N	1	0.0272(7)	*x*	*x*	3.6(4)
	CG(1)	1	0.375	*x*	*x*	5(1)
	Cl	*1/3*	0.3286(5)	*x*	0.2498(9)	11.1(7)
	Cd·Zn–C·N 2.07(1), C·N–C·N 1.16(3), CG(1)–Cl 1.73(2)					

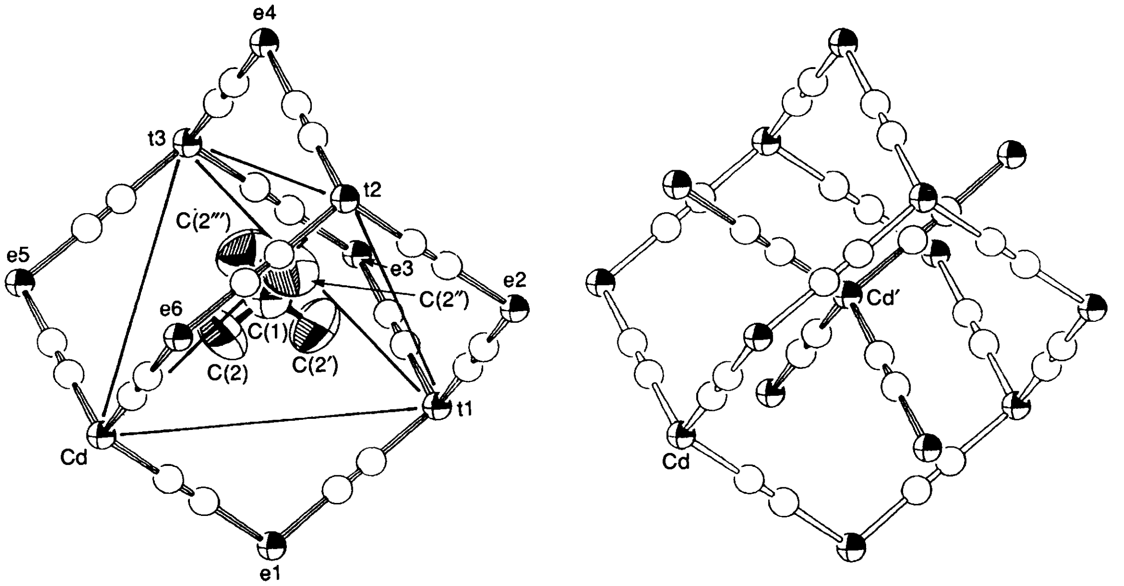
(3) $[NMe_4 \cdot G][CuZn(CN)_4]$ and $[NMe_4 \cdot G][CdCu(CN)_4]$

G	Atom	Occupancy[c]	*x*	*y*	*z*	$B_{eq}/Å^2$
$0.9CCl_4$	Cu	1	0.0	*x*	*x*	1.6(3)
	Zn	1	0.25	*x*	*x*	2.6(3)
	C(1)	1	0.094(3)	*x*	*x*	2.4(3)
	N(1)	1	0.150(2)	*x*	*x*	3.0(3)
	NG(1)	1	0.5	*x*	*x*	3.4(8)
	CG(1)	0.90(1)	0.429(1)	*x*	*x*	4.9(9)
	CG(1′)	0.10(1)	0.572(2)	*x*	*x*	6.6(9)
	CG(2)	0.90(1)	0.75	*x*	*x*	10(1)
	Cl	*0.90(1)/3*	0.792(1)	*x*	0.884(2)	22(1)
	Cu–C(1) 1.92(6), C(1)–N(1) 1.14(4), Zn–N(1) 2.04(4), NG(1)–CG(1) 1.45(2), NG(1)–CG(1′) 1.47(4), CG(2)–Cl 1.73(4)					

Table 3 (*continued*)

