Three-dimensional Framework Structures Built of Heptacyanotricadmate(II) Units providing Polyhedral Cavities for Guests: Classification of the Zeolite-like Structures†

Takafumi Kitazawa,[a] **Shin-ichi Nishikiori**[b] **and Toschitake Iwamoto***[,b]
[a] *Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274, Japan*
[b] *Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan*

A series of 17 inclusion compounds of composition $[am{\cdot}xG][Cd_3(CN)_7]$ ($x = 1$–2) has been obtained from the three-dimensional anionic $[Cd_3(CN)_7]^-$ host and guests of an onium cation am^+ and a neutral molecule G. The crystal structures of the inclusion compounds reveal a common feature for the host structures, *i.e.* an infinite chain with repeating –(CN)–Cd(t)–CN–Cd(o)–NC–Cd(t)– units, $-(T{-}O{-}T)_n-$, composed of tetrahedral Cd(t) and octahedral Cd(o) atoms linked by CN groups running along the mirror plane of the unit cell. The three-dimensional hosts are constructed through interchain connections between the mirror planes by out-of-plane CN groups. Six types of structure have been classified according to differences in the mode of bending at both ends of the T–O–T and T–T entities in the chain and in the mode of interchain connections building up the three-dimensional framework structures.

We have been developing a number of mineralomimetic structures built of $[Cd_x(CN)_y]^{2x-y}$ moieties based on the similarity between SiO_2 and $Cd(CN)_2$ in co-ordination and linking structures. Both have an AB_2 composition; A behaves as a tetrahedral centre and B links the A centres to build up a three-dimensional framework structure. We have determined the crystal structures of frameworks that are like pyrosilicate,[1a] inosilicate,[1b] cristobalite,[1c–g] clays[1d,e,h,i] and zeolites.[1d,e,h] The earlier three-dimensional host structures built of octahedral Cd and tetrahedral Cd or Hg in $[Cd(am)_2M'(CN)_4]{\cdot}2G$ [$(am)_2 = (NH_3)_2$ or $NH_2CH_2CH_2NH_2$ (en), M′ = Cd or Hg, G = C_6H_6 or $C_6H_5NH_2$] clathrates[1j–m] and in $[Cd(py)_2Cd(CN)_4]$ (py = pyridine)[1n] have tenorite(CuO)-like linkages for the CN groups among both co-ordination centres, as also reported by Robson and co-workers[2a] for $[NMe_4][CuPt(CN)_4]$. Analogous linkages among octahedral Zn^{2+} and trigonal $[C(CN)_3]^-$ form a double-framework of rutile-like three-dimensional lattices.[2b]

This paper describes the three-dimensional zeolite-like structures of 17 inclusion compounds. The three-dimensional hosts of common composition $[Cd_3(CN)_7]^-$ accommodate an onium cation am^+ and neutral guest molecule(s) G in polyhedral cavities to give compounds of composition $[am{\cdot}xG][Cd_3(CN)_7]$ ($x = 1$–2).

For natural and synthesized zeolites a large number of three-dimensional frameworks differing in topology and geometry have been classified according to the variations in chain structures found in the linkage of co-ordination tetrahedra sharing oxygen atoms;[3a] a classification of tectosilicates has also been proposed with the emphasis on their clathrate structures.[3b] Herein the structures are classified into six types according to the similarity of their structural features to those observed for zeolites. A linear linkage unit of –(CN)–Cd(t)–CN–Cd(o)–NC–Cd(t)– (T–O–T)‡ has been found for all the structures, where Cd(o) and Cd(t) are octahedral and tetrahedral cadmium atoms respectively. The T–O–T units make an infinite $-(T{-}O{-}T-)_n$ chain along the mirror plane. The three-dimensional host frameworks are built up by interconnection of the chains to adjacent mirror planes through the out-of-plane CN groups. Six types of host structures are derived from the variations in the modes of bending and interchain connection observed for the $-(T{-}O{-}T-)_n$ chains. Among the six types, type **IV** contains trigonal-bipyramidal five-co-ordinated Cd in addition to Cd(o) and Cd(t). The participation of the octahedral and trigonal-bipyramidal centres in the framework of the present zeolite-mimetic structures should be remarkably different from those of natural and synthesized zeolites.

Experimental

Preparation and Properties.—The inclusion compounds prepared, analysed and classified are listed in Table 1.

$[NMe_4{\cdot}xG][Cd_3(CN)_7]$ **I-1, II-1, IIIa-2, IIIb-1, IIIb-2, V-1, V-2** *and* **V-3**.—An aqueous solution, solution 1, prepared by dissolving $CdCl_2{\cdot}2.5H_2O$ (1.77 g, 7.75 mmol) and $K_2[Cd(CN)_4]$ (3.16 g, 10.72 mmol) in water (100 cm^3) was used as the source of the host complex in all of the preparations. After NMe_4I (1.35 g, 6.75 mmol) was dissolved in solution 1, the aqueous solution was filtered through a plastic membrane of 0.45 μm pore size; aliquots of *ca.* 30 cm^3 each were then placed on or below the organic layer of the respective guest species and allowed to stand in a refrigerator for a few days. Colourless plate-shaped crystals of the respective inclusion compounds were obtained.

$[SMe_3{\cdot}2G][Cd_3(CN)_7]$ **IIIa-1** *and* **V-4**. In place of NMe_4I, SMe_3I (0.55 g, 2.27 mmol) was used in the procedure above.

$[NEt_4{\cdot}CH_2Cl_2][Cd_3(CN)_7]$ **I-2**. To solution 1 NEt_4I (0.2 g, 1.2 mmol) was added to form a creamy suspension. The mixture became clear on the addition of appropriate amounts of citric acid and $NH_2(CH_2)_2OH$ to adjust the mixture to pH 10. The procedure was then similar to that above.

$[NH_2(CH_2)_3NMeH_2{\cdot}2CH_2Cl_2][Cd_3(CN)_7]$ **V-5**. The pH of solution 1 was adjusted to 8.7 by adding $NH_2(CH_2)_3NMeH$

---

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

‡ The notation T–O–T denotes a structure unit composed of a tetrahedron–octahedron–tetrahedron linkage sharing a connecting oxide anion in the chemistry of clay minerals, while in zeolite chemistry it sometimes denotes two tetrahedral centres such as Si, Al, linked with an oxide anion.

Table 1 The inclusion compounds of $[Cd_3(CN)_7]^-$ host and $[am{\cdot}xG]^+$ guest

		Analysis[b] (%)			
	$[am^a{\cdot}xG]^+$	C	H	N	Cl
I-1	$[NMe_4{\cdot}SnMe_4]^+$	23.00 (23.35)	3.10 (3.15)	14.15 (14.50)	
I-2	$[NEt_4{\cdot}CH_2Cl_2]^+$	25.95 (26.15)	2.95 (3.00)	15.50 (15.25)	9.35 (9.65)
I-3	$[Hdepn{\cdot}CHCl_3]^+$	23.35 (23.40)	2.60 (2.62)	16.80 (16.35)	13.35 (13.80)
II-1	$[NMe_4{\cdot}\textit{trans}\text{-}CHCl{=}CHCl]^+$	22.15 (22.60)	2.15 (2.05)	16.10 (16.25)	
II-2	$[Hdmpn{\cdot}CH_2ClCH_2Cl]^+$	23.15 (23.20)	2.60 (2.65)	17.50 (17.45)	
II-3	$[Hdepn{\cdot}C_6H_6]^+$	32.70 (32.95)	3.45 (3.60)	17.35 (17.30)	
IIIa-1	$[SMe_3{\cdot}2C_6H_6]^+$	34.75 (35.10)	3.15 (2.80)	12.90 (13.00)	
IIIa-2	$[NMe_4{\cdot}1.5C_6H_6]^+$	33.80 (33.80)	3.05 (3.00)	15.55 (15.75)	
IIIb-1	$[NMe_4{\cdot}C_6H_5Me]^+$	30.85 (31.55)	2.90 (2.95)	16.25 (16.35)	
IIIb-2	$[NMe_4{\cdot}\tfrac{2}{3}C_6H_3Me_3\text{-}1,3,5]^+$	29.95 (30.30)	2.75 (3.00)	16.70 (16.65)	
IV-1	$2[NMe_3H{\cdot}CH_2ClCH_2Cl]^{+c}$	22.25 (22.90)	2.15 (2.65)	16.90 (16.80)	
V-1	$[NMe_4{\cdot}2CH_2ClCH_2Cl]^+$	21.90 (22.75)	2.30 (2.55)	14.10 (14.15)	15.60 (17.90)
V-2	$[NMe_4{\cdot}2CH_2{=}CCl_2]^+$	22.20 (22.90)	2.10 (2.05)	15.45 (14.25)	17.25 (18.00)
V-3	$[NMe_4{\cdot}2EtCN]^+$	28.50 (29.00)	3.00 (3.15)	20.05(19.90)	
V-4	$[SMe_3{\cdot}2CH_2ClCH_2Cl]^+$	29.90 (21.15)	2.10 (2.15)	12.50 (12.35)	17.05 (17.85)
V-5	$[Hmpn{\cdot}2CH_2Cl_2]^+$	20.70 (20.05)	2.45 (2.20)	15.70 (16.20)	17.00 (18.20)
VI-1	$[Htmpn{\cdot}CH_2ClCH_2Cl]^+$	25.55 (25.60)	3.10 (3.10)	16.95 (16.80)	

[a] Hdepn = $NH_2(CH_2)_3N(C_2H_5)_2H^+$, Hdmpn = $NH_2(CH_2)_3N(CH_3)_2H^+$, Hmpn = $NH_2(CH_2)_3N(CH_3)H_2^+$ and Htmpn = $N(CH_3)_2(CH_2)_3N(CH_3)_2H^+$. [c] **IV-1** has the composition $[NMe_3H{\cdot}CH_2ClCH_2Cl]_2{\cdot}[Cd_6(CN)_{14}(NMe_3)]$.

(mpn) and citric acid. The procedure was then similar to that above.

$[NH_2(CH_2)_3NMe_2H{\cdot}CH_2ClCH_2Cl][Cd_3(CN)_7]$ **II-2**. The pH of solution 1 was adjusted to 8.5 by adding $NH_2(CH_2)_3NMe_2$ (dmpn) and citric acid. The procedure was then similar to that above.

$[NH_2(CH_2)_3NEt_2H{\cdot}G][Cd_3(CN)_7]$ **I-3** *and* **II-3**. The compound $NH_2(CH_2)_3NEt_2$ (depn) was used in place of dmpn in the above; the pH was adjusted to 8.7.

$[NMe_2(CH_2)_3NMe_2H{\cdot}CH_2ClCH_2Cl][Cd_3(CN)_7]$ **VI-1**. In solution 1 $NMe_2(CH_2)_3NMe_2$ (tmpn) and citric acid were dissolved to adjust the pH to 8.7. A small amount of colourless fine needle-like crystals, formed at room temperature, was filtered through the plastic membrane. The filtrate was placed over a layer of CH_2ClCH_2Cl and allowed to stand at room temperature for a few days.

$[NMe_3H{\cdot}CH_2ClCH_2Cl]_2[Cd_6(CN)_{14}(NMe_3)]$ **IV-1**. To solution 1 citric acid (1.55 g) and a 30% aqueous solution of NMe_3 (5.5 cm^3) were added until the pH became *ca.* 8.5. After filtration through the plastic membrane, the solution was placed over a layer of CH_2ClCH_2Cl and allowed to stand at room temperature for a few weeks.

The analytical data are included in Table 1. For some of the compounds non-stoichiometric accommodation of the neutral guests is suggested owing to unsatisfactory agreement with the calculated values.

The stability of the inclusion compounds under ambient conditions is similar to the clay-like structures described previously.[1d,e,i] In general, those compounds with the neutral guest G of higher boiling point are more stable, although they liberate the neutral guests gradually. Upon heating under ambient atmosphere they liberate neutral guests, decomposing to the onium heptacyanotricadmates whose powder diffraction patterns are not identical with the parent inclusion compounds. Hence, unlike zeolites, the integrity of the framework is not preserved after the liberation of the neutral guest.

Crystallography.—The crystal and selected experimental data are summarised in Table 2. In each experiment the crystal was coated with epoxy resin in order to prevent decomposition. During the intensity data collection three representative reflections were monitored after every 100 reflections; no significant decay was observed.

The cadmium atoms were located from Patterson maps; successive Fourier and Fourier difference syntheses were used to locate the other atoms. The structures were refined by least-squares procedures using SHELX 76.[4] All the host atoms were refined anisotropically and also the non-H guest atoms whose reflection data were of sufficient quality. Disorders in the orientation and occupancy were observed to a more or less extent for the guest molecules in some cases, mainly because of the non-coincidence of the molecular symmetry with the site symmetry of the cavity. Only isotropic refinement was possible for the guest atoms in such disorder; in some cases some of the non-H guest atoms could not be located; in the worst case no guest atoms could be refined for **I-3**.

