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Mineralomimetic chemistry of cyanometallates

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The structural similarity between $Cd_x(CN)_y$ and Si_xO_y in the A_xB_y composition, A taking tetrahedral positions linked successively with B to build up multi-dimensional structures such as 1D-chains, 2D-layers, or 3D-lattices, can be utilized in developing mineral-like but unprecedented inclusion or supramolecular structures using cadmium cyanide and cyanocadmate moieties as building blocks. Examples have been demonstrated with single crystal structures for such inclusion structures as silica-mimetic $Cd(CN)_2$ host clathrates, clay-mimetic 2D-layer and zeolite-mimetic 3D-lattice cyanocadmate host inclusion compounds.

INTRODUCTION

The mineralomimetic chemistry that the present authors have proposed is the chemistry of mineral-like structures prepared using materials that never give stable minerals in nature; the structures, properties and functions of artificially prepared mineralomimetic substances should be in some points similar to, but in other points different from, those occurring in nature.[1] Procedures which merely reproduce or modify the structure of natural minerals are not included in our mineralomimetic chemistry.

Mineralomimetic chemistry may be imagined as the counterpart of biomimetic chemistry, in which biosubstances, bioprocesses, biomechanisms, *etc.*, have been mimicked, much in relation to molecular recognition and inclusion, using chemical materials different from those existing in the real biosphere.

Our mineralomimetic chemistry using cyanometallates including cadmium cyanide is based on the similarity between $Cd(CN)_2$ and both SiO_2 and H_2O (ice). They all have the AB_2 composition, A takes a tetrahedral position, B bridges between a couple of A, and the three-dimensional (3D) structures built with the A-B-A linkages may exhibit inclusion ability. The aim of this presentation is to demonstrate what inclusion structures, both types, novel and already known in nature, have been materialised using cyanometallates. The structures to be demonstrated here were all determined by the single crystal X-ray diffraction method; well-defined single crystal structures are always necessary to understand and interpret the nature of the solid supramolecular structure.

As for the inorganic host inclusion compounds occurring in nature, there are bulk deposits of clathrate hydrates in certain regions of seabed and the Arctic regions; melanophlogite is a rare example of the silica mineral containing organic molecules as the guests in its polyhedral host isostructural to the host of clathrate hydrate type I. Clathrasils and zeosils are the artificial silica structures to copy the melanophlogite and zeolites.[2] Silicates also give us clays and zeolites, which are typical 2D and 3D host inclusion structures in nature.

The structural similarities between the 3D $Cd(CN)_2$ hosts we have materialised and the relevant polymorphs of both SiO_2 and H_2O are listed in Table 1. Apart from the similarity in topology, the Cd-CN-Cd span length of *ca.* 5.5 Å is longer by *ca.* 2.5 Å than those of the Si-O-Si and O-H ⋯ O in silica and ice, *ca.* 3 Å. The longer span makes the $Cd_x(CN)_y$ host structures less complicated in topography than those of the clathrate hydrates and clathrasils upon accommodating guests similar in the molecular dimensions. This is the remarkable feature of the $Cd_x(CN)_y$ which gives structures similar in some ways but dissimilar in others to the Si_xO_y structures occurring in nature.

SiO_2-MIMETIC $Cd(CN)_2$

The three polymorphs, quartz, tridymite and cristobalite are known as natural minerals of SiO_2; high-(H-) and low-(L-)temperature forms are additionally known for the respective polymorphs. The crystal packing is the most dense for L-quartz and the least for H-cristobalite. As listed in Table 2, the H-cristobalite-mimetic host

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Table 1 Mineralomimetic features of $Cd(CN)_2$

Cd(CN)₂	*SiO₂*	*H₂O*	*Space group*
Hc-host $Cd(CN)_2 \cdot G$	H-cristobalite	ice I_c	$Fd\bar{3}m$
Lc-host $Cd(CN)_2 \cdot G$	L-cristobalite		$P4_12_12$
Ht-host $Cd(CN)_2 \cdot 0.5G$	H-tridymite	ice I_h	$P6_3/mmc$
	melanophlogite	clathrate hydrate I	$Pm\bar{3}m$
	$46SiO_2 \cdot 8G$	$46H_2O \cdot [6X \cdot 2Y]$	
		clathrate hydrate II	$Fd\bar{3}m$
		$136H_2O \cdot [8X \cdot 16Y]$	
neat $Cd(CN)_2$[a]	anticuprite-type	(ice VII)	$Pn\bar{3}m$