G	Atom[b]	Occupancy[c]	x	y	z	$B_{eq}/Å^2$
None	Cu	1	0.0	x	x	5.5(2)
	Zn	1	0.25	x	x	3.05(6)
	C(1)	1	0.096(1)	x	x	4.3(3)
	N(1)	1	0.150(2)	x	x	5.8(4)
	NG(1)	1	0.5	x	x	3.4(8)
	CG(1)	1	0.572(1)	x	x	24.1(6)
	Cu–C(1) 1.94(2), C(1)–N(1) 1.09(6), Zn–N(1) 2.02(2), NG(1)–CG(1) 1.46(2)					
CCl_4	Cd	1	0.25	x	x	2.31(3)
	Cu	1	0.0	x	x	2.67(6)
	C(1)	1	0.0940(8)	x	x	3.2(2)
	N(1)	1	0.1463(8)	x	x	3.9(2)
	NG(1)	0.54(1)	0.75	x	x	4.2(6)
	NG(1′)	0.46(1)	0.5	x	x	4.6(6)
	CG(1)	*0.54(1)/3*	0.770(3)	x	0.868(2)	4.9(6)
	CG(1′)	*0.46(1)/3*	0.437(3)	x	0.417(4)	4.9(6)
	CG(2)	0.54(1)	0.5	x	x	4.4(6)
	CG(2′)	0.46(1)	0.75	x	x	4.3(6)
	Cl(1)	*0.54(1)/3*	0.4519(9)	x	0.368(1)	4.8(6)
	Cl(1′)	*0.46(1)/3*	0.806(2)	x	0.870(2)	9.6(8)
	Cu–C(1) 1.98(2), C(1)–N(1) 1.10(3), Cd–N(1) 2.19(2), NG(1)–CG(1) 1.48(2), NG(1′)–CG(1′) 1.48(2), CG(2)–Cl(1) 1.81(2), CG(2′)–Cl(1′) 1.75(2)					
(4) $Cd(CN)_2$ and $Zn(CN)_2$						
	Cd	1	0.25	x	x	11.23(7)
	C·N	1	0.0524(9)	x	x	10.5(1)
	Cd–C·N 2.159(9), C·N–C·N 1.143(19)					
	Zn	1	0.25	x	x	3.92(4)
	C·N	1	0.0557(7)	x	x	4.5(1)
	Zn–C·N 1.989(7), C·N–C·N 1.139(14)					

[a] Owing to the symmetry requirements of the respective space groups, the angles about the tetrahedral centres both in the host and guest should be the tetrahedral angle; those about the statistically distributed substituents in the tetrahedral and pseudo-tetrahedral guests have no significance. [b] C·N indicates 50% probability for each of the C and N atoms, 3C/Cl 75% C and 25% Cl, C/Cl 50% each of C and Cl and Cd·Hg 50% each of Cd and Hg. [c] Values for atoms statistically distributed due to the requirements of the space group are shown in italics.



(*a*) (*b*)

Fig. 1 Views of (*a*) the single host framework of $Cd(CN)_2 \cdot CMe_4$ and (*b*) the counterpart of the anticuprite-type double framework structure of $Cd(CN)_2$; thermal ellipsoids are of 50% probability and the approximate tetrahedron of the cavity is sketched in (*a*). In (*a*): Cd is at 1/8, 1/8, 1/8; the Cd atoms at the other three tripod vertices are t1 (5/8, 5/8, 1/8), t2 (5/8, 1/8, 5/8) and t3 (1/8, 5/8, 5/8); the Cd atoms on the expanded edges are e1 (3/8, 3/8, −1/8), e2 (7/8, 3/8, 3/8), e3 (3/8, 7/8, 3/8), e4 (3/8, 3/8, 7/8), e5 (−1/8, 3/8, 3/8) and e6 (3/8, −1/8, 3/8); all the Cd atoms are crystallographically equivalent in the space group $Fd\bar{3}m$; central carbon C(1) of the guest CMe_4 is at 3/8, 3/8, 3/8, those of the Me groups are C(2) [x, x, x (x = 0.307)], C(2′) (3/4 − x, 3/4 − x, x), C(2″) (3/4 − x, x, 3/4 − x) and C(2‴) (x, 3/4 − x, 3/4 − x). In (*b*): Cd is at 1/4, 1/4, 1/4, Cd′ at 3/4, 3/4, 3/4. The C and N atoms of the CN groups linking the Cd atoms (open ellipsoids) cannot be discriminated due to the symmetry requirements of the space groups $Fd\bar{3}m$ (*a*) and $Pn\bar{3}m$ (*b*) tetrahedron is surrounded by four other tetrahedra with face-to-face distances of $a/4 \times 3^{\frac{1}{2}}$ (*ca.* 1.8 Å); the distance between the centres of one cavity and another through the faces is $a \times 3^{\frac{1}{2}}/2$ (*ca.* 11 Å). Taking an ellipsoidal shape for the CN group with a maximum diameter of *ca.* 3.6 Å and a long axis of *ca.* 4.6 Å, the cavity has a wide opening of *ca.* 4 Å diameter toward the face. Owing to the expanded edges from the tripod vertex, the direction from the cavity centre toward the vertex allows the van der Waals distance of a guest to be a little less than $a \times 3^{\frac{1}{2}}/4$ (*ca.* 5.5 Å).