Another problem in the structure refinement was discrimination between the C and N atoms of the CN group linking tetrahedral Cd atoms on the mirror plane, as has usually been observed for the CN linkage between two tetrahedral centres.[5] Such a CN group is shown in parentheses in the chemical notations T–O–T and T–T. The space groups $R\bar{3}m$ and $P6_3/mmc$ for types **I** and **V** respectively predict that discrimination is impossible due to symmetry requirements. An inversion centre between the C and N atoms makes both atoms crystallographically equivalent; in $P6_3/mmc$ a mirror plane bisecting the Cd(t)–(CN)–Cd(t) linkage is added. When the space group of a lower symmetry was selected, *i.e.* $C2/m$ in place of $R\bar{3}m$, or *Bbmm* in place of $P6_3/mmc$, the relationship with the symmetry elements was unchanged. In some cases, although the space group applied allowed discrimination, significant selection was difficult from the X-ray data collected. When discrimination was impossible either theoretically or practically, the C and N atoms were refined together as an atom denoted by CN with 50% probability for each. When a Cd(t′)–N distance longer than Cd(t)–C was observed, with the difference being greater than the sum of three times their estimated standard deviations under acceptable convergence in the final refinement, the C and N atoms are described as having been discriminated. The atomic parameters refined are listed in Table 3.

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

Results

General.—All the space groups applied for the six types generate mirror planes as symmetry elements in the respective unit cells: the mirror planes vertical to the *c* axis in the orthorhombic systems and those vertical to the *a* or *b* axis in the trigonal and hexagonal systems in the axes setting applied. In other words, the unit-cell axes have been set for the sake of

Table 2 Crystal and selected experimental data for $[\text{am}\cdot x\text{G}][\text{Cd}_3(\text{CN})_7]$[a]

Type-number	**I-1**	**I-2**	**I-3**	**II-1**	**II-2**	**II-3**
am	NMe$_4$	NEt$_4$	NH$_2$(CH$_2$)$_3$NEt$_2$H	NMe$_4$	NH$_2$(CH$_2$)$_3$NMe$_2$H	NH$_2$(CH$_2$)$_3$NEt$_2$H
xG	SnMe$_4$	CH$_2$Cl$_2$	CHCl$_3$	*trans*-CHCl=CHCl	CH$_2$ClCH$_2$Cl	C$_6$H$_6$
Formula	$C_{15}Cd_3H_{24}N_8Sn$	$C_{16}Cd_3Cl_2H_{22}N_8$	$C_{15}Cd_3Cl_3H_{20}N_9$	$C_{14}Cd_3Cl_2H_{14}N_7$	$C_{14}Cd_3Cl_2H_{19}N_9$	$C_{20}Cd_3H_{19}N_9$
M	722.4	734.5	770.0	690.4	721.5	728.7
Crystal system	Trigonal	Trigonal	Trigonal	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$R\bar{3}m$ (no. 166)	$R\bar{3}m$ (no. 166)	$R\bar{3}m$ (no. 166)	$Pn2_1m$ (no. 31)	$Pn2_1m$ (no. 31)	$Pn2_1m$ (no. 31)
a/Å	8.849(1)	8.778(4)	8.850(3)	11.115(3)	11.026(5)	11.212(1)
b/Å	= a/Å	= a/Å	= a/Å	13.287(3)	13.54(1)	13.483(2)
c/Å	31.086(3)	30.64(3)	30.538(4)	8.664(3)	8.721(2)	8.694(2)
U/Å^3, Z	2108(1), 3	2044(2), 3	2071(1), 3	1280(2), 2	1032(1), 2	1314.3(6), 2
D_m,D_c/g cm^{-3} [b]	1.84(1), 1.83	1.79(2), 1.79	1.83(1), 1.85	1.80(1), 1.79	1.84(1), 1.82	1.81(1), 1.84
F(000)	1092	1056	1104	650	688	692
μ(Mo-Kα)/cm^{-1}	30.5	27.00	25.76	26.55	23.29	20.03
Crystal size/mm	0.25 × 0.25 × 0.20	0.30 × 0.20 × 0.15	0.40 × 0.30 × 0.20	0.25 × 0.20 × 0.15	0.25 × 0.25 × 0.25	0.40 × 0.20 × 0.15
Diffractometer	Rigaku AFC5	Rigaku AFC6A	Rigaku AFC5R	AFC6A	AFC6A	AFC5R
Scan range, 2θ/°	4–60	3–60	5–60	3–60	3–70	5–60
Peak scan width/°	1.470 + 0.3 tan θ	1.432 + 0.5 tan θ	1.418 + 0.3 tan θ	1.234 + 0.5 tan θ	1.298 + 0.5 tan θ	1.420 + 0.3 tan θ
Reflections measured	1558	1577	1539	2241	3390	2247
Reflections used, N_o	707, $> 3\sigma(F_o)$	669, $> 3\sigma(F_o)$	625, $> 3\sigma(F_o)$	1744, $> 4\sigma(F_o)$	2329, $> 3\sigma(F_o)$	2037, $> 4\sigma(F_o)$
No. of parameters, N_p	40	45	21	141	156	171
Weighting scheme	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$
g	0.007	0.0067	0.001 223	0.01	0.0012	0.002 262
R, R'	0.0816, 0.1294	0.0760, 0.1349	0.0690, 0.1061	0.0509, 0.0767	0.0508, 0.0649	0.0271, 0.0425
Goodness of fit[c]	1.293	1.432	2.232	6.912	1.260	0.818
Δ/e.s.d. max. (host)	0.174	0.441	0.003	0.087	0.493	0.005
Δ/e.s.d. max. (guest)	0.862	1.438		0.495	0.672	0.012
Max., min. residual electron density/e Å^{-3}	1.88, −5.81	1.38, −2.76	1.52, −1.05	2.45, −1.125	1.47, −1.21	1.19, −1.05

Type-number	**IIIa-1**	**IIIa-2**	**IIIb-1**	**IIIb-2**	**IV-1**[d]	**V-1**
am	SMe$_3$	NMe$_4$	NMe$_4$	NMe$_4$	2NMe$_3$H	NMe$_4$
xG	2C$_6$H$_6$	1.5C$_6$H$_6$	C$_6$H$_5$Me	$\frac{2}{3}$C$_6$H$_3$Me$_3$-1,3,5	2CH$_2$ClCH$_2$Cl	2CH$_2$ClCH$_2$Cl
Formula	$C_{22}Cd_3H_{21}N_7S$	$C_{20}Cd_3H_{21}N_8$	$C_{18}Cd_3H_{20}N_8$	$C_{17}Cd_3H_{20}N_8$	$C_{27}Cd_6Cl_4H_{39}N_{17}$	$C_{15}Cd_3Cl_4H_{20}N_8$
M	752.8	716.1	685.6	673.6	1416.0	791.4
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthohombic	Hexagonal
Space group	$Pnam$ (no. 62)	$Pnam$ (no. 62)	$Pnam$ (no. 62)	$Pnam$ (no. 62)	$Pnam$ (no. 62)	$P6_3/mmc$ (no. 194)
a/Å	21.934(7)	21.628(3)	22.33(2)	22.256(4)	43.39(1)	8.787(2)
b/Å	13.483(2)	13.998(3)	13.297(6)	13.489(4)	13.602(5)	= a/Å
c/Å	8.875(3)	8.945(1)	8.846(4)	8.868(3)	8.773(3)	20.97(3)
U/Å^3, Z	2698(2), 4	2708(1), 4	2627, 4	2662(1), 4	5177(3), 4	1404(1), 2
D_m,D_c/g cm^{-3}	1.82(1), 1.85	1.77(1), 1.76	1.69(1), 1.68	1.81(2), 1.80	1.74–1.86, 1.85	1.87(1), 1.87
F(000)	1448	1364	1312	1288	2704	756
μ(Mo-Kα)/cm^{-1}	24.10	23.29	23.32	25.41	25.25	26.26
Crystal size/mm	0.20 × 0.20 × 0.20	0.45 × 0.20 × 0.20	0.30 × 0.35 × 0.45	0.15 × 0.15 × 0.20	0.25 × 0.13 × 0.08	0.25 × 0.25 × 0.20
Diffractometer	AFC5	AFC5R	AFC6A	AFC5	AFC5R	AFC5
Scan range, 2θ/°	3–60	5–60	3–65	4–60	4–60	3–60
Peak scan width/°	1.300 + 0.14 tan θ	0.798 + 0.3 tan θ	0.996 + 0.5 tan θ	0.892 + 0.3 tan θ	0.966 + 0.3 tan θ	1.170 + 0.5 tan θ
Reflections measured	4557	10 852	4480	4467	8636	2440
Reflections used, N_o	1422, $> 4\sigma(F_o)$	2918, $> 4\sigma(F_o)$	3406, $> 3\sigma(F_o)$	1798, $> 3\sigma(F_o)$	3636, $> 4\sigma(F_o)$	560, $> 3\sigma(F_o)$
No. of parameters, N_p	185	182	148	197	301	45
Weighting scheme	Unit weight	$w = 1/\sigma^2$	Unit weight	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$
g				0.001 26	0.0027	0.001 119
R, R'[c]	0.0809, 0.0984	0.0550, 0626	0.0555, 0.0700	0.0634, 0.0748	0.0749, 0.0906	0.0678, 0.0815
Goodness of fit[c]	9.391	1.175	4.278	1.255	1.646	1.686
Δ/e.s.d. max. (host)	0.361	0.059	0.058	0.249	0.327	0.139
Δ/e.s.d. max. (guest)	0.418	0.672	0.764	0.648	0.914	0.691
Max., min. residual electron density/e Å^{-3}	1.48, −1.47	0.94, −1.87	1.47, −1.85	1.43, −1.03	2.29, −1.67	1.57, −1.35

Table 2 (*contd.*)

Type-number	V-2	V-3	V-4	V-5	VI-1
am	NMe_4	NMe_4	SMe_3	$NH_2(CH_2)_3NMeH_2$	$NMe_2(CH_2)_3NMe_2H$
*x*G	$2CH_2{=}CCl_2$	2EtCN	$2CHCl_2CHCl_2$	$2CH_2Cl_2$	CH_2ClCH_2Cl
Formula	$C_{15}Cd_3Cl_4H_{16}N_8$	$C_{16}Cd_3H_{25}N_{10}$	$C_{14}Cd_3Cl_4H_{13}N_7S$	$C_{13}Cd_3Cl_4H_{17}N_9$	$C_{16}Cd_3Cl_2H_{23}N_9$
M	787.4	703.7	794.4	778.4	749.6
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Orthorhombic
Space group	$P6_3/mmc$ (no. 194)	$P6_3/mmc$ (no. 194)	$P6_3/mmc$ (no. 194)	$P6_3/mmc$ (no. 194)	$Pb2_1m$ (no. 26)
a/Å	8.775(5)	8.714(5)	8.814(4)	8.775(2)	10.817(5)
b/Å	= *a*/Å	= *a*/Å	= *a*/Å	= *a*/Å	27.553(1)
c/Å	20.546(8)	20.437(8)	20.567(3)	20.546(8)	9.048(2)
U/Å^3, Z	1370(1), 2	1344(1), 2	1384(1), 2	1370(1), 2	2697(2), 4
$D_m D_c$/g cm^{-3}	1.90(2), 1.91	1.72(2), 1.74	1.89(2), 1.91	1.87(1), 1.88	1.86(2), 1.85
F(000)	748	670	748	740	1440
μ(Mo-Kα)/cm^{-1}	26.26	23.28	27.10	26.46	25.25
Crystal size/mm	0.20 × 0.15 × 0.10	0.20 × 0.20 × 0.10	0.30 × 0.25 × 0.15	0.25 × 0.20 × 0.10	0.10 × 0.10 × 0.07
Diffractometer	AFC6A	AFC5	AFC5	AFC6A	AFC5
Scan range, 2θ/°	3–60	3–60	3–60	3–60	4–60
Peak scan width/°	1.245 + 0.5 tan θ	1.300 + 0.03 tan θ	1.245 + 0.5 tan θ	1.340 + 0.5 tan θ	0.756 + 0.3 tan θ
Reflections measured	2410	924	2348	2339	4545
Reflections used, N_o	680, > 3σ(F_o)	569, > 3σ(F_o)	475, > 4σ(F_o)	636, > 3σ(F_o)	1996, > 4σ(F_o)
No. of parameters, N_p	35	44	49	34	176
Weighting scheme	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$	$w = 1/(\sigma^2 + gF^2)$
g	0.012	0.006	0.001 119	0.000 111 9	0.0027
R, *R′*	0.0680, 0.0705	0.0444, 0.0666	0.0728, 0.0705	0.0781, 0.0831	0.0859, 0.1089
Goodness of fit[c]	1.889	0.767	1.889	2.971	1.473
Δ/e.s.d. max. (host)	0.339	0.313	0.339	0.02	0.190
Δ/e.s.d. max. (guest)	0.891	0.508	0.891	1.55	0.697
Max., min. residual electron density/e Å^{-3}	1.55, −0.55	0.59, −1.36	1.57, −1.35	1.57, −1.35	2.17, −1.78

[a] Conditions in common: *T* 293 K; graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) from sealed tube (AFC5 and AFC6A) or a rotating anode (AFC5R); α = β = 90° and γ = 120° for trigonal **I-1** to **I-3** and hexagonal **V-1** to **V-5**; α = β = γ = 90° for orthorhombic **II-1** to **II-3**, **IIIa-1** to **IIIb-2**, **IV-1** and **VI-1**. [b] Density was measured by the flotation method in $CHBr_3$–C_6H_3-Me_3-1,3,5. [c] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}$; goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$. [d] Composition of **IV-1**: $[NMe_3H{\cdot}CH_2ClCH_2Cl]_2[Cd_6(CN)_{14}(NMe_3)]$.