[a] Cuprite Cu_2O and ice VII have double-framework (self-clathrate) structures.

structures of $Cd(CN)_2$, $CdM(CN)_4$ (M = Hg, Zn) and $[MCu^I(CN)_4]^-$ (M = Cd, Zn) accommodate a number of organic guest molecules; the negative charge of the $[MCu^I(CN)_4]^-$ host is neutralised by accommodating the NMe_4^+ cation in the cavity as one of the guest components;[3,4] Hoskins and Robson[5] reported the neutral-guest-free structure of $[NMe_4][CuZn(CN)_4]$. Since the neat $Cd(CN)_2$ has a double framework structure of anticuprite-type *i.e.*, a self-clathrate structure, the clathrate is given by the apparent replacement of one framework by the guest molecules, as shown in Figure 1.

As has been discussed in detail,[4] the Hc-host (H-cristobalite-mimetic host) has the cavity approximated to a tetrahedron. It is reasonable that the tetrahedral and pseudo-tetrahedral guests such as $CMe_{4-n}Cl_n$ (n = 0 - 4), NMe_4^+ are accommodated in the tetrahedral cavity. However it is rather curious that the Hc-host of the space group $Fd\bar{3}m$ accommodates such guest as $CHMeClCH_2Cl$, $CHMe_2CH_2Cl$, $CFCl_2CF_2Cl$, $CHCl_2CHCl_2$, CCl_3CF_3, which have molecular symmetries considerably lower than T_d, without distortion of the host lattice from the face-centred cubic symmetry.

The distortion from Hc- to Lc-host (low-cristobalite-mimetic host) is induced upon accommodating $CHCl_2CH_2Cl$, $CHMe_2Br$ or $CHMe_2CN$ as the guest:[6] the

Table 2 $Cd(CN)_2 \cdot G$ and analogous clathrates, and related cyanides

H-Cristobalite-like host structures							
$Cd(CN)_2 \cdot G$:[a] space group $Fd\bar{3}m$ (No. 227), $Z = 8$							
G	a/Å	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	M	G	a/Å
Hg	CCl_4	12.7138(5)	*cyclo*-C_6H_{12}	12.734(1)	Zn	CCl_4	12.243(2)
$[CuM(CN)_4] \cdot [NMe_4 \cdot G]$: space group $F\bar{4}3m$ (No. 216), $Z = 4$							
M	G	a/Å	G	a/Å	M	G	a/Å
Zn	CCl_4	11.771(2)	no	11.671(2)[b]	Cd	CCl_4	12.189(2)
L-Cristobalite-like host structures							
$Cd(CN)_2 \cdot G$: space group $P4_12_12$ (No. 92)							
G	a/Å	c/Å	Z	G	a/Å	c/Å	Z
$CHCl_2CH_2Cl$	8.978(3)	11.924(3)	4	$CHMe_2Br$	9.124(3)	11.335(3)	4
$CHMe_2CN$	12.481(6)	12.719(6)	8				
H-Tridymite-like host structure							
$Cd(CN)_2 \cdot 0.5(Bu^n{}_2O \cdot H_2O)$: space group $P6_3/mmc$ (No. 194) $Z = 4$							
a/Å = 8.888(3)	c/Å = 14.945(6)						
Anticuprite-type $M(CN)_2$ structures							
$Cd(CN)_2$ and $Zn(CN)_2$: space group $Pn\bar{3}m$ (No. 224), $Z = 2$							
	a/Å		a/Å				
$Cd(CN)_2$	6.300(1)[b]	$Zn(CN)_2$	5.9086(7)[b]				

[a] The chemical formulae of the guests have been modified as methane derivatives Cabcd with the substituents from lighter a to heavier d except for *cyclo*-C_6H_{12} and *cyclo*-$C_6H_{11}Me$.