The neutral mixed-metal host $[CdM(CN)_4]$ (M = Hg or Zn) has essentially the same cavity as that in the $Cd(CN)_2$ host with random distributions of Cd and M at the tetrahedral centres. The cubic lattice parameter *a* for $[CdHg(CN)_4]{\cdot}2G$ is practically the same as that of $Cd(CN)_2{\cdot}G$ in the respective pairs where G = CCl_4 and cyclohexane. When M is Zn, the value of *a* for $[CdZn(CN)_4]{\cdot}2CCl_4$ is reduced by *ca.* 4% from that for $Cd(CN)_2{\cdot}CCl_4$ due to the smaller ionic radius of Zn^{2+} than that of Cd^{2+}.

Although the framework of the negatively charged host $[CuM(CN)_4]$ (M = Cd or Zn) has substantially the same extension as that of $Cd(CN)_2$ as host, crystallographic discrimination is possible both between the heavy atoms Cu and M and between C and N of the CN in the applied space group $F\bar{4}3m$. The Cu^I is co-ordinated to the C atom of the CN groups to preserve the tetrahedral integrity of $Cu^I(CN)_4$, as ^{13}C magic angle spinning NMR spectroscopy for ^{13}C, ^{15}N-enriched $[NMe_4][CuZn(CN)_4]$ has shown.[3e]

In previous work by Hoskins and Robson,[2a] the cationic guest compound $[NMe_4][CuZn(CN)_4]$ was reported in which half the total cavities were vacant. Here, besides confirmation of the half-filled/half-vacant structure, the additional accommodation of the neutral CCl_4 into the remaining cavities has been confirmed for the previously reported $[CuZn(CN)_4]^-$ and the novel $[CdCu(CN)_4]^-$ host.

As noted in previous work,[2a] two kinds of cavities are formed in the negatively charged $[CuM(CN)_4]^-$ hosts, since the M^{2+} and Cu^+ are located at positions crystallographically independent of each other. With respect to the cavity approximating the tetrahedron in the adamantane-like skeleton, one cavity is topped by Cu^+ at every tripod vertex, the other by M^{2+}; the former is designated Cu_4M_6 and the latter M_4Cu_6. In $[NMe_4][CuZn(CN)_4]$ the cationic guest was reported to prefer Zn_4Cu_6 to Cu_4Zn_6. This has been confirmed in this work, although some residual electron density remained in the Cu_4Zn_6 according to the final Fourier-difference map. The preference is sustained in the CCl_4 clathrate $[NMe_4{\cdot}0.9CCl_4][CuZn(CN)_4]$ where NMe_4^+ is accommodated in Zn_4Cu_6, CCl_4 in Cu_4Zn_6. However, a disorder in the distribution of the cationic and the neutral guests has been observed in the novel $[NMe_4{\cdot}CCl_4][CdCu(CN)_4]$. At the final stage of the structure refinement the occupancy ratio 0.54:0.46 was obtained for $NMe_4^+ : CCl_4$ in Cd_4Cu_6.

