Silica-mimetic Polymorphism of the $Cd(CN)_2$ Host Lattice depending on the Guest G in $Cd(CN)_2{\cdot}xG$ Clathrates†

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The single-crystal structures have been determined for the $Cd(CN)_2$ host clathrates $Cd(CN)_2{\cdot}xBu^n{}_2O{\cdot}yH_2O$ (x, $y \approx 0.5$) **1**, $Cd(CN)_2{\cdot}0.5Bu^i{}_2O$ **2a**, $Cd(CN)_2{\cdot}0.5(Pr^iCH_2CH_2)_2O$ **2b**, $Cd(CN)_2{\cdot}Pr^iCl$ **2o**, $Cd(CN)_2{\cdot}CHCl_2CH_2Cl$ **3a**, $Cd(CN)_2{\cdot}Pr^iBr$ **3b** and $Cd(CN)_2{\cdot}Pr^iCN$ **4**, prepared in order to mimic the polymorphism of SiO_2 by $Cd(CN)_2$. The hexagonal $P6_3/mmc$ host lattice of **1** is isostructural with the high-temperature form of tridymite, accommodating the dibutyl ether guest in the channel cavity extending along the c axis and the water molecule is hydrogen bonded to the ether in the cage neighbouring the channel. The cubic $Fd\bar{3}m$ host lattice of **2** in the high-temperature cristobalite structure provides two neighbouring tetrahedral cavities for the respective alkyl ether guests in **2a** and **2b**; the structure of **2o** is the same. The cubic $Fd\bar{3}m$ lattice is transformed into the tetragonal $P4_12_12$ one in **3** and **4**, similar to the deformation from high- to low-temperature cristobalite, the lattice of **4** ($Z = 8$) being more distorted than those of **3a** and **3b** ($Z = 4$). The polymorphic behaviour of these $Cd(CN)_2$ lattices is discussed in terms of the geometry and function of the guest molecules.

The $Cd(CN)_2{\cdot}G$ clathrates that we have reported previously[1] have a three-dimensional host lattice of space group $Fd\bar{3}m$ isomorphous to the high-temperature form of cristobalite (H-cristobalite). Although the $Cd(CN)_2$ host provides a cavity approximating to a regular tetrahedron for each guest G, the accommodated guests exhibit not only tetrahedral or pseudo-tetrahedral symmetry, *e.g.* $CMe_{4-n}Cl_n$ ($n = 0$–4), but also molecular symmetries considerably lower than T_d, *e.g.* Pr^iCl, Pr^iCH_2Cl, $CHMeClCH_2Cl$, $CFCl_2CF_2Cl$, $CHCl_2CHCl_2$, $Bu^tCH_2CH_3$. Since the Cd–CN–Cd span of *ca.* 5.5 Å, longer than the Si–O–Si span of *ca.* 3.2 Å, makes the cavity considerably voluminous, appropriate guests are necessary to stabilise the three-dimensional framework structure of the silica-mimetic $Cd(CN)_2$ by filling up the cavity. It is theoretically possible for $Cd(CN)_2$ to mimic polymorphs of SiO_2 such as L-cristobalite, high- and low-temperature forms of tridymite and quartz, if guests of appropriate shape and size are available. We attempted to induce the transformation of the $Cd(CN)_2$ host into other SiO_2-like polymorphs using guest molecules of different sizes, shapes and symmetries. Two modifications of the L-cristobalite-like host in the space group $P4_12_12$ were obtained in $Cd(CN)_2{\cdot}G$ where $G = CHCl_2CH_2Cl$ or Pr^iBr ($Z = 4$) or Pr^iCN ($Z = 8$) respectively. The host of the dual guest clathrate $Cd(CN)_2{\cdot}xBu^n{}_2O{\cdot}yH_2O$ was found to have a H-tridymite ($P6_3/mmc$) structure. The hosts in $Cd(CN)_2{\cdot}0.5G$ where $G = Bu^i{}_2O$ or $(Pr^iCH_2CH_2)_2O$ are isomorphous to the previously reported $Fd\bar{3}m$ high-temperature cristobalite-like host, accommodating one guest molecule in two neighbouring cavities. This paper discusses the transformation of the three-dimensional $Cd(CN)_2$ host lattice upon change of the guest molecules based on single-crystal structures.

Recent theoretical studies[2] on host–guest interactions in Hofmann-type,[2a] Hofmann-en-type[2b] and $Cd(CN)_2$[2b] host clathrates also stimulated us to design and synthesise novel supramolecular structures. The $Cd(CN)_2{\cdot}G$ clathrate is the simplest in composition among the CN-bridged multi-dimensional clathrate structures so far developed by this group[1,3] and others.[4] Simpler systems appear to be more suitable for theoretical discussions than more complicated ones. However, a simple composition does not always mean a simple structure for supramolecular compounds.