[b] Hoskins and Robson reported a = 11.609 Å for $[NMe_4][CuZn(CN)_4]$, and a = 6.301(1) and 5.9002(9) Å for $Cd(CN)_2$ and $Zn(CN)_2$, respectively, with the space group $P\bar{4}3m$ (No. 215); as for the details see refs. *4* and *5*.

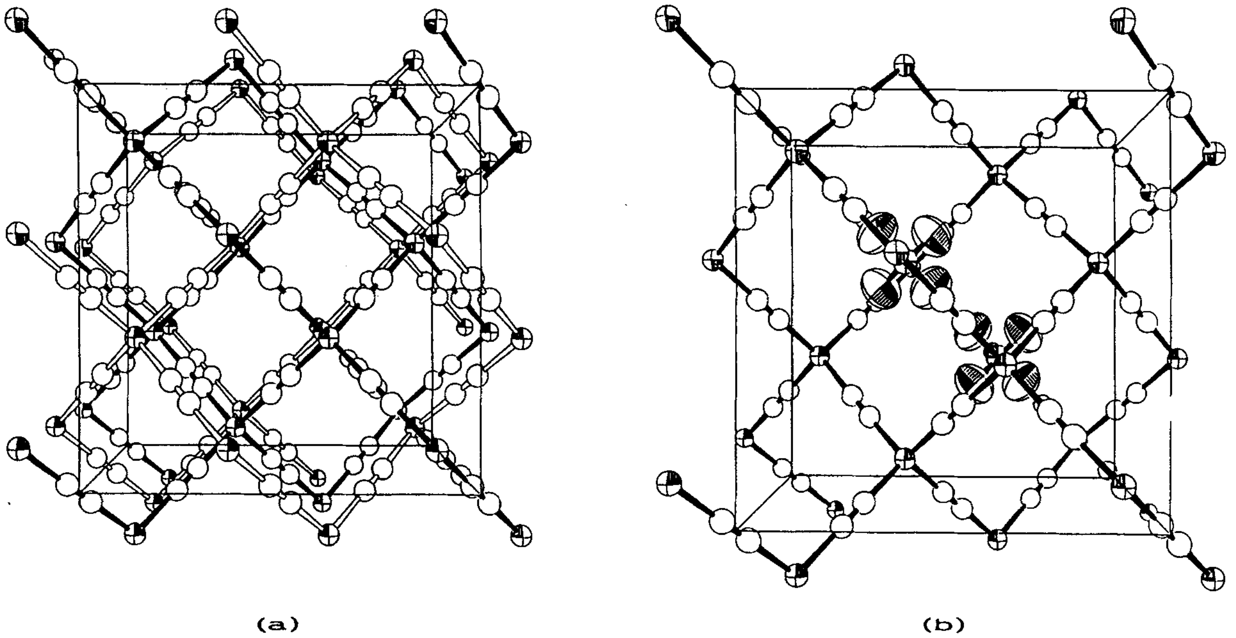

Figure 1 (a) The anticuprite-type double framework (self-clathrate) structure of $Cd(CN)_2$; one lattice with solid bonds and another with open bonds; Cd atoms with thermal peripheries. (b) The Hc-host clathrate structure of $Cd(CN)_2 \cdot CMe_4$; the lattice with open bonds in (a) has been replaced by the guest molecules; thermal peripheries are shown for Cd and guest C atoms.

distortion from the cubic $Fd\bar{3}m$ space group to the tetragonal $P4_12_12$ is just the same as that from H- to L-cristobalite. The structural change corresponding to the phase transition from cristobalite to tridymite is brought about by using a guest with a longer aliphatic chain, for instance dibutyl ether.[6] The hexagonal ($P6_3/mmc$) host, isomorphous to H-tridymite and ice I_h, gives a channel character to its cavity so that the guest aliphatic chain appears to pass through the chair form opening of the cavity along the crystal c axis. Thus, the thermodynamical distortion and phase transition in the silica structures have been mimicked in the $Cd(CN)_2$ host structures by chemical regulation, *i.e.*, by changing the guest molecules. The three structures of the $Cd(CN)_2$ hosts, Hc-, Lc- and Ht-modifications, are compared with one another in Figure 2.