Orientation of the Guest Molecules.—(*a*) *Tetrahedral guests in tetrahedral cavities.* Two typical modes of orientation, A and B, are possible for a tetrahedral guest in the tetrahedral cavity of $Cd(CN)_2$ and analogous hosts, as shown in Fig. 2. The tetrahedral guest extends its substituent from the tetrahedral centre toward the face of the cavity tetrahedron in mode A, but toward the vertex in B. Mode A is seen in the anticuprite structure of $Cd(CN)_2$ itself (see Fig. 1): a pair of the frameworks is coupled by mutual penetration of the vertex of one tetrahedron into the face of the other. The only tetrahedral guest adopting this mode is NMe_4^+ in the half-filled structure of the $[CuZn(CN)_4]^-$ host.[2a] Since the substituent protruding from the centre of a cavity should suffer steric repulsion from that in the next cavity if it is occupied by another guest, mode A is possible only when the next cavity is vacant, for the guest species examined so far in this work. In mode B the tetrahedral guest is just enclosed in the tetrahedral cavity vertex by vertex and face by face.

Examples of mode B and intermediate situations between A and B have been observed for the series of guests $CMe_{4-n}Cl_n$ (n = 0–4) in the $Cd(CN)_2$ host. Views along the three-fold axis of the tetrahedral cavity are compared for n = 0–4 in Fig. 3.

The CMe_4 molecule (n = 0) adopts mode B: each of the C–C (Me) bonds is extended toward each of the tripod vertices of the cavity as if the tetrapod of the guest skeleton supports the adamantane-like host skeleton on the inside without any direct chemical bonds. In other words, the methyl group is encapped by the Cd[–(CN)–Cd]$_3$ tripod. The distance of 5.524(3) Å ($= a \times 3^{\frac{1}{2}}/4$) between the cavity centre and the Cd atom at the tripod vertex is appropriate to accommodate the CMe moiety with a van der Waals contact. Since the direction toward the face of the cavity tetrahedron is left vacant, considerable void space remains in the crystal packing of $Cd(CN)_2{\cdot}CMe_4$.

On the other hand, the CCl_4 molecule (n = 4) distributes its C–Cl bonds about the three-fold axis of the crystal giving an occupancy of 1/3 at the refined atomic position x, x, z [x = 0.3341(4), z = 0.2495(7)] of Cl. The C–Cl bond, 1.756(9) Å, is not only too long to be encapped by the tripod vertex but also too long for a mode A orientation due to the repulsion from the neighbouring guest. Hence this bond directed toward the face of the cavity tetrahedron is forced to deviate from the axis toward the face centre, but is distributed about the three-fold axis in order to reduce the repulsive interaction. This distributed orientation is designated mode A′.

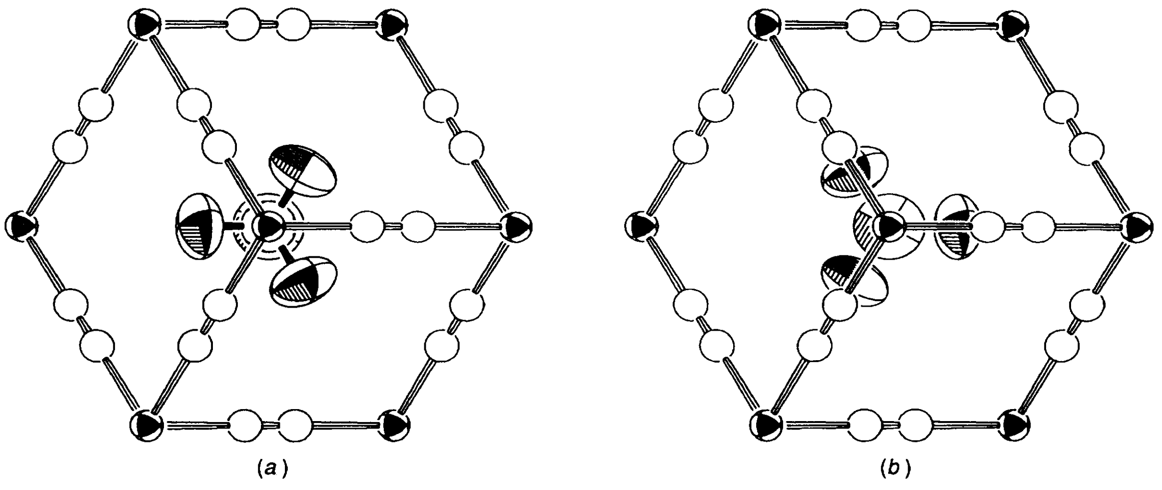

(*a*) (*b*)