Table 3 Atomic parameters[a]

Atom[b]	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}/Å^{2}[c]	Occupancy[d]
I-1: $[NMe_4 \cdot SnMe_4][Cd_3(CN)_7]$					
Cd(o)	0.0	0.0	0.0	2.36(4)	
Cd(t)	0.0	0.0	0.409 85(4)	2.69(3)	
CN(1)	0.0	0.0	0.480 1(4)	3.7(3)	
N(1)	0.127 6(7)	= −*x*/*a*	0.041 2(4)	4.8(3)	
C(1)	0.196 3(8)	= −*x*/*a*	0.055 3(4)	4.0(3)	
Sn	0.0	0.0	0.221 7(2)	6.9(1)	0.5
C(2)	0.0	0.0	0.290 2(6)	7.1(3)	0.5
C(3)	0.136(2)	= −*x*/*a*	0.205(2)	12.2(6)	0.5
N(2)	0.0	0.0	0.246(1)	3.3(5)	0.5
C(4)	0.0	0.0	0.293(1)	7.8(6)	0.5
C(5)	0.083(2)	= −*x*/*a*	0.223(2)	9.7(6)	0.5
I-2: $[NEt_4 \cdot CH_2Cl_2][Cd_3(CN)_7]$[e]					
Cd(o)	0.0	0.0	0.0	3.81(5)	
Cd(t)	0.0	0.0	0.408 22(4)	3.70(4)	
CN(1)	0.0	0.0	0.482 0(6)	4.7(4)	
N(1)	0.127 1(8)	= −*x*/*a*	0.043 6(4)	6.6(2)	
C(1)	0.193 4(9)	= −*x*/*a*	0.055 0(4)	5.3(2)	
CN(2)	0.0	0.0	0.194(2)	14.5(4)	0.5
Cl(1)	0.0	0.0	0.137(2)	22.7(4)	0.25
Cl(2)	0.097(2)	= −*x*/*a*	0.224(1)	15.5(4)	0.25
[*CN(2)*	0.0	0.0	0.194(2)	14.5(4)	0.5]
C(2)	0.043(4)	= −*x*/*a*	0.238(2)	18.5(4)	0.167
C(3)	0.0	0.0	0.284(2)	9.3(4)	0.5
C(4)	−0.080(3)	= −*x*/*a*	0.166(2)	18.5(4)	0.5
C(5)	0.099(4)	= 2*x*/*a*	0.144(3)	21.6(4)	0.5
I-3: $[NH_2(CH_2)_3NEt_2H \cdot CHCl_3][Cd_3(CN)_7]$[f]					
Cd(o)	0.0	0.0	0.0	3.81(4)	
Cd(t)	0.0	0.0	0.409 85(4)	3.91(3)	
CN	0.0	0.0	0.480 1(4)	5.6(4)	
N(1)	0.127 1(8)	= −*x*/*a*	0.043 6(4)	6.6(4)	
C(1)	0.193 4(9)	= −*x*/*a*	0.055 0(4)	4.8(4)	
II-1: $[NMe_4 \cdot$*trans*-$CHCl{=}CHCl][Cd_3(CN)_7]$					
Cd(o)	0.228 99(9)	0.0	0.0	2.36(3)	
Cd(t)	0.074 0(1)	0.403 2(1)	0.0	2.70(4)	
Cd(t′)	0.493 3(1)	0.635 0(1)	0.0	2.85(4)	
N(1)	0.096(1)	−0.048 1(9)	0.191(1)	4.1(2)	
N(2)	0.361(1)	0.058(1)	0.190(1)	4.5(2)	
N(3)	0.139(2)	0.161(1)	0.0	4.7(2)	
N(4)	0.333(2)	0.849(1)	0.0	4.3(2)	
C(1)	0.035(1)	−0.062 8(9)	0.293(1)	3.0(2)	
C(2)	0.413(1)	0.089(1)	0.289(2)	4.0(2)	
C(3)	0.117(1)	0.240(1)	0.0	3.4(2)	
C(4)	0.390(1)	0.776(1)	0.0	3.4(2)	
CN(1)	0.243(1)	0.486(1)	0.0	4.2(2)	
CN(2)	0.328(2)	0.535(2)	0.0	5.1(2)	
Cl(1)	1.045(1)	0.683(1)	0.0	10.4(2)	
Cl(2)	0.705(1)	0.824(2)	0.064(2)	11.7(2)	0.5
C(5)	0.897(2)	0.714(2)	0.0	9.8(2)	
C(6)	0.850(2)	0.804(2)	0.0	8.4(2)	
N(5)	0.260(2)	0.669(2)	0.5	7.3(2)	
C(7)	0.364(2)	0.600(2)	0.5	9.2(2)	
C(8)	0.354(2)	0.749(2)	0.5	9.0(2)	
C(9)	0.199(2)	0.709(2)	0.366(2)	9.9(2)	
II-2: $[NH_2(CH_2)_3NMe_2H \cdot CH_2ClCH_2Cl][Cd_3(CN)_7]$					
Cd(o)	0.222 32(6)	0.0	0.0	2.24(2)	
Cd(t)	0.069 47(7)	0.397 49(8)	0.0	2.85(2)	
Cd(t′)	0.486 63(7)	0.635 35(8)	0.0	3.21(3)	
N(1)	0.100 2(6)	−0.046 0(5)	0.190 7(7)	4.01(8)	
N(2)	0.365 3(6)	0.058 3(6)	0.191 3(7)	4.52(8)	
N(3)	0.149 3(8)	0.161 5(6)	0.0	4.30(8)	
N(4)	0.333 7(7)	0.850 8(7)	0.0	4.03(8)	

Table 3 (*contd.*)

Atom[b]	*x*/*a*	*y*/*b*	*z*/*c*	$B_{eq}/Å^{2}$[c]	Occupancy[d]
C(1)	0.041 2(6)	−0.065 6(6)	0.291 5(7)	3.57(8)	
C(2)	0.418 2(6)	0.087 3(6)	0.291 4(8)	3.78(8)	
C(3)	0.118 9(8)	0.240 6(7)	0.0	3.86(8)	
C(4)	0.383 9(8)	0.777 0(7)	0.0	3.76(8)	
CN(1)	0.244 0(9)	0.482 1(8)	0.0	4.59(9)	
CN(2)	0.325 9(7)	0.531 8(8)	0.0	4.39(9)	
Cl(1)	−0.041 6(6)	0.175 1(6)	0.5	12.5(1)	
Cl(2)	0.298 4(6)	0.313 8(6)	0.441 7(9)	12.0(2)	0.5
C(5)	0.107(1)	0.237(1)	0.427(1)	13.3(1)	0.5
C(6)	0.169(1)	0.280(1)	0.447(1)	9.6(1)	
N(5)	0.299(1)	0.863(1)	0.5	7.6(1)	0.5
N(6)	0.553(1)	0.855(1)	0.5	12.8(1)	0.5
C(7)	0.425 0(9)	0.821(1)	0.5	16.5(1)	
C(8)	0.513(1)	0.735(1)	0.5	12.7(1)	0.5
C(9)	0.302(1)	0.840(1)	0.423(1)	6.7(1)	0.25
C(10)	0.380(1)	0.713(1)	0.467(1)	18.1(1)	0.25
C(11)	0.297(1)	0.730(1)	0.378(1)	11.5(1)	0.25
N(7)	0.257 9(9)	0.667(1)	0.5	13.3(1)	
C(12)	0.193(1)	0.663(1)	0.350(1)	8.8(1)	0.5
C(13)	0.213(1)	0.587(1)	0.404(1)	15.3(1)	0.5
II-3: $[NH_2(CH_2)_3NEt_2H{\cdot}C_6H_6][Cd_3(CN)_7]$					
Cd(o)	0.233 76(4)	0.0	0.0	1.79(2)	
Cd(t)	0.067 88(4)	0.399 23(5)	0.0	2.01(2)	
Cd(t′)	0.485 72(4)	0.632 46(5)	0.0	2.04(2)	
N(1)	0.100 8(4)	−0.041 9(4)	0.192 3(6)	3.2(2)	
N(2)	0.367 9(4)	0.050 7(4)	0.192 5(5)	3.1(2)	
N(3)	0.157 9(7)	0.161 7(5)	0.0	3.2(3)	
N(4)	0.322 5(6)	0.841 7(5)	0.0	2.9(2)	
C(1)	0.039 2(5)	−0.061 2(4)	0.292 7(6)	2.8(2)	
C(2)	0.420 0(4)	0.081 7(4)	0.293 3(6)	2.5(2)	
C(3)	0.123 5(6)	0.242 0(6)	0.0	2.5(3)	
C(4)	0.376 5(7)	0.769 1(6)	0.0	2.5(2)	
CN(1)	0.239 1(6)	0.482 7(6)	0.0	3.4(3)	
CN(2)	0.327 2(6)	0.524 3(6)	0.0	2.8(2)	
C(5)	0.360 7(8)	0.376 0(6)	0.422(1)	5.5(4)	
C(6)	0.279 9(8)	0.315 7(9)	0.341(1)	5.8(4)	
C(7)	0.207 0(9)	0.259(1)	0.415(2)	6.8(5)	
N(5)	0.286 0(7)	0.861 7(7)	0.5	4.4(4)	
C(8)	0.407(1)	0.842(1)	0.459(2)	4.3(6)	0.5
C(9)	0.445 8(8)	0.744 0(9)	0.5	4.3(3)	
C(10)	0.368 2(9)	0.660(1)	0.461(1)	3.7(5)	0.5
N(6)	0.241 9(6)	0.666 0(5)	0.5	3.1(3)	
C(11)	0.229 2(2)	0.632(1)	0.320(2)	3.6(4)	0.5
C(12)	0.158(1)	0.615 3(8)	0.407(2)	3.3(4)	0.5
C(13)	0.129 3(7)	0.671 6(6)	0.253(1)	4.1(3)	
IIIa-1: $[SMe_3{\cdot}2C_6H_6][Cd_3(CN)_7]$					
Cd(o)	0.130 7(1)	0.314 5(2)	0.25	2.7(1)	
Cd(t)	0.227 2(1)	0.933 9(2)	0.25	3.0(1)	
Cd(t′)	0.023 6(1)	0.683 6(2)	0.25	3.1(1)	
N(1)	0.062 8(9)	0.282(2)	0.046(3)	4.1(6)	
N(2)	0.203(1)	0.360(2)	0.056(3)	4.1(6)	
N(3)	0.092(1)	0.472(2)	0.25	3.2(6)	
N(4)	0.170(1)	0.153(2)	0.25	3.3(6)	
C(1)	0.031(1)	0.291(2)	−0.050(3)	3.5(6)	
C(2)	0.226(1)	0.387(2)	−0.047(3)	3.5(6)	
C(3)	0.066(2)	0.542(3)	0.25	4.7(6)	
C(4)	0.192(2)	0.082(3)	0.25	3.7(6)	
CN(1)	0.111(2)	0.783(3)	0.25	5.2(6)	
CN(2)	0.149(2)	0.833(3)	0.25	3.8(6)	
C(5)	0.399(2)	0.054(3)	0.178(4)	9.8(6)	
C(6)	0.364(2)	0.122(2)	0.101(3)	7.8(6)	
C(7)	0.334(2)	0.194(3)	0.178(4)	8.9(6)	
C(8)	0.493(4)	0.490(5)	0.25	16.9(6)	
C(9)	0.470(3)	0.473(4)	0.104(4)	20.9(6)	
C(10)	0.438(4)	0.390(3)	0.146(5)	18.3(6)	
C(11)	0.428(4)	0.315(4)	0.25	18.1(6)	

Table 3 (*contd.*)