Experimental

The clathrates $Cd(CN)_2{\cdot}xBu^n{}_2O{\cdot}yH_2O$ **1** (x, $y \approx 0.5$), $Cd(CN)_2{\cdot}xG$ [$G = Bu^i{}_2O$ **2a** or $(Pr^iCH_2CH_2)_2O$ **2b**, $x \approx 0.5$], $Cd(CN)_2{\cdot}G$ ($G = CHCl_2CH_2Cl$ **3a**, Pr^iBr **3b** or Pr^iCN **4**) were prepared and the single-crystal structure determinations carried out by methods similar to those described previously.[1a] The products, similar to those of the high-temperature crystobalite-like host, were so unstable under ambient conditions that their compositions were estimated from the results of the crystal-structure determinations and density measurements. The single-crystal structure refinement was also carried out for one of the previously reported clathrates, $Cd(CN)_2{\cdot}Pr^iCl$ **2o**. The presence of water in **1** and its absence in the other compounds was ascertained by Fourier-transform IR spectroscopy.

We again encountered the problems found in previous work:[1a,3a] discrimination between C and N in the Cd–(CN)–Cd linkages in the hosts and disorder in the molecular orientation of the guests. All the relevant C and N atoms were assumed to have 50% probability of being C and N and denoted as C•N; the linkage involving C•N is denoted as Cd–(CN)–Cd. Discrimination is essentially impossible for compounds **1** and **2** owing to the symmetry requirements of the space groups $P6_3/mmc$ and $Fd\bar{3}m$, but theoretically possible for **3** and **4** in the space group $P4_12_12$. However, the crystallographically independent Cd–C•N distances determined had insignificant differences, *e.g.* in **3a** between 2.17(2) and 2.19(2) Å, so that they were practically indistinguishable in the present structure refinement.

Refinement of the guest molecule was impossible for compounds **1**, **2a** and **2b** owing to the high degree of disorder, although some significant peaks in electronic density (1.20–0.4 e $Å^{-3}$), statistically distributed according to the symmetry reqirements of the relevant space groups, were observed in the

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

Table 1 Crystal and experimental data for $Cd(CN)_2{\cdot}xG$[a]

	1	**2a**	**2b**	**2o**	**3a**	**3b**	**4**
xG	0.5 ($Bu^n{}_2O{\cdot}H_2O$)	$0.5Bu^i{}_2O$	0.5 ($(Pr^iCH_2CH_2)_2O$)	Pr^iCl	$CHCl_2CH_2Cl$	Pr^iBr	Pr^iCN
Formula	$C_6H_{10}CdN_2O$	$C_6H_9CdN_2O_{0.5}$	$C_7H_{11}CdN_2O_{0.5}$	$C_5H_7N_2CdCl$	$C_4H_3CdCl_3N_2$	$C_5H_7BrCdN_2$	$C_6H_7CdN_3$
M	238.57	229.56	243.59	242.99	297.85	287.44	233.55
Crystal system	Hexagonal	Cubic	Cubic	Cubic	Tetragonal	Tetragonal	Tetragonal
Space group	$P6_3/mmc$	$Fd\bar{3}m$	$Fd\bar{3}m$	$Fd\bar{3}m$	$P4_12_12$	$P4_12_12$	$P4_12_12$
a^b/Å	8.888(3)	12.645(8)	12.69(1)	12.638(6)	8.978(6)	9.124(1)	12.483(7)
c/Å	14.945(6)				11.934(3)	11.335(3)	12.719(3)
U/Å^3, Z	1022.4(8), 4	2022(1), 8	2042(3), 8	2018.4(9), 8	961.0(6), 4	943.7(3), 4	1982(2), 8
D_c, D_m/g cm^{-3}	1.54, 1.29–1.48	1.51, 1.49(3)	1.58, 1.59(3)	1.60, 1.58(2)	2.06, 2.04(1)	2.20, 2.03(1)	1.56, 1.57(2)
μ(Mo-Kα)/cm^{-1}	20.78	21.00	20.86	23.60	30.44	63.34	21.39
Crystal size/mm	0.50 × 0.40 × 0.40	0.30 × 0.30 × 0.20	0.25 × 0.22 × 0.20	0.35 × 0.35 × 0.25	0.18 × 0.18 × 0.15	0.20 × 0.18 × 0.13	0.45 × 0.40 × 0.30
Scan width/°	1.10 + 0.30 tan θ	1.57 + 0.30 tan θ	1.63 + 0.30 tan θ	1.63 + 0.30 tan θ	1.00 + 0.30 tan θ	1.47 + 0.30 tan θ	1.52 + 0.30 tan θ
Scan range, 2θ/°	3–55	3–55	3–55	3–60	4–60	4–60	4–60
hkl ranges	0–20, 0–14, 0–10	0–10, 1–13, 0–8	1–14, 0–10, 0–8	1–14, 0–10, 0–8	0–13, 0–13, 0–17	0–13, 0–13, 0–16	0–15, 0–12, 0–16
N_o[c]	537	512	155	190	906	906	1738
N_r[c] for $I > n\sigma(I)$	194, 3	75, 3	76, 2	60, 3	271, 2.5	209, 3	829, 3
No. of parameters, N_p	14	7	5	9	56	43	91
R,[d] R'[d]	0.082, 0.106	0.072, 0.074	0.068, 0.070	0.073, 0.084	0.043, 0.025	0.057, 0.068	0.046, 0.044
Goodness of fit[d]	9.19	7.41	7.64	7.38	1.22	3.65	2.91
Maximum shift/e.s.d.	0.30	0.01	0.09	0.32	0.32	0.32	1.09
Maximum peak/e Å^{-3}	0.45	0.31	0.34	0.77	0.49	0.87	0.40