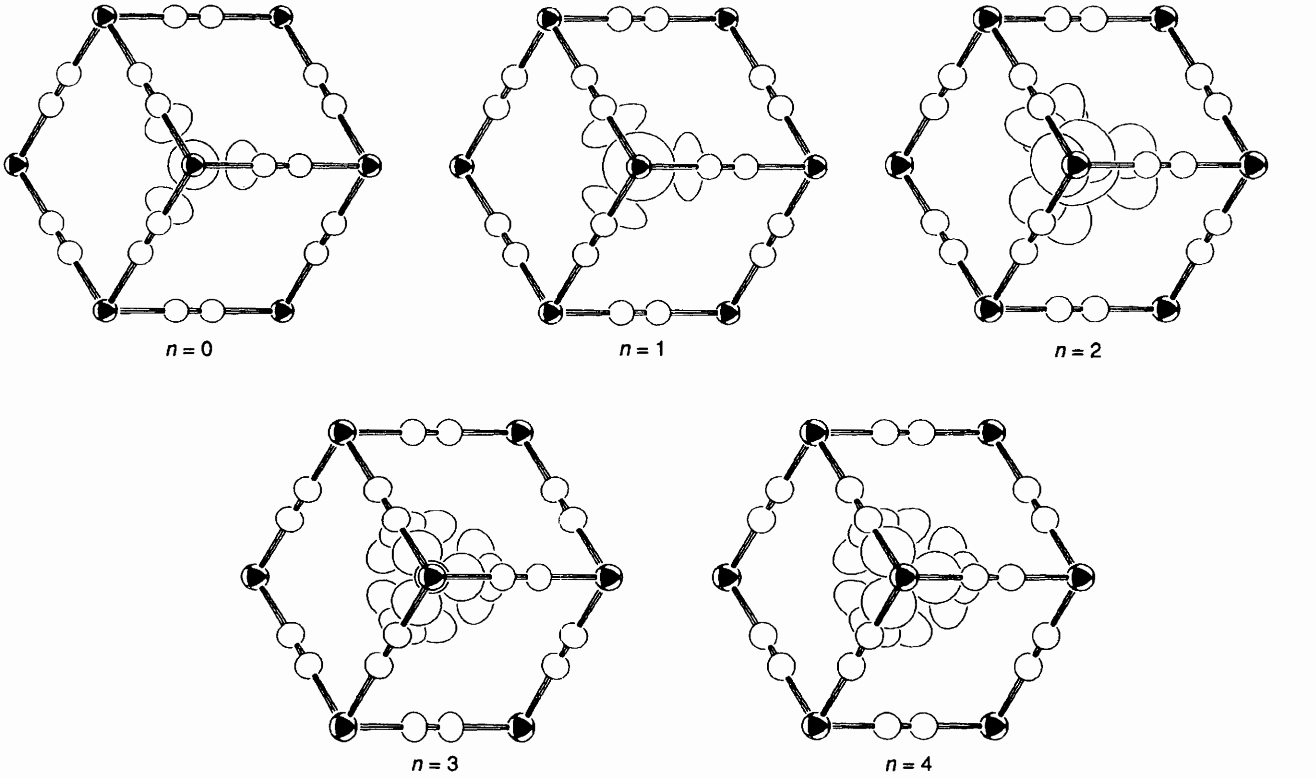
Fig. 2 Orientation modes of a tetrahedral guest in the approximated tetrahedral cavity: (*a*) A; (*b*) B. The views are from the top of the tripod vertex along the three-fold axis to the counterface of the approximate tetrahedron. Anisotropic sections are shown for tetrahedral co-ordination centres (Cd, Cu, Hg or Zn) and the guest atoms