Atom[b]	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}/Å^2 [c]	Occupancy[d]
S	0.316(2)	0.561(3)	0.25	21.5(6)	
C(12)	0.350(3)	0.678(3)	0.25	9.9(6)	
C(13)	0.242(2)	0.619(4)	0.25	14.7(6)	
C(14)	0.375(3)	0.614(5)	0.138(6)	11.2(6)	0.5
IIIa-2: [NMe$_4$·1.5C$_6$H$_6$][Cd$_3$(CN)$_7$]					
Cd(o)	0.130 00(3)	0.312 64(5)	0.25	2.24(3)	
Cd(t)	0.228 61(3)	0.933 90(5)	0.25	2.64(3)	
Cd(t′)	0.024 90(3)	0.680 11(6)	0.25	2.50(3)	
N(1)	0.063 2(3)	0.284 6(5)	0.053 0(7)	3.8(2)	
N(2)	0.201 8(3)	0.358 1(5)	0.062 8(7)	3.5(2)	
N(3)	0.094 9(5)	0.469 1(7)	0.25	4.1(3)	
N(4)	0.167 8(4)	0.154 2(6)	0.25	3.1(3)	
C(1)	0.032 6(3)	0.294 6(6)	−0.047 4(9)	3.3(2)	
C(2)	0.225 2(3)	0.387 1(5)	−0.043 2(8)	2.9(2)	
C(3)	0.069 5(5)	0.538 5(8)	0.25	3.5(3)	
C(4)	0.187 7(5)	0.078 5(8)	0.25	3.0(3)	
CN(1)	0.105 7(5)	0.780 9(8)	0.25	3.8(3)	
CN(2)	0.146 9(5)	0.832 1(8)	0.25	3.7(3)	
C(5)	0.393 4(6)	0.053 3(9)	0.325(2)	9.0(3)	
C(6)	0.363 9(5)	0.120(1)	0.402(1)	8.0(3)	
C(7)	0.332 9(5)	0.193 1(8)	0.330(2)	8.8(3)	
C(8)	0.518(2)	0.514(3)	0.25	11.9(3)	0.574(4)
C(9)	0.504(2)	0.494(2)	0.403(3)	15.6(3)	0.574(4)
C(10)	0.461(1)	0.410(2)	0.405(2)	13.8(3)	0.574(4)
C(11)	0.467(2)	0.367(2)	0.25	9.1(3)	0.574(4)
N(5)	0.314 1(7)	0.596 1(9)	0.25	7.0(3)	
C(12)	0.356(1)	0.661(2)	0.173(2)	13.1(3)	0.6667
C(13)	0.265(1)	0.614(2)	0.134(2)	14.1(3)	0.6667
C(14)	0.332(1)	0.516(1)	0.162(2)	13.8(3)	0.6667
IIIb-1: [NMe$_4$·C$_6$H$_5$Me][Cd$_3$(CN)$_7$]					
Cd(o)	0.146 05(2)	0.340 57(5)	0.25	2.64(2)	
Cd(t)	0.206 82(3)	0.929 18(5)	0.25	2.77(2)	
Cd(t′)	0.004 37(3)	0.693 39(5)	0.25	2.95(2)	
N(1)	0.077 6(3)	0.302 3(6)	0.061 7(7)	5.0(1)	
N(2)	0.214 5(3)	0.378 3(5)	0.061 4(6)	4.5(1)	
N(3)	0.099 4(5)	0.499 2(6)	0.25	4.6(1)	
N(4)	0.178 9(4)	0.175 7(6)	0.25	4.1(1)	
C(1)	0.048 3(3)	0.300 0(6)	−0.042 1(7)	4.2(1)	
C(2)	0.241 9(3)	0.393 1(5)	−0.042 4(7)	3.6(1)	
C(3)	0.066 4(5)	0.560 2(7)	0.25	4.3(1)	
C(4)	0.187 7(4)	0.093 4(6)	0.25	3.1(1)	
CN(1)	0.075 9(4)	0.807 5(6)	0.25	5.2(1)	
CN(2)	0.120 4(4)	0.849 4(6)	0.25	3.4(1)	
C(5)	0.476 3(9)	0.423(1)	0.25	10.7(1)	
C(6)	0.448 3(7)	0.462(1)	0.375(1)	10.2(1)	
C(7)	0.395 8(7)	0.520 4(9)	0.390(1)	9.3(1)	
C(8)	0.370 7(8)	0.559(1)	0.25	9.5(1)	
C(9)	0.316 4(9)	0.622(1)	0.25	12.7(1)	
N(5)	0.376 1(5)	0.160(1)	0.25	8.3(1)	
C(10)	0.443 0(8)	0.163(1)	0.25	12.0(1)	
C(11)	0.356 1(9)	0.047(1)	0.25	15.4(1)	
C(12)	0.346 4(8)	0.166(1)	0.112(1)	15.2(1)	
IIIb-2: [NMe$_4$·$\frac{2}{3}$C$_6$H$_3$Me$_3$-1,3,5][Cd$_3$(CN)$_7$]					
Cd(o)	0.142 25(6)	0.336 9(1)	0.25	3.00(5)	
Cd(t)	0.211 81(6)	0.933 81(9)	0.25	3.09(6)	
Cd(t′)	0.008 35(6)	0.693 7(1)	0.25	3.35(6)	
N(1)	0.072 2(5)	0.297 1(9)	0.063(1)	5.2(3)	
N(2)	0.209 4(5)	0.379 6(8)	0.061(1)	4.8(3)	
N(3)	0.097 9(8)	0.494(1)	0.25	5.5(3)	
N(4)	0.177 4(8)	0.175(1)	0.25	4.8(3)	
C(1)	0.044 3(6)	0.298(1)	−0.042(2)	4.7(3)	
C(2)	0.237 1(6)	0.399 2(9)	−0.043(2)	4.2(3)	
C(3)	0.067(1)	0.556(1)	0.25	4.6(3)	
C(4)	0.189 7(7)	0.095(1)	0.25	4.1(3)	
CN(1)	0.087 1(8)	0.804(1)	0.25	5.5(3)	
CN(2)	0.129 8(7)	0.848(8)	0.25	3.4(3)	

Table 3 (*contd.*)

Atom[b]	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}/Å^2 [c]	Occupancy[d]
C(5)	0.5	0.5	0.0	11.3(3)	
C(6)	0.498(2)	0.489(3)	0.25	8.1(3)	0.5
C(7)	0.372(2)	0.571(3)	0.25	7.6(3)	0.5
C(8)	0.461(1)	0.512(2)	0.130(2)	8.8(3)	0.5
C(9)	0.403(1)	0.549(2)	0.116(2)	9.7(3)	0.6667
C(10)	0.315(2)	0.626(3)	0.25	9.7(3)	0.6667
C(11)	0.246(2)	0.646(4)	0.25	8.6(3)	0.6667
C(12)	0.435(3)	0.530(4)	0.25	8.6(3)	0.1667
C(13)	0.342(2)	0.566(3)	0.143(3)	8.5(3)	0.1667
C(14)	0.459(2)	0.556(3)	0.015(4)	8.3(3)	0.1667
N(5)	0.375 6(8)	0.186(2)	0.25	7.3(3)	
C(15)	0.419(2)	0.267(2)	0.25	13.7(3)	
C(16)	0.427(2)	0.117(2)	0.25	13.1(3)	
C(17)	0.342(1)	0.164(2)	0.117(2)	12.5(3)	
IV-1: 2[$NMe_3H{\cdot}CH_2ClCH_2Cl$][$Cd_6(CN)_{14}(NMe_3)$]					
Cd(o)	0.064 55(4)	0.314 6(1)	0.25	2.78(7)	
Cd(o′)	0.192 73(4)	0.836 3(1)	0.75	2.43(6)	
Cd(t1)	0.012 91(4)	0.694 8(1)	0.25	2.91(7)	
Cd(t1′)	0.231 29(4)	0.238 0(1)	0.75	2.82(7)	
Cd(t2)	0.116 54(4)	0.934 7(1)	0.25	2.83(7)	
Cd(p)	0.119 66(4)	0.496 7(1)	0.75	3.44(8)	
N(1)	0.087 3(5)	0.158(1)	0.25	3.8(3)	
N(2)	0.045 0(5)	0.471(1)	0.25	5.0(3)	
N(3)	0.168 2(5)	0.681(1)	0.75	4.2(3)	
N(4)	0.211 7(5)	0.000(2)	0.75	4.2(3)	
N(5)	0.166 8(6)	0.360(2)	0.75	4.3(4)	
N(6)	0.031 0(3)	0.275(1)	0.442(2)	4.5(3)	
N(7)	0.098 6(3)	0.375(1)	0.439(2)	4.7(3)	
N(8)	0.159 1(3)	0.882(1)	0.560(2)	4.3(3)	
N(9)	0.227 0(3)	0.794(1)	0.558(2)	4.4(3)	
C(1)	0.097 2(5)	0.082(2)	0.25	3.6(3)	
C(2)	0.033 5(6)	0.545(2)	0.25	3.7(3)	
C(3)	0.153 5(6)	0.616(2)	0.75	4.3(3)	
C(4)	0.220 0(5)	0.079(2)	0.75	3.5(3)	
C(5)	0.185 3(6)	0.319(2)	0.75	3.7(3)	
C(6)	0.015 0(3)	0.280(1)	0.543(2)	3.4(3)	
C(7)	0.107 6(4)	0.417(1)	0.539(2)	4.8(3)	
C(8)	0.144 5(3)	0.901(1)	0.457(2)	3.2(3)	
C(9)	0.241 5(4)	0.772(1)	0.457(2)	3.5(3)	
CN(1)	0.054 8(6)	0.791(2)	0.25	4.2(4)	
CN(2)	0.076 2(6)	0.832(2)	0.25	4.3(4)	
N(10)	0.075 2(5)	0.599(2)	0.75	5.1(3)	
C(10)	0.049 5(9)	0.538(3)	0.75	9.9(4)	
C(11)	0.076 0(6)	0.661(2)	0.895(3)	7.6(4)	
Cl(1)	0.263 2(3)	0.005 4(8)	0.25	10.7(4)	
Cl(2)	0.174 4(2)	0.133(1)	0.25	10.9(4)	
Cl(3)	0.433(1)	0.427(3)	0.25	12.6(4)	
Cl(4)	0.472(1)	0.509(3)	0.033(4)	8.2(4)	0.5
C(12)	0.223 0(7)	0.038(3)	0.25	13.1(4)	
C(13)	0.212 2(8)	0.097(3)	0.312(4)	11.4(4)	0.5
C(14)	0.478(1)	0.449(3)	0.25	15.0(4)	
C(15)	0.455 0(8)	0.440(2)	0.112(3)	7.7(4)	0.5
N(16)	0.178 4(9)	0.511(3)	0.25	12.0(4)	
N(17)	0.381 1(5)	0.686(1)	0.25	3.9(4)	
C(16)	0.177(1)	0.412(4)	0.25	17.3(4)	
C(17)	0.194 5(9)	0.518(3)	0.387(3)	17.0(4)	
C(18)	0.414 9(7)	0.694(2)	0.25	7.2(4)	
C(19)	0.368 9(6)	0.637(2)	0.393(2)	8.1(4)	
V-1: [$NMe_4{\cdot}2CH_2ClCH_2Cl$][$Cd_3(CN)_7$]					
Cd(o)	0.0	0.0	0.0	2.45(6)	
Cd(t)	0.3333	0.6667	0.116 1(1)	2.76(5)	
CN	0.3333	0.6667	0.222 3(9)	4.2(5)	
N(1)	0.128 4(9)	= 2*x*/*a*	0.060 4(5)	4.5(4)	
C(1)	0.195 9(9)	= 2*x*/*a*	0.081 0(6)	3.7(4)	
Cl	0.553 8(9)	= 2*x*/*a*	0.170 6(7)	15.5(5)	0.6667
C(2)	0.618(2)	= 2*x*/*a*	0.097(1)	11.0(6)	0.6667
N(2)	0.0	0.0	0.25	6.6(6)	
C(3)	0.0	0.0	0.320(1)	9.0(6)	0.5
C(4)	0.085(2)	= 2*x*/*a*	0.218(2)	10.9(6)	0.5

Table 3 (*contd.*)