[a] Details in common: Rigaku AFC-5S diffractometer, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), ω–2θ scan at 295 K for epoxy-resin coated single crystal, TEXSAN software package[5] installed on the diffractometer for Lorentz polarisation-corrected reflections; densities measured by the flotation method in a bromoform–mesitylene mixture immediately after the crystals were removed from the mother-liquor. [b] $\alpha = \beta = 90°$ for all cases; $\gamma = 120°$ for **1** and 90° for the others. [c] N_o = Number of reflections measured; N_r = number of reflections used. [d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$; $w = 4F_o{}^2/[\sigma(F_o{}^2)]^2$; goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_r - N_p)]^{\frac{1}{2}}$.

Table 2 Refined atomic parameters *

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
1							
Cd	0.33	0.67	0.0663(2)	*C*(2)	0	0	0.3873
C·N(1)	0.33	0.67	0.215(2)	*C*(3)	0.08	0.16	0.3486
C·N(2)	0.464(2)	0.928	0.015(1)	*C*(4)	0.06	0.12	0.25
O(1)	0.33	0.67	0.75	*C*(5)	0.59	0.21	0.25
C(1)	0	0	0.5	*C*(6)	0.35	0.12	0.25
2a							
Cd	0.125	0.125	0.125	*C*(1)	0.375	0.375	0.375
C·N	0.0271(9)	0.0271	0.0271	*C*(2)	0.452	0.452	0.452
O(1)	0.5	0.5	0.5	*C*(3)	0.266	0.375	0.375
2b							
Cd	0.125	0.125	0.125	*C*(2)	0.449	0.449	0.449
C·N	0.0258(5)	0.0258	0.025 8	*C*(3)	0.306	0.306	0.306
O(1)	0.5	0.5	0.5	*C*(4)	0.238	0.375	0.375
C(1)	0.375	0.375	0.375				
2o							
Cd	0.125	0.125	0.125	*C*	0.42(2)	0.42	0.42
C·N	0.026(2)	0.026	0.026	*Cl*	0.321(5)	0.321	0.321
3a							
Cd	0.2963(2)	0.2963	0	*Cl*(2)	0.6098(7)	0.8466(8)	0.1249(5)
C·N(1)	0.261(2)	0.122(2)	0.127(1)	*C*(1)	0.79(1)	0.74(1)	0.03(1)
C·N(2)	0.234(2)	0.014(2)	0.174(1)	*C*(2)	0.68(1)	0.69(1)	0.043(5)
Cl(1)	0.888(7)	0.911(7)	0.979(3)				
3b							
Cd	0.3179(3)	0.3179	0	*Br*	0.9044(5)	0.9044	0
C·N(1)	0.274(3)	0.139(3)	0.116(3)	*C*(1)	0.755(6)	0.755	0
C·N(2)	0.242(3)	0.029(4)	0.168(2)	*C*(2)	0.627(5)	0.785(5)	0.055(7)
4							
Cd	−0.039 54(6)	0.244 20(7)	0.087 09(5)	N	0.105(1)	0.835(1)	0.036(1)
C·N(1)	0.069 6(8)	0.345 5(8)	0.189 4(7)	C(1)	0.034(2)	0.790(1)	0.098(1)
C·N(2)	−0.115 8(9)	0.370 8(8)	−0.009 6(9)	C(2)	−0.003(2)	0.741(3)	0.227(2)
C·N(3)	0.086 3(7)	0.145 1(7)	0.018 4(8)	C(3)	−0.101(2)	0.814(2)	0.178(2)
C·N(4)	−0.125 1(7)	0.164 5(8)	0.215 4(7)	C(4)	−0.045(2)	0.660(2)	0.136(2)

* C·N indicates 50% probability for each of the C and N atoms; disordered atoms are shown in italics. In clathrates **1**, **2a** and **2b** disordered guest atoms have been located at fixed positions with fixed anisotropic thermal parameters; *Cl* in **2o** is statistically distributed with the probability of [(2C + Cl)/3]/4.