Disorder is inevitable for the distribution of the substituents in the structures where n = 1–3. The deviation from T_d symmetry in the molecular structures of the mixed Cl–Me derivatives makes the thermal parameters of the central CG(1) atom, fixed at 3/8, 3/8, 3/8, greater than that observed for $n = 0$, *i.e.* $B_{eq} = 5.6(3)$ Å^2. Thus $B_{eq} = 11(2)$ for $n = 1$, 12(1) for $n = 2$ and 8.3(6) Å^2 for $n = 3$. Although the thermal parameter is extremely large [26(2) Å^2] for the guest atom 3C/Cl when $n = 1$ with an occupancy ratio of 3:1 for C:Cl at x, x, x [$x = 0.3058(13)$], the orientation of the guest molecule is similar to that when $n = 0$. When $n = 2$ the guest atom C/Cl (C:Cl = 2:2) moves to position x, x, z [$x = 0.2892(16)$, $z = 0.3356(25)$], distributed about the three-fold axis similar to that in the case of CCl_4 when $n = 4$. However, the relation between the values of x and z is reversed when $n = 2$ ($x < z$) from that when $n = 4$ ($x > z$). This means that the guest atom C/Cl when $n = 2$ comes closer to the tripod vertex than the Cl when $n = 4$. This mode is designated B′. When $n = 3$ two kinds of atomic positions were assigned: one on x, x, x to the methyl C, the other on x, x, z ($x > z$) to the Cl of $CMeCl_3$, modes B and A′ apparently being mixed. Similar mixing of modes has been observed for $Cd(CN)_2 \cdot CCl_3CF_3$ for which the a dimension of 12.767(2) Å is the longest among the present series of clathrates.

The preference for mode B is interpreted in terms of the steric fitting between the CH_3 or CF_3 group of the guest and the $Cd[-(CN)-Cd]_3$ tripod vertex of the cavity. The effect should be stronger for F than H, because the protrusion of an F atom is more distinct than that of an H atom in view of its larger van der Waals radius. The mixed mode B–A′ has been observed only for guests monosubstituted with the fitting group (CH_3 or CF_3), $CMeCl_3$ and CCl_3CF_3. When the fitting group is fixed at the tripod vertex, the remaining CCl_3 moiety can rotate about the molecular three-fold axis, which coincides with the crystal three-fold axis from the central CG(1) atom to the tripod vertex, to reduce the steric repulsion from the neighbouring guests. If two of the four substituents are the fitting groups in mode B orientation, the remaining two Cl atoms should suffer too much steric repulsion. Hence the guest when $n = 2$ adopts mode A′.

(*b*) *Ice-mimetic character of the* $Cd(CN)_2$ *host in the* $Cd(CN)_2 \cdot CMe_{4-n}Cl_n$ *clathrates.* The a dimension decreases monotonously from 12.757(2) Å for $Cd(CN)_2 \cdot CMe_4$ to 12.714(1) Å for $Cd(CN)_2 \cdot CCl_4$ in the $CMe_{4-n}Cl_n$ guest series; the host framework becomes successively more compact upon replacement of Me by Cl in the guest molecule. This may be due to the smaller van der Waals radius of Cl (*ca.* 1.8 Å) than that of Me (*ca.* 2.2 Å). However, the thermal parameter B_{eq} of Cd in the host, increases from 4.03(2) for $n = 0$ through 4.2(1), 4.9(1) and 5.37(7) for $n = 1$, 2 and 3 to 6.06(3) Å^2 for $n = 4$. A similar trend is also seen in the thermal parameters of C·N. Even for the anticuprite $Cd(CN)_2$ structure, extremely large thermal parameters of 11.23(7) Å^2 for Cd and 10.5(1) Å^2 for C·N have been obtained in comparison with those of 3.92(4) and 4.5(1) Å^2 for $Zn(CN)_2$. Concerning the three-dimensional framework, the more compact structure of $Cd(CN)_2$ gives rise to the increase in thermal parameters. Taking the orientation of the guest molecules into account, the degree of disorder increases more in the more-compact host. That the more-compact packing gives the higher entropy state resembles the melting of ice. The rigid structure when $n = 0$ with the less-compact packing may be called 'van der Waals ice', because the host skeleton, the structure of which is isomorphous to cubic ice I_c, is stabilised in terms of thermal displacement with the guest neopentane molecule adopting a rigid orientation inside the cavity in van der Waals contact with the host skeleton.