Atom[b]	x/a	y/b	z/c	$B_{\mathrm{eq}}/\text{Å}^{2}$ [c]	Occupancy[d]
V-2: $[NMe_4\cdot 2CH_2{=}CCl_2][Cd_3(CN)_7]$[g]					
Cd(o)	0.0	0.0	0.0	2.73(3)	
Cd(t)	0.3333	0.6667	0.114 76(7)	3.02(4)	
CN	0.3333	0.6667	0.222(1)	3.9(5)	
N(1)	0.127 7(7)	$= 2x/a$	0.060 6(5)	4.0(3)	
C(1)	0.194 4(9)	$= 2x/a$	0.081 1(5)	3.6(3)	
Cl	0.571 06(4)	$= 2x/a$	0.170 9(7)	15.7(7)	0.6667
N(2)	0.0	0.0	0.25	11(2)	
C(2)	0.0	0.0	0.301(6)	13(2)	
C(3)	0.103(2)	$= 2x/a$	0.208(2)	15(2)	
V-3: $[NMe_4\cdot 2EtCN][Cd_3(CN)_7]$					
Cd(o)	0.0	0.0	0.0	2.23(3)	
Cd(t)	0.3333	0.6667	0.119 58(5)	2.47(2)	
CN(1)	0.3333	0.6667	0.223 4(7)	4.7(2)	
N(1)	0.127 5(5)	$= 2x/a$	0.061 8(3)	3.6(2)	
C(1)	0.195 0(5)	$= 2x/a$	0.085 4(3)	3.0(2)	
CN(2)	0.653(2)	$= 2x/a$	0.200(2)	17.2(2)	0.6667
CN(3)	0.723(2)	$= 2x/a$	0.091(2)	22.2(2)	0.6667
N(2)	0.0	0.0	0.25	12.9(3)	
C(2)	0.0	0.0	0.322 2(9)	11.6(3)	0.5
C(3)	0.075(2)	$= 2x/a$	0.203(2)	14.7(3)	0.5
V-4: $[SMe_3\cdot 2CH_2ClCH_2Cl][Cd_3(CN)_7]$					
Cd(o)	0.0	0.0	0.0	3.84(8)	
Cd(t)	0.3333	0.6667	0.113 7(1)	4.03(6)	
CN	0.3333	0.6667	0.222(1)	5.4(8)	
N(1)	0.126(1)	$= 2x/a$	0.061 5(7)	6.3(7)	
C(1)	0.194(1)	$= 2x/a$	0.079 8(8)	4.6(6)	
Cl	0.562(1)	$= 2x/a$	0.170 9(7)	19.5(6)	0.6667
C(2)	0.717(3)	$= 2x/a$	0.092(2)	12(1)	0.6667
S	0.0	0.0	0.216(1)	11.9(8)	0.5
C(3)	0.098(7)	$= 2x/a$	0.233(6)	10(3)	0.25
C(4)	0.19(2)	0.18(2)	0.25	13(3)	0.5
V-5: $[NH_2(CH_2)_3NMeH_2\cdot 2CH_2Cl_2][Cd_3(CN)_7]$[h]					
Cd(o)	0.0	0.0	0.0	3.4(1)	
Cd(t)	0.3333	0.6667	0.113 6(1)	3.60(9)	
CN	0.3333	0.6667	0.225 0(9)	5.3(9)	
N(1)	0.122 6(9)	$= 2x/a$	0.065 1(5)	4.3(7)	
C(1)	0.195 0(9)	$= 2x/a$	0.081 4(6)	3.8(3)	
Cl(1)	0.576 2(9)	$= 2x/a$	0.170 6(7)	5.4(9)	0.3333
Cl(2)	0.702(2)	$= 2x/a$	0.097(1)	8(1)	0.3333
VI-1: $[NMe_2(CH_2)_3NMe_2H\cdot CH_2ClCH_2Cl][Cd_3(CN)_7]$					
Cd(o)	0.340 5(3)	0.0	0.0	2.8(1)	
Cd(o′)	0.135 3(3)	0.737 0(1)	0.5	2.8(1)	
Cd(t1)	0.162 1(3)	0.194 1(2)	0.0	2.9(1)	
Cd(t1′)	0.603 3(3)	0.301 1(2)	0.0	4.7(2)	
Cd(t2)	0.368 1(3)	0.551 6(2)	0.5	3.4(1)	
Cd(t2′)	0.066 7(3)	0.939 7(2)	0.5	2.9(1)	
N(1)	0.742(3)	0.580(1)	0.0	4.4(4)	
N(2)	0.410(3)	0.920(1)	0.0	3.5(4)	
N(3)	0.790(2)	0.478(1)	0.199(3)	3.9(4)	
N(4)	0.525(3)	0.524(1)	0.197(3)	5.3(4)	
N(5)	0.218(3)	0.659(1)	0.5	4.4(4)	
N(6)	1.060(3)	0.817(1)	0.5	4.5(4)	
N(7)	0.994(3)	0.716(1)	0.319(3)	4.2(4)	
N(8)	0.275(3)	0.762(2)	0.342(3)	7.8(4)	
C(1)	0.768(3)	0.618(1)	0.0	3.5(4)	
C(2)	0.426(4)	0.881(1)	0.0	3.5(4)	
C(3)	0.840(2)	0.464(1)	0.299(3)	3.7(4)	
C(4)	0.474(3)	0.534(1)	0.298(3)	5.5(4)	
C(5)	0.267(3)	0.623(2)	0.5	5.1(4)	
C(6)	1.058(3)	0.858(1)	0.5	3.3(4)	
C(7)	0.940(2)	0.711(1)	0.211(3)	4.2(4)	
C(8)	0.309(3)	0.772(2)	0.228(3)	6.5(4)	

Table 3 (*contd.*)

Atom[b]	x/a	y/b	z/c	B_{eq}/Å^2 [c]	Occupancy[d]
CN(1)	0.581(3)	0.761(2)	0.0	3.0(4)	
CN(2)	0.673(3)	0.742(2)	0.0	3.3(4)	
CN(3)	0.209(3)	0.498(1)	0.5	2.8(4)	
CN(4)	0.120(3)	0.478(3)	0.5	2.3(4)	
Cl(1)	0.055(2)	0.074(7)	0.5	9.5(4)	
Cl(2)	0.384(3)	0.138(1)	0.374(3)	10.7(4)	0.5
Cl(3)	0.100(3)	0.608(1)	0.054(3)	12.2(4)	0.5
Cl(4)	0.385(3)	0.638(1)	0.0	15.2(4)	
C(9)	0.200(3)	0.106(2)	0.5	8.8(4)	
C(10)	0.246(3)	0.102(2)	0.378(4)	4.8(4)	0.5
C(11)	0.236(3)	0.639(2)	0.114(3)	5.2(4)	0.5
C(12)	0.233(3)	0.615(2)	0.0	6.0(4)	
N(9)	0.124(4)	0.329(2)	0.0	10.4(4)	
N(10)	0.173(4)	0.472(2)	0.0	11.6(4)	
N(11)	0.357(3)	0.296(2)	0.5	9.4(4)	
N(12)	0.491(3)	0.382(2)	0.5	7.2(4)	
C(13)	0.109(4)	0.355(3)	0.147(4)	8.4(4)	0.5
C(14)	0.207(4)	0.360(2)	0.092(4)	6.8(4)	0.5
C(15)	−0.018(4)	0.331(2)	0.0	11.4(4)	
C(16)	−0.032(4)	0.387(2)	0.0	10.2(4)	
C(17)	0.065(4)	0.433(2)	0.0	10.5(4)	
C(18)	0.173(4)	0.527(2)	0.021(5)	8.0(4)	0.5
C(19)	0.254(4)	0.477(3)	0.128(4)	8.4(4)	0.5
C(20)	0.288(4)	0.251(2)	0.5	10.0(4)	
C(21)	0.449(4)	0.264(3)	0.434(4)	7.1(4)	0.5
C(22)	0.276(4)	0.295(3)	0.362(4)	7.1(4)	
C(23)	0.274(4)	0.323(3)	0.5	10.5(4)	
C(24)	0.356(4)	0.370(2)	0.5	10.3(4)	
C(25)	0.585(4)	0.401(3)	0.389(4)	7.7(4)	
C(26)	0.460(4)	0.397(3)	0.346(4)	7.8(4)	

[a] Atoms are arranged in the order of host cyanocadmate, neutral guest and onium guest separated by a broken line in each compound; disordered atoms are shown in italic. [b] The notation CN is for the atom with 50% each probability of C and N. [c] The value is B_{iso}/Å^2 for the guest atoms in **I-2**, and CN(2) and CN(3) in **V-3**. [d] Occupancy for the atom in disorder statistically distribed. [e] Both central C of CH_2Cl_2 and N of NEt_4 have been located on the same position as CN(2). [f] Guest atoms could not be refined. [g] Carbon atoms of $CH_2{=}CCl_2$ could not be refined. [h] Onium guest and C of CH_2Cl_2 could not be refined.

comparison of the respective structures with related mirror planes. An infinite chain composed of –(NC)–Cd(t)–CN–Cd(o)–NC–Cd(t)– (T–O–T) units is found along each of these mirror planes. In type **IV** an infinite chain of P–O–T units is also added: a trigonal-bipyramidal five (or penta)-co-ordinated Cd(p) is formed by co-ordination of NMe_3 to one of the tetrahedral Cd atoms. The CN groups out of the mirror plane bridge Cd(o) on the mirror plane and Cd(t) atoms on adjacent planes and *vice versa*. The Cd(o) atoms always take CdN_6 co-ordination, *i.e.* Cd(o) is linked with N atoms of the CN bridges to six Cd(t) atoms which include Cd(p). An ambiguous case is for Cd(o′) and Cd(t2′) in **VI-1**, as mentioned later.

The intra- and inter-chain Cd–(CN)–Cd linkages frame the polygonal faces of polyhedral cavities, although some of the polygons such as tetragons, pentagons and hexagons with Cd vertices and –CN– edges are significantly deformed and puckered. Polygons in the following description of cavity structure include those of chair- and boat-form topologically closed structures.

The bond distances and angles in the host structures are not unusual except for some that are considerably distorted. The Cd(o)–N distances are within the range 2.29–2.42 Å with angles 90 ± 5°; the corresponding distances Cd(t)–C are 2.17–2.28 Å with angles 109.5 ± 10°. Because of orientational disorder of the CN group between the tetrahedral Cd atoms, the Cd–(CN) distances are in the range 2.12–2.30 Å. In **VI-1**, exceptionally short Cd(o′)–N(8) [2.19(3) Å] and long Cd(t1′)–C(8) distances [2.41(3) Å] were obtained, which suggest that the orientation of the C(8)–N(8) group is reversed. However, since no significant improvement in the refinement was achieved assuming the reversed orientation, the present assignment has been tentatively adopted.

Type **I** *Structures*.—The reflection data supported the Laue class $\bar{3}m$. Based on the obverse setting of the hexagonal axes, the observed reflections satisfied the conditions $-h + k + l = 3n$. Among three possible space groups $R3m$, $R32$ and $R\bar{3}m$, the best convergence was given for $R\bar{3}m$, although essentially identical results were obtained for all three. The Cd(o) atom was located at the origin with $\bar{3}m$ site symmetry and Cd(t) at 0, 0, z with $3m$ symmetry. As the space group was $R\bar{3}m$ discrimination between the C and N atoms of CN linking crystallographically equivalent Cd(t) atoms was impossible.

Cross-linking of the –(T–O–T–)$_n$ chains produces a cavity surrounded by three O–T$_2$–O tetragons and three chair-form O–(T–T)$_2$–O hexagons to be denoted by [4^36^3], as shown in Fig. 1. In shape the cavity resembles the adamantane-like cavity of the cristobalite-like host[1c–g] but capped by a Cd(t)(–CN–)$_3$ moiety on a chair-form hexagon. Since only one kind of crystallographically independent cavity IA is formed in type **I**, each of the onium and neutral guests distributes with 50% probability in a cavity, *i.e.* the distribution of the guest species is random.*

---

* In **I-1**, the N–C bond lengths in NMe_4^+ and Sn–C in $SnMe_4$ were constrained at 1.46(2) and 2.14(2) Å, respectively, in the final stage of the refinement. When space group $R3m$ (no. 160) was applied, discrimination between the C and N atoms of CN and between the cavities accommodating the respective guests were theoretically possible, however the results did not show any significant differences. As for the guests in **I-2**, the N atom of NEt_4 and C atom of CH_2Cl_2 were located on the same coordinates as CN; the C–C and C–N bond lengths in NEt_4^+ and C–Cl in CH_2Cl_2 were constrained at 1.54(3), 1.48(3) and 1.76(3) Å, respectively, in the final refinement, where all the host atoms were refined anisotropically and the non-H guest atoms isotropically. It was extremely difficult to refine significant atomic parameters for the onium guest $Hdepn^+$ and the neutral guest $CHCl_3$ in **I-3**: only the host structure was refined anisotropically.

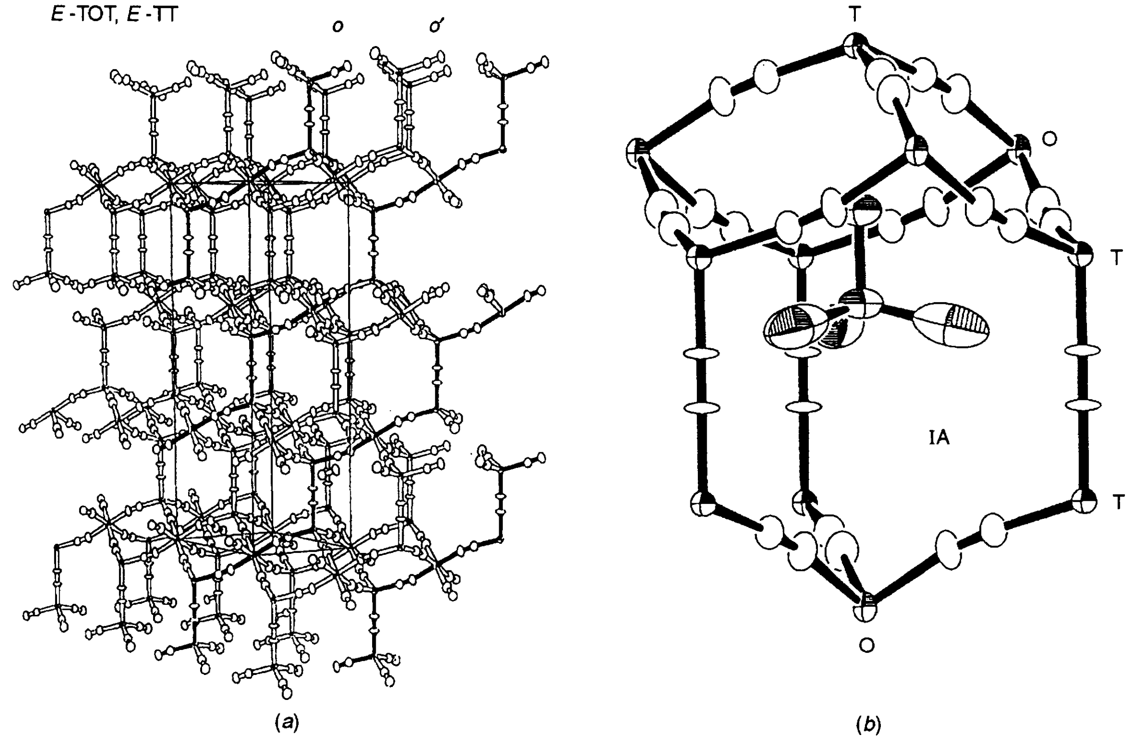

Fig. 1 (*a*) The host structure of type **I**; the -(T-O-T-)$_n$ chains running along the mirror plane (2*x*, *x*, *z*) are shown by solid lines. (*b*) NMe_4^+ in cavity IA of **I-1**; O and T refer to the octahedral and tetrahedral Cd atoms respectively. Anisotropic peripheries are shown for the Cd and guest atoms