Fourier-difference maps after the refinements of the respective host structures. By including non-H guest atoms fixed at the peak positions with fixed isotropic thermal parameters, only the host atoms were refined anisotropically. The guests in the other compounds, except for **4**, were also disordered to more or less extent so that the refined atomic coordinates should be read as tentative.

No significant differences were observed in the enantiomorphic discrimination between the space groups $P4_12_12$ and $P4_32_12$ for compounds **3** and **4** so that we excluded anomalous dispersion terms in the final structure refinements for **3a**, **3b** and **4** according to the instruction in the TEXSAN software package.[5]

The crystallographic and experimental data are listed in Table 1, refined atomic parameters in Table 2.

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

Results

Structure of Clathrate **1**.—The hexagonal host framework of clathrate **1** is isostructural to those of H-tridymite and hexagonal ice I_h. As is illustrated in Fig. 1, this framework provides two kinds of cavities for the guests. One [$6b^36c^2$] is surrounded by three boat-form (6b) hexagons edged with Cd–(CN)–Cd linkages at the sides and two chair-form (6c) hexagons at the top and bottom, the other [$6b^3$] being surrounded by three boat-form hexagons similar to cavity V A in the previously reported zeolite-like series type V.[3a] The array of the first type of cavities gives a channel extending along the *c* axis through the opening of the chair-form hexagon, which is effectively wider for the alkyl chain than that of the boat form.

The guest $\mathrm{Bu^n_2O}$ is considerably disordered in the channel. The distribution of the scattered peaks observed in the Fourier-difference map suggests the guest ether molecules are arranged linearly, but at random channel by channel, along the *c* axis with their skeletons passing through the opening of the chair form. The *c* dimension of the unit cell, 14.945(6) Å, equivalent to two times the dimension of the cavity unit along the *c* axis, is slightly shorter than the dimension of the guest along its skeleton in the all-*trans* conformation (*ca.* 16 Å), but acceptable if some parts of the skeleton are twisted by adopting *gauche* conformations. The water molecule appears to be accommodated in the [$6b^3$] cavity, and hydrogen bonded with any one or two of the ether O atoms in the surrounding channels: IR $\tilde{\nu}_{max}$/cm^{-1} 3412w (br) and 1626w (br) (H_2O).

Full occupation by the guests gives the limiting composition $\mathrm{Cd(CN)_2{\cdot}0.5(Bu^n_2O{\cdot}H_2O)}$. The effective volume of the cavity

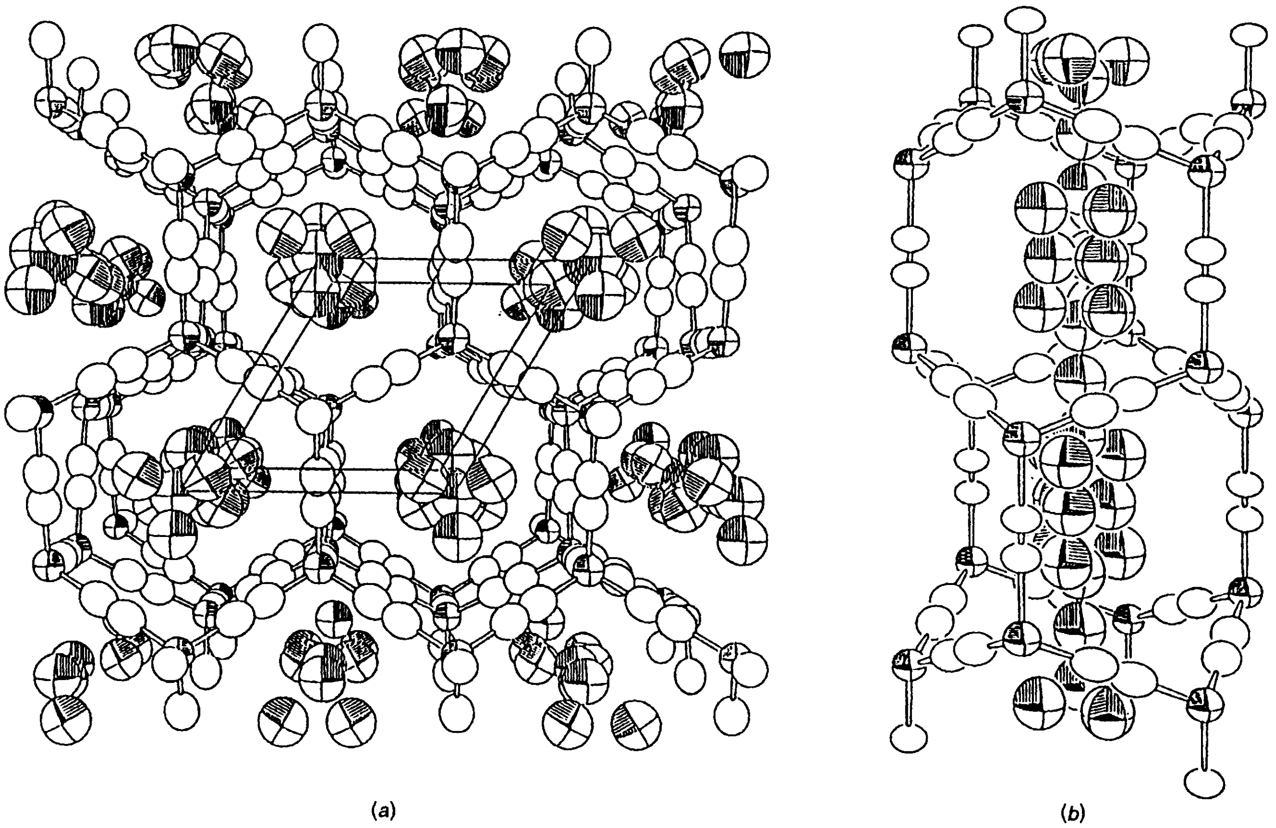
(a) (b)