The structure when $n = 0$ appears to be the first example where the orientation-labile neopentane molecule adopts a rigid orientation in the solid state at ambient temperature. The corresponding structure of neat neopentane is highly disordered at low temperature approximating a sphere.[7] The C–C(Me) distance of 1.508(11) Å when $n = 0$, being shorter than that of 1.539(2) Å in the gaseous state,[8] is apparently due to thermal oscillation of the methyl group, the carbon atom CG(2) of which has a considerably large thermal parameter of 14.6(4) Å^2.


$n = 0$ $n = 1$ $n = 2$

$n = 3$ $n = 4$

Fig. 3 Orientations of $CMe_{4-n}Cl_n$ molecules in the tetrahedral cavity for the $Cd(CN)_2 \cdot CMe_{4-n}Cl_n$ series; the direction of the view is the same as that in Fig. 2; anisotropic sections are shown for Cd atoms. The guest is CMe_4 in $n = 0$, CMe_3Cl in $n = 1$, CMe_2Cl_2 in $n = 2$, $CMeCl_3$ in $n = 3$ and CCl_4 in $n = 4$

(*c*) *Other* $Cd(CN)_2$ *host clathrates.* The single-crystal structures have been refined for the $Cd(CN)_2\cdot G$ clathrates where $G = CCl_3CF_3$, $CHCl_2CHCl_2$ and cyclohexane; the *a* dimensions of the cubic unit cells have been refined for single crystals of the clathrates where $G = CHCl_3$, $CHMe_2Cl$, $CHMeCl_2$, $CHMe_2CH_2Cl$, $CHMeClCH_2Cl$, $CFCl_2CF_2Cl$, CMe_3Et and methylcyclohexane on the four-circle diffractometer under experimental conditions kept as similar as possible to one another.

The structure refinement ceased at the stage where the host structure had been confirmed as isostructural with those already refined [*i.e.* $Cd(CN)_2\cdot CMe_{4-n}Cl_n$, $n = 0$–4]; the disorder of the respective guests was too great to obtain any significant information on the molecular orientations.

(*d*) *Mixed-metal host clathrates.* The orientation of the guests in the neutral mixed-metal hosts $[CdHg(CN)_4]$ and $[CdZn(CN)_4]$ is quite similar to that in the $Cd(CN)_2$ host.

As for the mode A orientation of NMe_4^+ in the half-filled/half-vacant anionic host clathrate $[NMe_4][CuZn(CN)_4]$, the *a* dimension of the $F\bar{4}3m$ unit cell, 11.671(2) Å, is contracted to *ca.* 91.5% [lit.,[2a] 11.609(3) Å, to 91.0%] of that of $Cd(CN)_2\cdot CMe_4$ due to the smaller ionic radii of Zn^{2+} and Cu^+ than of Cd^{2+}. The contraction appears to be critical for the tetrahedral guest to adopt either orientation mode A or B. The distance from the centre of the tripod vertex of the tetrahedral cavity $a \times 3^{\frac{1}{2}}/4 = 5.054$ Å (5.027 Å from the literature value) might be too short for the N–C(Me) bond [1.46(2) Å] to be directed toward the tripod vertex, in comparison with the 5.524(3) Å distance and C–C bond length of 1.507(11) Å for $Cd(CN)_2\cdot CMe_4$.

On additional accommodation of the neutral guest CCl_4, the *a* dimension is elongated by 0.1 Å. Both guests adopt the mode A′ orientation, *i.e.* the N–C(Me) and the C–Cl bonds directed toward the tetrahedral face of the cavities are distributed about the three-fold axis of the crystal, similar to the situation with CCl_4 in the $Cd(CN)_2$ host. The guests in $[NMe_4\cdot CCl_4][CdCu(CN)_4]$ also adopt mode A′ with $a = 12.189(2)$ Å and $a \times 3^{\frac{1}{2}}/4 = 5.278$ Å, which are reduced by *ca.* 4% from the values for $Cd(CN)_2\cdot CCl_4$.

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