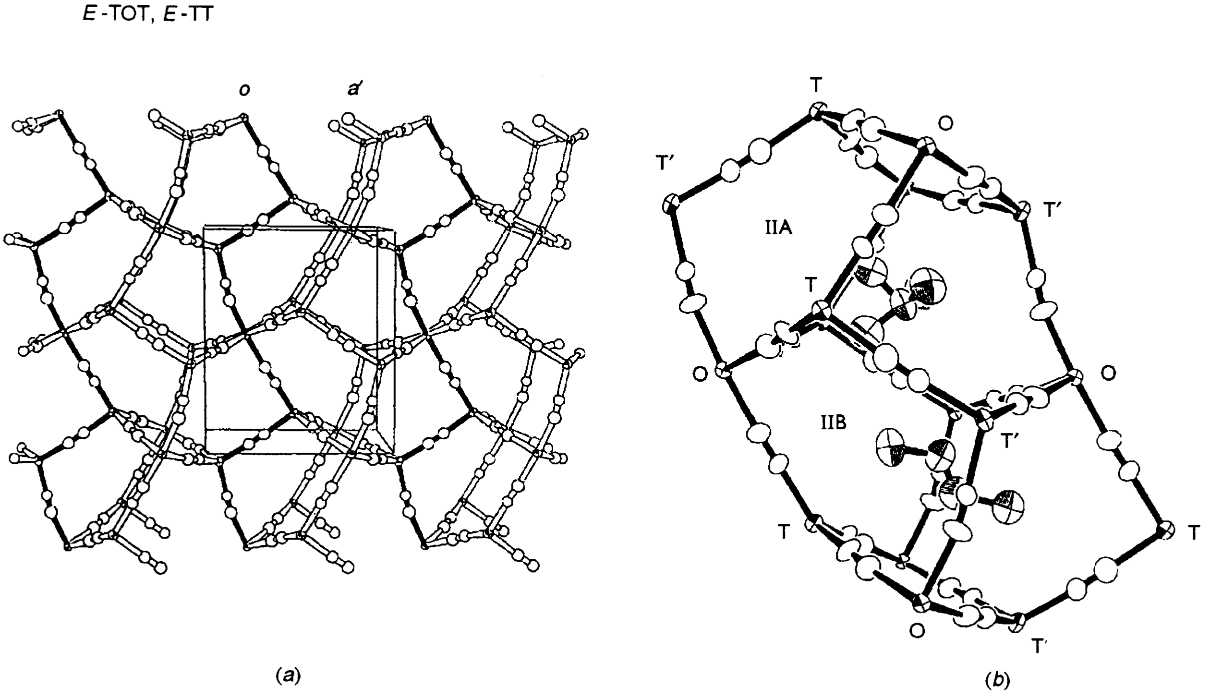

Fig. 2 (*a*) The host structure of type **II**; the -(T-O-T-)$_n$ chains running along the mirror plane at *c* = 0.5 are shown by solid lines. (*b*) NMe_4^+ in IIA and *trans*-ClHC=CHCl in IIB of **II-1**. Anisotropic peripheries are shown for the Cd and guest atoms

Type **II** *Structures*.—The observed systematic absences were consistent with space groups $Pn2_1m$ (no. 31) and *Pnmm* (no. 59); the non-centrosymmetric $Pn2_1m$ gave chemically acceptable results uniquely. Discrimination between Cd(t) and Cd(t'), and the C and N atoms of CN linking Cd(t) and Cd(t') was possible in this space group; Cd(t) is in a CdC_4 co-ordination and Cd(t') in CdC_3N. The Cd(t)-C and Cd(t')-N distances on the mirror plane are 2.19(2) and 2.28(2) Å for **II-1**, 2.21(1) and 2.28(1) Å for **II-2**, and 2.214(8) and 2.313(8) Å for **II-3**. If the criterion is strictly applied, the discrimination is inadequate for **II-1**.

Crystallographically independent but topologically the same two kinds of cavities are formed, as shown in Fig. 2. One, cavity IIA [$4^15^46^1$], is surrounded by a T-O_2-T' tetragon at the top, two T-O-T-O-T'- and two T'-O-T'-T-O- pentagons at the sides, and an O-(T-T')$_2$-O hexagon at the bottom; the other, IIB [$4^15^46^1$], by the O-(T-T')$_2$-O hexagon shared with IIA at the top, a T-O_2-T' tetragon at the bottom and two O-T-T'-O-T-

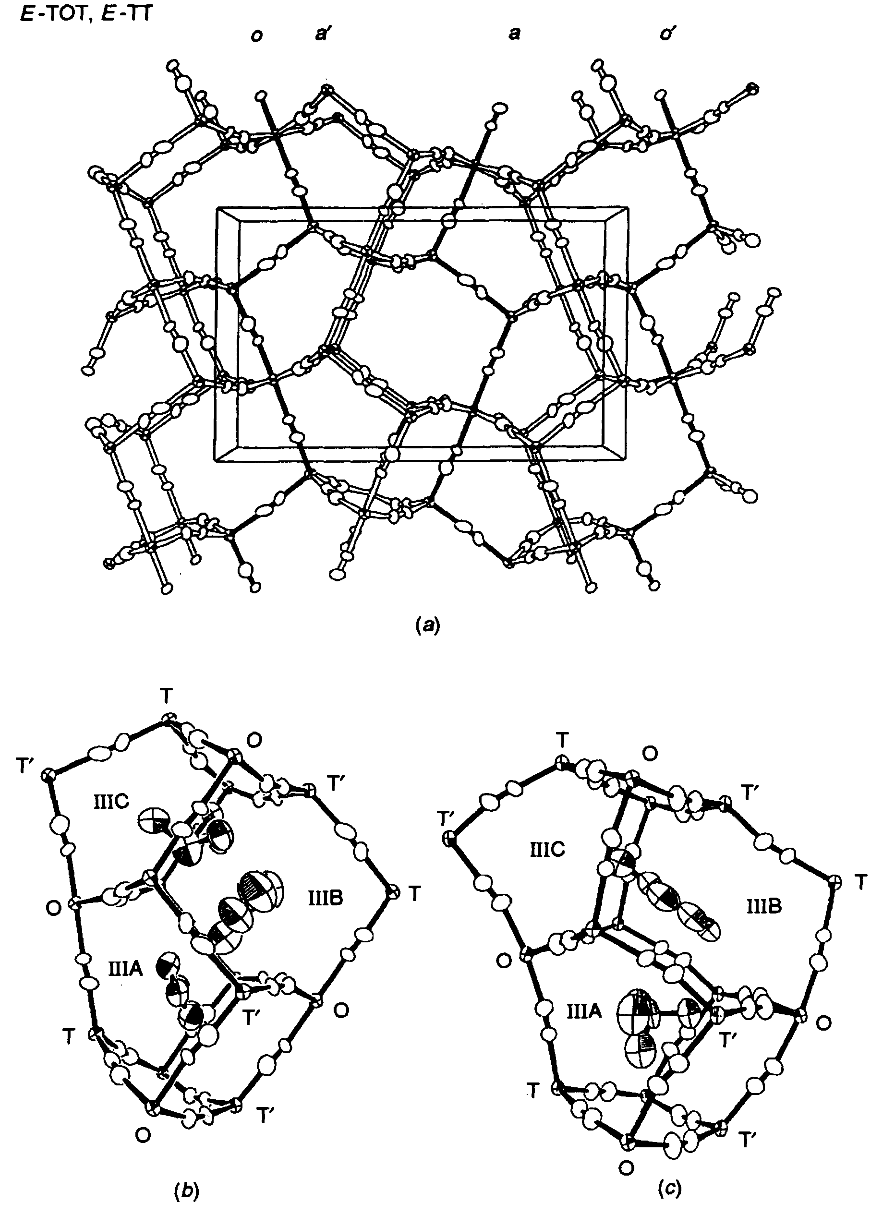

Fig. 3 (*a*) The host structures of type **III**; the -(T-O-T-)$_n$ chains running along the mirror plane at c = 0.25 are shown by solid lines. (*b*) C_6H_6 in IIIA, C_6H_6 in IIIB and NMe_4^+ in IIIC of **IIIa-2**. (*c*) NMe_4^+ in IIIA and MeC_6H_5 in IIIB through IIIC for **IIIb-1**. Anisotropic peripheries are shown for the Cd and guest atoms

and two O–T–T′–O–T′– pentagons at the sides. With respect to the co-ordination polyhedra, both cavities are surrounded by seven tetrahedra and four octahedra. In spite of the equivalence in topology between cavities IIA and IIB, the respective onium guests NMe_4^+, $Hdmpn^+$ and $Hdepn^+$ always prefer cavity IIA regardless of their molecular geometries.*

Type **III** *Structures*.—The observed systematic absences were consistent with space groups *Pna*2$_1$ (no. 33) and *Pnam* (no. 62); the latter was chosen because it gave chemically acceptable results. Although in theory the space group allowed discrimination between the C and N atoms of CN linking Cd(t) and Cd(t′), in practice it was ambiguous. The assumed Cd(t)–C and Cd(t′)–N distances were 2.21(4) and 2.35(5) Å for **IIIa-1**, 2.27(1) and 2.25(1) Å for **IIIa-2**, 2.209(9) and 2.204(9) Å for **IIIb-1** and 2.16(2) and 2.30(2) Å for **IIIb-2**. Considerable ambiguities remain except for **IIIb-2**. There are also three kinds of crystallographically independent Cd atoms, Cd(o), Cd(t) and Cd(t′).

Three kinds of cavities, IIIA, IIIB and IIIC, can be defined, although the mutual openings are rather wide, as shown in Fig. 3. Cavity IIIA [$4^3 5^2 6^1$] is surrounded by an O–(T–T′)$_2$–O hexagon at the top, two O–T–T′–O–T– pentagons at the sides and three tetragons, one T–O$_2$–T′ at the bottom and two T′–O$_2$–T′ at the sides; IIIB [$6^2 8^1$] by an O–(T′–T–O)$_2$–T′ octagon from the bottom through to the top and two O–T′–T–O–T′–T– hexagons at the sides; IIIC [$5^2 6^1$] by a T–(T–O)$_2$–O hexagon from the bottom through to the top and two O–T′–T–O–T–

---

* Both $Hdmpn^+$ and $Hdepn^+$ appear to form an intramolecular hydrogen bond between the amino group and the substituted amino group in the cavity: the N–N distance is 2.69(2) Å for $Hdmpn^+$ and 2.76(2) Å for $Hdepn^+$. When the coiled skeletons are viewed from the amino group to the substituted amino group, the projection of the coil is in a clockwise orientation for $Hdmpn^+$ and counterclockwise for $Hdepn^+$ along the c axis of the given unit-cell setting. Refinement with the counterclockwise orientation of $Hdmpn^+$ gave the reversed Cd(t)–C and Cd(t′)–N distances, 2.27(1) and 2.24(1) Å, respectively. Although the clockwise orientation has been adopted in the final results, the problem of CN discrimination has not been solved.

pentagons at the sides. According to the positions of the respective guests in these cavities, type **III** compounds are divided into two sub-groups, **IIIa** and **IIIb**. In **IIIa**, the onium guest is accommodated in cavity IIIC and the benzene molecules are in IIIB and IIIA; in **IIIb** the onium in IIIA, and the substituted benzene guest places the benzene ring in IIIB and the substituent(s) in IIIC. Hence, the limiting formula is given by [am·2G][$Cd_3(CN)_7$] for the former and [am·G][$Cd_3(CN)_7$] for the latter, although non-stoichiometric occupation of the aromatic guests was observed for both sub-groups.*

Type **IV** *Structure*.—Only one example has been obtained for this type, which differs remarkably from the other five because of the participation of trigonal-bipyramidal five-coordinate Cd(p). The space group *Pnam* was chosen similarly to type **III**. As shown in Fig. 4, there are six crystallographically independent Cd atoms, two Cd(o,o′), three Cd(t1, t1′, t2) and one Cd(p) in the unit cell with the extremely long *a* dimension of 43.39(1) Å. The five-co-ordination of Cd(p) is attained by ligation of the unidentate neutral NMe_3. Two kinds of chain unit, T–O–T and P–O–T, are observed running along the mirror planes: T–O–T of Cd(t1)–Cd(o)–Cd(t2) and P–O–T of Cd(p)–Cd(o′)–Cd(t1′). According to the symmetry requirements of the space group, T and P chains are alternately arranged at c = 0.25 and 0.75 Å along the *a* axis in the repeating order of T, P, P and T. The Cd(t1′)–CN–Cd(p) distance of 5.99(2) Å is unusually long, but the Cd(t1′)–C and Cd(p)–N distances of 2.28(2) and 2.76(2) Å make discrimination between the C and N atoms clear. Discrimination for the CN group linking Cd(t1) to Cd(t2) was impossible as the distances Cd–(CN) 2.24(2) Å were the same.