Fig. 1 Structure of the host clathrate **1**: (*a*) perspective view along the *c* axis and (*b*) the channel cavity accommodating disordered $Bu^n{}_2O$. The guest $Bu^n{}_2O$ is shown as a tentative image from the statistically distributed peaks of electron densities

in the $Cd(CN)_2$ host structure is given by $U/2Z$ Å^3 based on the double-framework self-clathrate structure of neat $Cd(CN)_2$;[1a] the value of 128 Å^3 for **1** is similar to those of the high-temperature cristobalite-like host clathrates previously reported.[1a]

Structures of Clathrates **2a**, **2b** *and* **2o**.—The branched-chain aliphatic ether guests $Bu^i{}_2O$ (**2a**) and $(Pr^iCH_2CH_2)_2O$ (**2b**) are accommodated in the host, although it was impossible to establish any definite molecular structures from the X-ray data. The observed electron densities for the guest in the Fourier-difference map were interpreted in terms of a statistical distribution occupying a couple of adjacent tetrahedral cavities at random in such a manner that the branched parts are in the cavities and the central O between the cavities, as in Fig. 2. The cavity tetrahedron in the host is surrounded by four other cavities with a confronting face-to-face distance of $a\sqrt{3}/24$ (*ca.* 0.9 Å) and centre-to-centre distance of $a\sqrt{3}/4$ (*ca.* 5.5 Å). The peak observed at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (and equivalent positions: the middle point of the face-to-face separation) in the Fourier-difference map, 0.6 and 0.5 e Å^{-3}, supports this idea, taking the statistical distribution of the O atom with 0.25 occupancy into account. The mode of one guest in two cavities leads to the limiting composition $Cd(CN)_2{\cdot}0.5G$.

The structure of the $2Cd(CN)_2{\cdot}4,4'$-bipy complex[6] is similar to those of **2a** and **2b**. The 4,4′-bipyridine ligand, with its skeleton in two neighbouring tetrahedral cavities, bridges between two Cd atoms of the $Cd(CN)_2$ high-temperature cristobalite-like host framework, in which the Cd atom has five co-ordination.

The structure of clathrate **2o**, with one guest in one cavity, is similar to those of the high-temperature cristobalite-like host $Cd(CN)_2{\cdot}G$ clathrates determined previously.[1a]

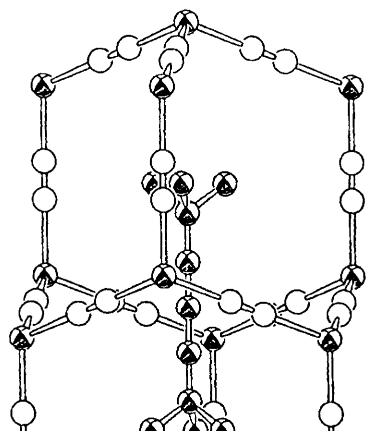

Fig. 2 A hypothetical view of the guest $Bu^i{}_2O$ occupying two neighbouring cavities of the host in clathrate **2a**; the Me groups are shown as disordered about the three-fold axis with 2/3 probability

Structures of Clathrates **3a**, **3b** *and* **4**.—Two modifications have been observed for the L-cristobalite-like host, as illustrated in Fig. 3. The straight Cd–(CN)–Cd linkage in the high-temperature cristobalite-like host is bent in these structures to induce the transformation of the framework of **2** without change in topology.