SILICATE(Si_xO_y)-MIMETIC $Cd_x(CN)_y$

Among a number of the silicate modifications, neso-silicate (discrete SiO_4^{4-}), soro-silicate (dimeric $Si_2O_7^{6-}$,

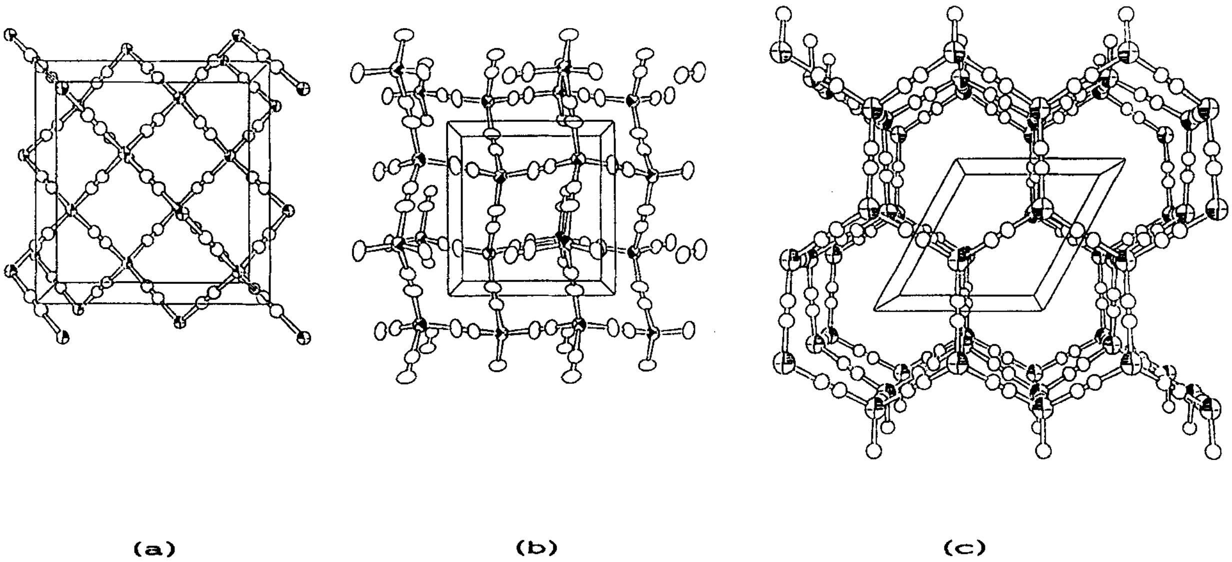

Figure 2 Projections along the c axis for (a) H-cristobalite-like (space group $Fd\bar{3}m$), (b) L-cristobalite-like ($P4_12_12$) and (c) H-tridymite-like ($P6_3/mmc$) $Cd(CN)_2$ host structures; thermal peripheries are shown for Cd atoms.

pyrosilicate) and ino-silicate (polymeric 1D $[SiO_3^{2-}]_\infty$) have been mimicked by cyanocadmates.

Ziegler and Babel[7] reported the crystal structure of $K_2[Cd(CN)_4]$ as a cyanospinel. In its AB_2X_4 composition A (= Cd) accepts tetrahedral coordination from the -CN groups and B (K) accepts octahedral coordination from the N of the CN groups; the arrangement of the CN groups in the unit cell is similar to that of the O^{2-} in spinel $MgAl_2O_4$.

Tetraphenylphosphonium heptacyanodicadmate[8] gives the crystal structure composed of the discrete PPh_4^+ and $[Cd_2(CN)_7]^{3-}$, the latter taking a staggered conformation similar to the pyrosilicate anion $Si_2O_7^{6-}$. The tetraphenylstibinium salt[9] $[SbPh_4]_2[Cd(CN)_3]_2$ is composed of two sets of discrete crystallographically independent $SbPh_4^+$ cations and anionic 1D $[Cd(CN)_3^-]_\infty$ chains. The $Cd(CN)_4$ tetrahedra are successively linked to one another by sharing two vertices each to extend the chain in a manner similar to that observed in pyroxenes. The reason why the tetraphenyl-onium salts of the group 15 elements P and Sb have structures different from each other may be ascribed to the tendency of Sb(V) to take a trigonal bipyramidal conformation: a weak interaction between the Sb and an unbridged N of the CN group is suggested from the Sb-N distances of 3.20(2) and 3.43(3) Å.