Five kinds of cavities IIA [$4^15^46^1$], IIB [$4^15^46^1$], IIIA [$4^35^26^1$], IIIB [6^28^1] and IIIC [5^26^1], similar to but distorted from those in types **II** and **III**, are formed in the host framework. The ligating NMe_3 occupies IIIA; IIA and IIIB accommodate respectively a CH_2ClCH_2Cl molecule, and each of IIB and IIIC an NMe_3H^+. Similarly to type **III**, the CH_2ClCH_2Cl molecule in IIIB appears to be non-stoichiometric from the accuracies of the refined parameters; the values of the measured densities were scattered also.

Type **V** *Structures*.—The diffraction data supported the Laue class 6/*mmm*; the space group *P*6_3/*mmc* was chosen as the most reasonable for the host framework in the high symmetry. As shown in Fig. 5, there are two kinds of cavities, the smaller VA [6^3] and the larger VB [4^66^3], in the framework. Cavity VA, surrounded by three O–(T–T)$_2$–O boat-form hexagons, *i.e.* an O–(T–T)$_3$–O cage, has the shape of bicapped trigonal prism, in which the onium guest is accommodated. Cavity VB has the shape of a truncated trigonal prism surrounded by three boat-form hexagons of VA cavities at the sides but capped by three T–O_2–T tetragons at the top and three at the bottom so as to expand the cavity volume from VA. A pair of the neutral guests are accommodated in VB. Both the cationic and neutral guests are highly disordered in each compound; their molecular symmetries have little correlation with the site symmetry of the cavity centre.

With respect to the pyrosilicate-like T–T unit of the (-NC–)$_3$Cd–(CN)–Cd(–CN–)$_3$ moiety, it takes a staggered conformation in trigonal type **I**, but an eclipsed one in hexagonal type **V**.

Type **VI** *Structure*.—The space group *Pb*2_1*m* (no. 26) was chosen as the most reasonable among those possible from the observed systematic absences including *Pbm*2 (no. 28) and *Pbmm* (no. 51). Two formula units are crystallographically independent of the long *b* dimension, 27.553(1) Å in the unit cell. Discrimination between the C and N atoms of CN linking Cd(t) and Cd(t′) was practically impossible.

Although four kinds of crystallographically independent cavities are formed, two each of the four are topologically the same as each other so as to be classified as VIA and VIB, as shown in Fig. 6. Cavity VIA [$4^15^46^1$] is topologically the same as IIA in type **II**: an O–(T–T′)$_2$–O hexagon at the top, two each of O–T–T′–O–T– and O–T–T′–O–T′– pentagons at the sides and a T–O_2–T′ tetragon at the bottom. The disordered CH_2ClCH_2Cl molecule is accommodated in VIA. Cavity VIB [4^36^3] shares the hexagon with VIA at the bottom and is surrounded by two O–T–T′–O–T′–T– hexagons and three T–O_2–T′ tetragons; the onium guest Htmpn$^+$ forms an intramolecular hydrogen bond in cavity VIB.

Discussion

Classification of the Host Structures.—Three ways of bending the –(T–O–T–)$_n$ chains on the mirror planes in the host structures have been observed [in type **IV** –(P–O–T–)$_n$ is considered as –(T–O–T–)$_n$]: (*a*) *E*–TOT,*E*–TT for types **I–IV**, (*b*) *E*–TOT,*Z*–TT for type **V** and (*c*) *Z*–TOT,*E*–TT for type **VI**, as illustrated in Fig. 7. The notation *E*–TOT denotes that the chain bends in opposite directions at the ends of the T–O–T unit; *Z*–TOT denotes that the chain bends in the same direction. When the T–O–T units are coupled with opposite bending at the T–T junction, the mode is *E*–TT. Hence it is impossible to extend a sequence of *Z*–TOT and *Z*–TT as infinite chain on a plane.

As has been illustrated in Figs. 1–6, the relative arrays of the respective chains on the same and adjacent planes gives the varieties of the structures from type **I** to type **VI**. In type **I**, the array of *E*–TOT,*E*–TT chains on a mirror plane generates the same array on an adjacent plane by an appropriate parallel translation. In type **II**, the selected chain is correlated with that on the adjacent plane by a 2_1 screw rotation, *i.e.*, the direction of bending is alternately reversed between the planes. If the chain

---

* The structure of **IIIa-1** was solved with full occupation of the benzene molecules in cavities IIIA and IIIB, however SMe_3^+ is distributed statistically with respect to the mirror plane in cavity IIIC. The C_6H_6 molecules in IIIB cavities are arranged along the *c* axis of the crystal with an alternate deviation from the centre of the cavity to the hexagonal face shared with cavity IIIA; the deviation appears to lessen the steric repulsion between the C_6H_6 molecules in the next cavity along the *c* axis. The thermal amplitudes of the C_6H_6 molecules in IIIB appear to be about twice as large as those of C_6H_6 in IIIA.

It appears that the repulsion is stronger in **IIIa-2** than in **IIIa-1**, since the C_6H_6 in IIIB of **IIIa-1** is located at the cavity centre with a refined occupancy factor of 0.57 and considerably greater thermal amplitudes than those in IIIA. The occupancy of *ca.* 0.5 means that the occupied and vacant cavities IIIB are alternately arranged. This may be due to the invasion of the Me groups of NMe_4^+ in IIIC to IIIB through the hexagonal opening to such an extent as to lessen the effective volume of IIIB. With this respect SMe_3^+ in **IIIa-1** should be less effective than NMe_4^+.

In contrast with the former sub-group, the onium is accommodated in cavity IIIA and the aromatic guests in IIIB for **IIIb-1** and **IIIb-2**. The aromatic plane of the guest in IIIB takes an orientation rotated by 90° about the *c* axis from that in the **IIIa** sub-group; the Me group of C_6H_5Me in **IIIb-1** is located at a position similar to the onium guest in **IIIa**. One of the Me groups from the $C_6H_3Me_3$-1,3,5 molecule in **IIIb-2** invades cavity IIIC similarly to that of C_6H_5Me, but leaves the remaining two Me groups related to the mirror plane in cavity IIIB to bring about great repulsion between the neighbouring guests along the *c* axis. The occupancy was refined to 0.667: two thirds of the total IIIB cavities should be occupied by the mesitylene molecules. Moreover, the molecule is distributed statistically at two positions in the IIIB cavity: the Me group invades IIIC to a greater extent in one than the other with a ratio of 1 : 3. The deeper position reduces the repulsion between the neighbouring mesitylenes. If a neighbouring cavity is vacant, the less deep position should be energetically stable. When both positions were arranged in order, a superlattice structure with at least three times the *c* dimension should have been obtained from the reflection data. It was not. Hence the occupancies of the cavity and the position are both in disorder in the crystal analysed.

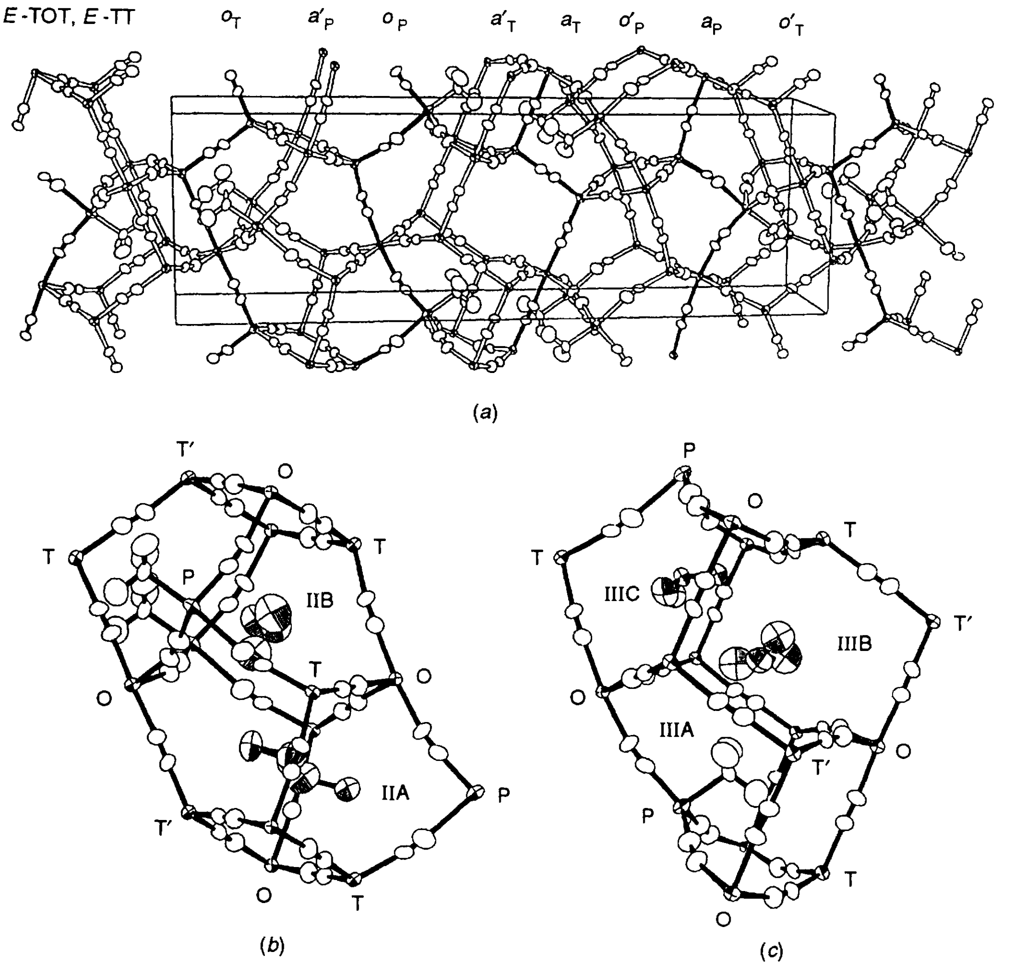

Fig. 4 (*a*) The host structure of type **IV**; the $-(\text{T–O–T–})_n$ and $-(\text{P–O–T–})_n$ chains running along the mirror plane at $c = 0.25$ are shown by solid lines. (*b*) CH_2ClCH_2Cl in IIA and NMe_3H^+ in IIB and (*c*) NMe_3 in IIIA, CH_2ClCH_2Cl in IIIB and NMe_3H^+ in IIIC of **IV-1**. Anisotropic peripheries are shown for the Cd and guest atoms

first selected is seen to take an '*ortho*' arrangement *o*, those on the adjacent planes are in the '*anti*' arrangement *a*. This mode of array may be denoted *o*–*a*' with the prime for the chain on the adjacent plane, where the difference between T and T', or T and P, is neglected. In type **III**, the chains in *o* and *a* are alternately arranged on the same plane along the *a* axis, but the interplane arrangement is *o*–*a*'–*a*–*o*'. In type **IV**, the arrangement is *o*–*a*'–*o*–*a*'–*a*–*o*'–*a*–*o*' to make the *a* dimension the longest among types **II**, **III** and **IV**; discriminating the T and P chains gives o_T–a'_P–o_P–a'_T–a_T–o'_P–a_P–o'_T. The *a* dimension is approximately two times that of type **II** for type **III** and three times that for type **IV**. In type **V**, the *E*–TOT,*Z*–TT chains are arranged in the *o*–*o*' mode. Type **VI** is the only example of *Z*–TOT,*E*–TT with the *o*–*a*' arrangement.

Comparison with Zeolite Structures.—Although the number of the structures analysed were still limited to 17 for the $[Cd_3(CN)_7]^-$ host inclusion compounds, at least six variations in the structural pattern have been found on the basis of the difference in bending and relative arrangement of the $-(\text{T–O–T–})_n$ chains. The non-stoichiometric character of the neutral guest molecules observed for some examples suggests that the behaviour of the guests is similar to those adsorbed in real zeolite frameworks. The negative charge of the host and the cationic guest inside the framework also show similarity to real zeolites.

The resemblance of the cyanometal complex framework structures with zeolites in adsorption behaviour has been reported for $K_2Zn_3[Fe(CN)_6]_2\cdot xH_2O$[6] and $Zn_3[Co(CN)_6]_2\cdot 12H_2O$.[7] Reversible adsorption behaviour was observed on their dehydrated complexes for some small inorganic and organic molecules. The structures of these host complexes[8,9] have disorder to a more or less extent with regard to the alkali-metal cations and water molecules.