The distortion in clathrates **3a** and **3b**, from the cubic $Fd\bar{3}m$

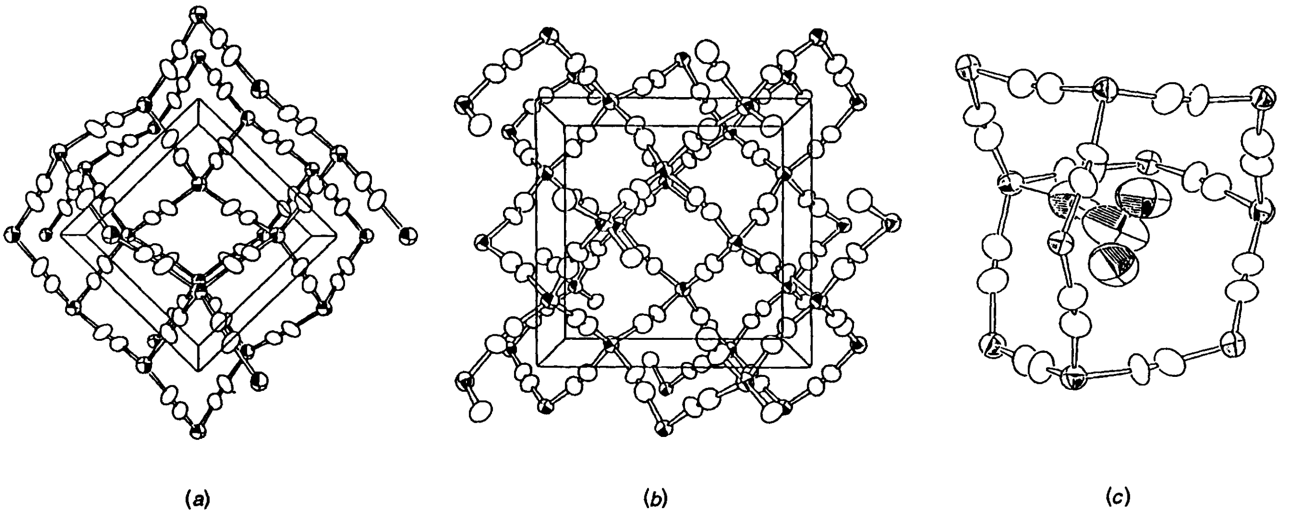
(a) (b) (c)

Fig. 3 Structures of L-cristobalite-like host clathrates: (*a*) framework of **3a**, (*b*) framework of **4** and (*c*) the fifth co-ordination of Pr^{i}CN to Cd in **4**

high-temperature cristobalite-like host framework ($Z = 8$) to the tetragonal $P4_12_12$ L-cristobalite-like host framework ($Z = 4$) is the same as that which occurs when H-cristobalite is transformed into L-cristobalite with a decrease in Z from 8 to 4.[7] The bond angles about the Cd atom range from 101.5(6) to 113.9(2)° for **3a** and from 96(2) to 127(2)° for **3b**. Upon the distortion of the lattice from the cubic to the tetragonal, the lattice parameter a of the former decreases to $a/\sqrt{2}$ and c is compressed to *ca.* 90% of a of the former; the atomic coordinates of Cd change from 0, 0, 0* to x, x, 0. This means they are on the planes at $c = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$ related by the 4_1 screw operation. The unit-cell dimensions of **3a** (G = $CHCl_2CH_2Cl$) and **3b** (G = Pr^iBr) may be compared with that of the high-temperature cristobalite-like host $Cd(CN)_2{\cdot}Pr^iCH_2Cl$, a = 12.692(2) Å.[1a] The a dimension of 8.978(6) Å in **3a** is ≈12.692/$\sqrt{2}$ (=8.975) Å; that of 9.124(1) Å in **3b** is 1.6% longer than 8.975 Å. The c dimension in **3a** is compressed to 11.934(3) Å, 94% of a in the cubic lattice, and that in **3b** to 11.335(3) Å, 89%. Owing to this compression the $U/2Z$ value decreases from *ca.* 130 Å^3 to *ca.* 120 Å^3.

Another index to measure the degree of distortion is given by conversion of the tetragonal cell of the present L-cristobalite-like host to an unconventional C-face-centred tetragonal cell which is equivalent to the tetragonally deformed $Fd\bar{3}m$ cell.[7] The positional parameters of the Cd atom x, x, 0 [x = 0.2963(2) in **3a**, 0.3179(3) in **3b**] in the tetragonal cell are then converted into X, 0, 0 in the face-centred tetragonal cell with X = 0.0463(2) and 0.0679(3). The deviation of X from 0 reflects a degree of distortion in the present L-cristobalite-like host framework from that of the high-temperature cristobalite-like host, being similar to that from H- to L-cristobalite, 0.050.

The tetragonal $P4_12_12$ unit cell of clathrate **4** ($Z = 8$) is given by the distortion of the $Fd\bar{3}m$ cubic lattice ($Z = 8$) as a whole with a decrease in the a ($= b$) dimension and an increase in c: a = 12.483(7) and c = 12.719(3) Å. The doubling in Z is caused by the displacement of the Cd atoms from the special position x, x, 0 in **3** to a general position x, y, z in **4**. The effective fractional displacements of the Cd atoms in **4** are *ca.* ±0.01 and ±0.04 along the a, ±0.01 and ±0.04 along the b, and ±0.09 and ±0.16 Å along the c direction, respectively. The Cd atoms are displaced on the mirror planes in the original $Fd\bar{3}m$ unit cell by the transformation from host **2** to host **3**, as in that from H- to L-cristobalite. The further distortion in **4** occurs three-dimensionally, in particular along the c axis to a greater extent than along the ab plane; the $U/2Z$ value of 124 Å^3 increases slightly from those in series **3**. Hence the distortion from **2** to **4** is not exactly equivalent to the transformation from H- to L-cristobalite. The distortions from **2** to **3** and **4** are compared in Fig. 4.

The reason why clathrate **4** is distorted further is interpreted in terms of the interaction between the Cd and N of the guest Pr^{i}CN with the Cd–N distance of 2.80(1) Å, which suggests the Cd is five-co-ordinate. Co-ordination of the guest as a fifth ligand from the cavity to the host Cd atom has previously been seen in $[NMe_3H{\cdot}CH_2ClCH_2Cl]_2[Cd_6(CN)_{14}(NMe_3)]$,[3a] $5Cd(CN)_2{\cdot}4H_2O{\cdot}4C_6H_{11}OH$[3c] and $2Cd(CN)_2{\cdot}$4,4′-bipy.[6] As for the cristobalite (diamondoid) lattice $[Cu_3(en)_2(CN)_4]{\cdot}H_2O$[8] $\{=[Cu^{II}(en)_2(H_2O)][Cu^I(CN)_2]_2\}$ has the negatively charged $[Cu(CN)_2{}^-]_n$ lattice more distorted than that of **4**, the lattice accommodating the $[Cu(en)_2(H_2O)]^{2+}$ cation in the cage as the guest.

Discussion

Since the present and related $Cd(CN)_2$ host clathrates are obtained under similar preparation conditions, it is obvious that the structural variations of the $Cd(CN)_2$ host are induced upon accommodating guest molecules. As for the functions of the guest in selecting host structure, the molecular shape, size and possible conformation, Lewis basicity, lipo- or hydro-philic character, freedom of motion in the cavity, *etc.* may be taken into account.

We have previously obtained dialkyl ether guest clathrates of the three-dimensional $Cd(CN)_2$ hosts $8Cd(CN)_2{\cdot}6H_2O{\cdot}6G$ $\{=3Cd_{oc}(H_2O)_2{\cdot}Cd[Cd(CN)_4]_4{\cdot}6G$; G = $Pr^i{}_2O$ or $Et_2O\}$ and $3Cd(CN)_2{\cdot}2H_2O{\cdot}2Pr^n{}_2O$ $[=Cd_{oc}(H_2O)_2{\cdot}2Cd(CN)_3{\cdot}2Pr^n{}_2O]$.[3b] These hosts involve not only tetrahedral but also octahedral cadmium (Cd_{oc}) ligated by a couple of aqua ligands protruding into the cavities, to which the ether O is hydrogen bonded. The straight alkyl chain of $Bu^n{}_2O$ being longer than those of Et_2O and $Pr^n{}_2O$ prefers the H-tridymite-like host with the channel cavity accompanied by the hydrogen-bonded water in **1** to such a host involving aqua-ligated Cd_{oc}. When the longer chain is branched, the high-temperature cristobalite-like host **2** is favourable for the accommodation of the alkyl groups of $Bu^i{}_2O$ (**2a**) and $(Pr^iCH_2CH_2)_2O$ (**2b**) in two neighbouring cavities.