Another kind of three-dimensional framework built of nonacyanotetracadmate $[Cd_4(CN)_9]^-$ has recently been discovered with a 3:1 ratio of Cd(t) and Cd(o) which host K^+ and EtCN as guests to give the clathrate $[K\cdot 4EtCN][Cd_4(CN)_9]$.[10] The host has the –O–T–T'–T''– chains running along the mirror planes vertical to the *b* axis of the *Pnma* unit cell with an *o*–*a*'–*a*–*o*' array; the interchain connections by the out-of-plane cyanides give cavities with wider openings than those in the present structures. A heteropolycyanometalate host has also been demonstrated in $[(H_3O)_3(H_2O)_{11}][CdCu_2(CN)_7]$,[11] in which the pyrite-like three-dimensional framework structure built of octahedral Cd^{2+} and pyrosilicate-like $[Cu_2(CN)_7]^{5-}$ interpenetrates into the three-dimensional framework of the hydrogen-bonded partly protonated water molecules. The three-dimensional framework discovered in an early example of supramolecular crystallography, $[Cu(H_2O)(en)_2][Cu_2(CN)_4]$, resembles the zeolite structure more than the present series, because its negatively charged host is comprised of tetrahedral Cu^I only as the co-ordination centre.[5b]

In conclusion no reasonable relationship between the structural modification of the host and the molecular structures of the relevant onium and neutral guests for the present 17 inclusion compounds has been obtained. The structural chemistry of iso- and hetero-polycyanometalates appears to have much more to be explored.

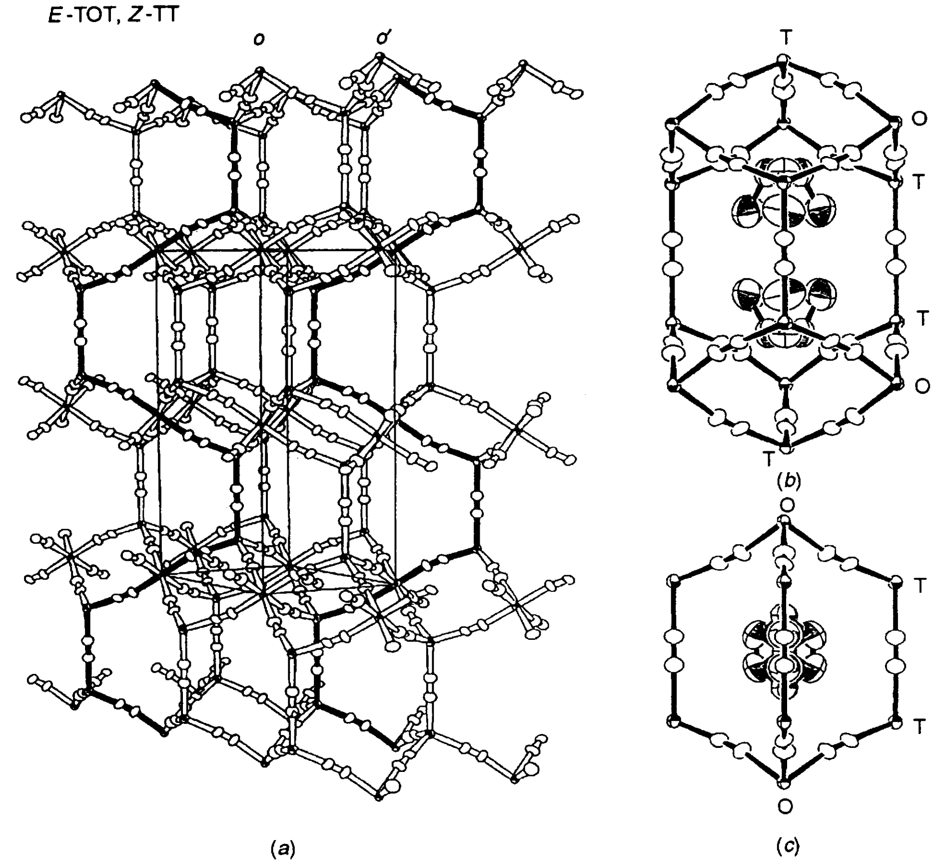

Fig. 5 (*a*) The host structure of type **V**; the -(T-O-T-)$_n$ chains running along the mirror plane [11$\bar{1}$0] are shown by solid lines. (*b*) A pair of disordered CH_2ClCH_2Cl in VB and (*c*) disordered NMe_4^+ in VA of **V-1**. Anisotropic peripheries are shown for the Cd and guest atoms

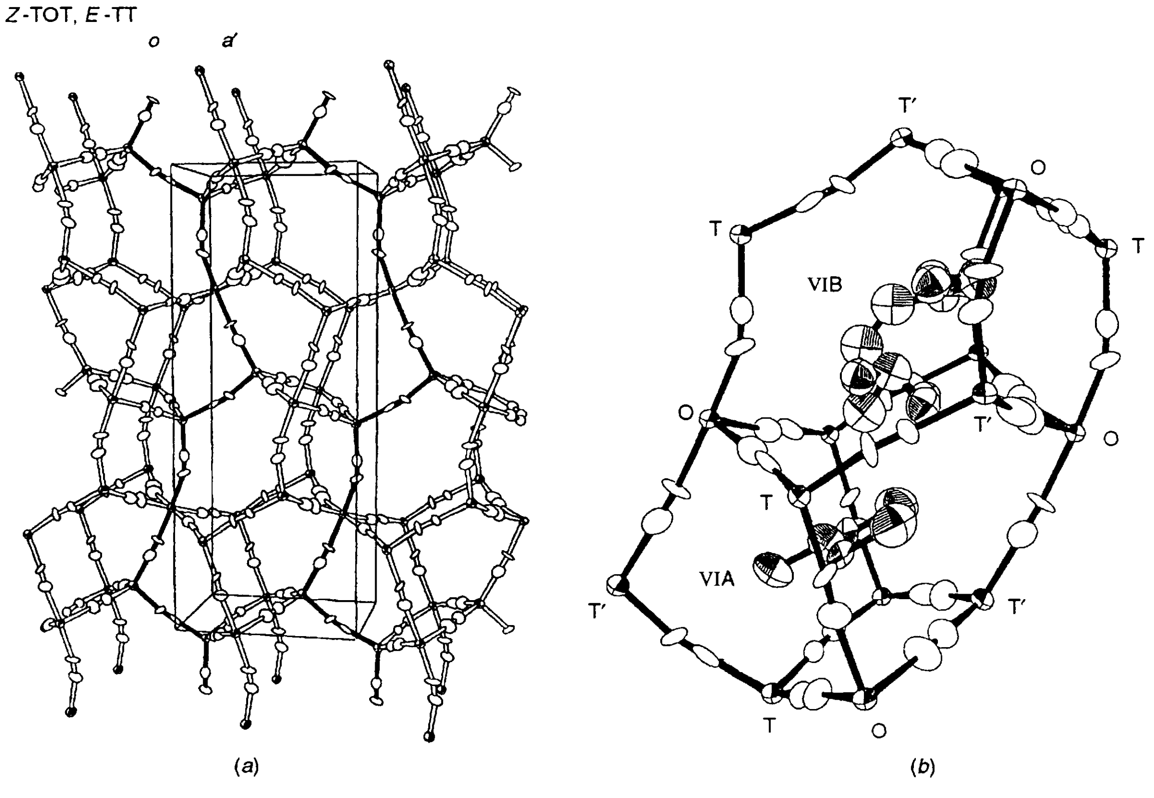

Fig. 6 (*a*) The host structure of type **VI** and (*b*) disordered CH_2ClCH_2Cl in VIA and disordered $NMe_2(CH_2)_3NMe_2H^+$ in VIB for **VI-1**. Anisotropic peripheries are shown for the Cd and guest atoms

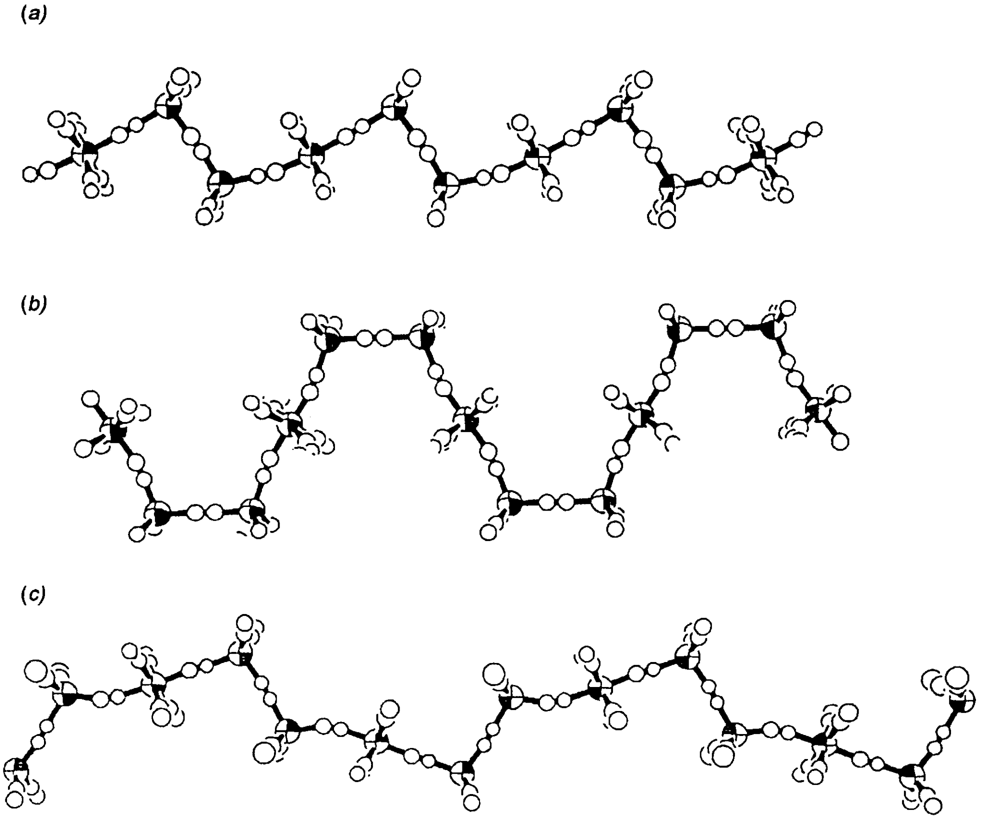

Fig. 7 Bending modes of -(T-O-T-)$_n$ chains on a mirror plane: (*a*) *E*-TOT,*E*-TT in types **I–IV**, (*b*) *E*-TOT,*Z*-TT in type **V** and (*c*) *Z*-TOT,*E*-TT in type **VI**

References

1 (*a*) T. Kitazawa and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 1993, 309; (*b*) T. Kitazawa, M. Akiyama, M. Takahashi and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 1993, 1112; (*c*) T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *Chem. Lett.*, 1988, 1729; (*d*) T. Iwamoto, in *Chemistry of Microporous Crystals*, eds. T. Inui, S. Namba and T. Tatsumi, Kodansha-Elsevier, Tokyo, 1991, pp. 3–10; (*e*) T. Iwamoto, T. Kitazawa, S. Nishikiori and R. Kuroda, in *Chemical Physics of Intercalation II, NATO ASI Series, B, Physics*, eds. P. Bernier, J. E. Fischer, S. Roth and S. A. Solin, Plenum, New York, 1993, vol. 305, pp. 325–332; (*f*) T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1992, 413; (*g*) T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, 1994, 1029; (*h*) T. Kitazwa, S. Nishikiori, R. Kuroda and T. Iwamoto, *Chem. Lett.*, 1988, 459; (*i*) T. Kitazawa, S. Nishikiori and T. Iwamoto, *Mater. Sci. Forum*, 1992, **91–93**, 257; (*j*) R. Kuroda, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 13; (*k*) T. Iwamoto, *Chem. Lett.*, 1973, 723; (*l*) S. Nishikiori and T. Iwamoto, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1985, **3**, 2283; (*m*) H. Yuge and T. Iwamoto, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1972, **14**, 217; (*n*) H. Yuge and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, 1993, 2841.

2 (*a*) R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 762; (*b*) S. R. Batten, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1991, 445.

3 (*a*) J. V. Smith, *Chem. Rev.*, 1988, **88**, 149; (*b*) F. Liebau, H. Gies, R. P. Gunawardane and B. Marler, *Zeolites*, 1986, **6**, 373.

4 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

5 (*a*) D. T. Cromer and A. C. Larson, *Acta Crystallogr., Sect. B*, 1973, **29**, 251; (*b*) R. J. Williams, A. C. Larson and D. T. Cromer, *Acta Crystallogr., Sect. B*, 1972, **28**, 858.

6 P. Cartraud, A. Cointot and A. Renaud, *J. Chem. Soc., Faraday Trans.*, 1981, **77**, 1561.

7 G. Boxhoorn, J. Moolhuysen, J. G. F. Coolegem and A. van Santen, *J. Chem. Soc., Chem. Commun.*, 1985, 1305.

8 P. Gravereau, E. Garnier and A. Hardy, *Acta Crystallogr., Sect. B*, 1979, **35**, 2843.

9 D. F. Mullica, W. O. Milligan, G. W. Beall and W. L. Reeves, *Acta Crystallogr., Sect. B*, 1978, **34**, 3558.

10 T. Kitazawa, H. Sugisawa, M. Takeda and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1993, 1855.

11 S. Nishikiori and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1993, 1555.

Received 26*th May* 1994; *Paper* 4/03143A