Selection of the L-cristobalite-like host is delicate: the molecular dimensions differ to small extents from the guests

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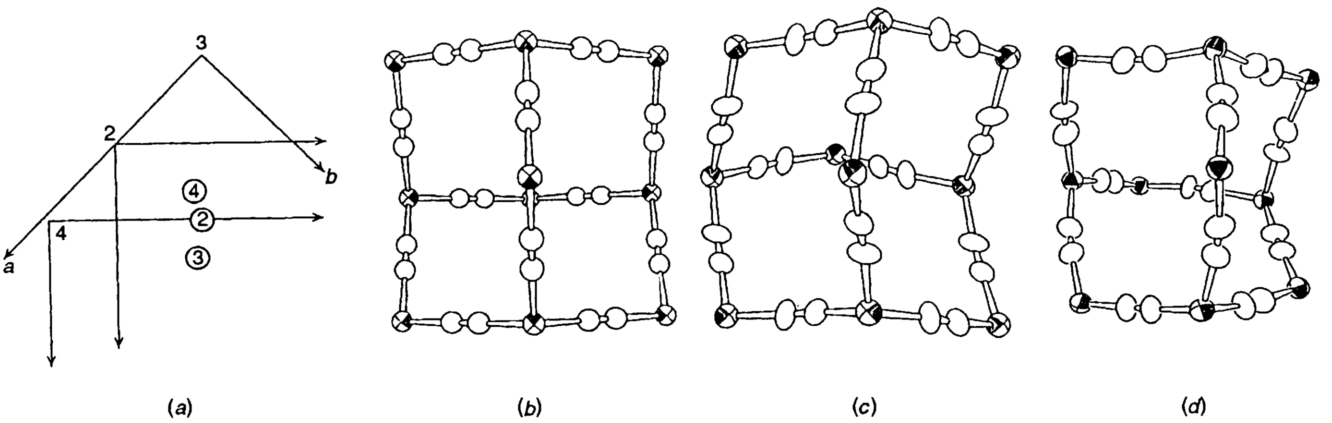
* The coordinates 0, 0, 0 are given as origin choice 1 of the unit cell in the International Tables;[7] origin choice 2 has been applied for our high-temperature cristobalite-like host structures so that the coordinates have been given as $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ in Table 2.



(*a*) (*b*) (*c*) (*d*)

Fig. 4 Deformation from high-temperature cristobalite-like host **2** to L-cristobalite-like hosts **3** and **4**: (*a*) viewed along the *c* axis. Atom Cd(2) in **2** at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$; Cd(3) in **3** shifts by *ca.* 0.05 Å along the *a* axis on the coordinates of **2**; the origin of the coordinates of **3** has been set at $-\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ on the coordinates of **2** accompanied with a clockwise rotation of 45° about the *c* axis. Atom Cd(4) in **4** shifts by *ca.* −0.04, −0.01 and 0.09 Å along the *a*, *b* and *c* axes, respectively on the coordinates of **2**; the origin of the coordinates of **4** has been set at −0.105, 0.25, 0.09 on the coordinates of **2**. Had no deformation occurred, the positions of atoms Cd(2) to Cd(4) would have coincided with one another independent of the origin setting. (*b*)–(*d*) Cavities in **2**, **3** and **4**, respectively

CHX_2Y (X, Y = Me, Cl in **2o**; Cl, CH_2Cl in **3a**; Me, Br in **3b**; Me, CN in **4**) including those accommodated in the high-temperature cristobalite-like host such as $CHMe_2CH_2Cl$ (Bu^iCl: X, Y = Me, CH_2Cl), $CHMeClCH_2Cl$ (X, X′, Y = Me, Cl, CH_2Cl), $CHCl_2CHCl_2$ (X, Y = Cl, $CHCl_2$).[1a] Assuming the shape of a tetrahedral molecule like CMe_4 to be a sphere, the degree of deformation from a sphere increases in the order $CHMe_2Cl$ (Pr^iCl), $CHMe_2Br$ (Pr^iBr) and $CHMe_2CN$ (Pr^iCN) in **2o**, **3b** and **4**, respectively. Hence, the distortion of the structure from that of a high-temperature cristobalite-like to a L-cristobalite-like host seems to be reasonable, particularly when taking the behaviour of $CHMe_2CN$ as the fifth ligand to the Cd atom into account. The difference between $CHMe_2CH_2Cl$ in the former host and $CHCl_2CH_2Cl$ in **3a** (the latter) appears to be critical. Chiral discrimination of $CHMeClCH_2Cl$ isomers in the L-cristobalite-like host, either in space group $P4_12_12$ or $P4_32_12$, was impossible because the guest selects the high-temperature cristobalite-like host.[1a]

With regard to the silica-mimetic structure of supramolecular mixed-metal cyanides, it should be noted that $Co[Au(CN)_2]_2$ with an AB_2 composition as well as $Cd(CN)_2$ has the six-fold interpenetrating self-clathrate structure of a quartz-mimetic three-dimensional lattice.[9] The *ca.* 11 Å span of Co–NC–Ag–CN–Co, longer than the *ca.* 5.5 Å of Cd–NC–Cd, appears to be favourable for six-fold interpenetration without any other guests.

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