SILICATE$[M_x(SiO_y)_z]$-MIMETIC $Cd(o)_xCd(t)_y(CN)_z$

Isopolycyanopolycadmates $[Cd_x(CN)_y]^{2x-y}$ can mimic silicate structures composed of tetrahedral silicate moieties and octahedral coordination centres such as Mg^{2+}, Fe^{2+}. The divalent cadmium cation is a most versatile Lewis acid, accepting the Lewis base N of the bridging CN group to extend multi-dimensional structures with cyanometallate anions. Not only tetrahedral Cd(t) but also octahedral Cd(o) atoms are involved in the mineralomimetic isopolycyanopolycadmates so that the general composition $Cd(o)_xCd(t)_y(CN)_z$ is more appropriate. Clay-like 2D and zeolite-like 3D host structures have been materialised.

PHYLLO-SILICATE-MIMETIC LAYERS LIKE CLAYS

Table 3 summarises the clay-like layer structures classified into three types, type I to type III;[1] type III includes a sub-series type III′. Each of the layer structures is built by the cross-linking of T-O-T units, each unit involving two tetrahedral Cd(t) and an octahedral Cd(o) atoms sharing the bridging CN groups, -NC-Cd(t)-CN-Cd(o)-NC-Cd(t)-(CN)-, like the T-O-T unit in clay structures. The respective layers are shown in Figure 3.

Table 3 Clay-like 2D layer structures

Type	*Space group*	*Compound*
I	*C2/m*	$[Cd_3(CN)_7)\{NH_2(CH_2)_3NMe_2H\}]\cdot C_6H_5F$
	C2/m	$[Cd_3(CN)_7)\{NH_2(CH_2)_3NMe_2H\}]\cdot C_6H_6$
	C2/m	$[Cd_3(CN)_7)\{NH_2(CH_2)_3NMe_2H\}]\cdot CCl_4$
	C2/m	$[Cd_3(CN)_7)\{NH_2(CH_2)_3NMe_2H\}]\cdot Me_2$-$CHCH_2OH$
II	*R3m*	$[Cd_3(CN)_8]\cdot[2NMe_4\cdot Cl_2C{=}CCl_2]$
	C2/m	$[Cd_3(CN)_8]\cdot[2NHMe_3\cdot C_6H_6]$
	C2/m	$[Cd_3(CN)_{6+x}I_{2-x}]\cdot[2NMe_4\cdot Cl_2C{=}CCl_2]$ ($x = 0.29$)
III	*Pnam*	$[Cd_3(CN)_7(H_2O)]\cdot SMe_3$
	Pnam	$[Cd_3(CN)_{6+y}I_{1-y}(H_2O)]\cdot SMe_3$ ($y = 0.49$)
III	*Cmca*	$[Cd_3(CN)_8\{NH_2(CH_2)_3NMeH_2\}_2]\cdot[2C_6H_6\cdot C_6H_6]$

Type I has a neutral host layer of composition $[Cd_3(CN)_7dmtnH]$. The monoprotonated diamine ligand $dmtnH^+$ [= $NH_2(CH_2)_3NMe_2H^+$] coordinates to Cd(o) at the NH_2 group, extending its tail on the surface of the layer, and forming a hydrogen bond at the NMe_2H^+ with the N of a CN group protruding from the adjacent layer. The neutral guest molecules are intercalated between the layers pillared by the hydrogen bond.

The negative charge of the Type II layer, $[Cd_3(CN)_8]^{2-}$, is neutralised by onium cations intercalated between the layers along with the neutral guest. Type III has no neutral guests but the trimethylsulphonium cation is accommodated in the cavity formed inside the layer itself. The intralayer cavity has a structure similar to those in the zeolite-like host structures to be mentioned later.

An unprecedented structure of type III′ $\{[Cd_3(CN)_8(mtnH_2)_2]\cdot 2C_6H_6\}\cdot C_6H_6$ [$mtnH_2^+$ = $NH_2(CH_2)_3NMeH_2^+$] accommodates the guest C_6H_6 molecules in the intralayer cavity and in the concave part of the layer surface in a 2:1 ratio, in each formula unit.[10] Each of the $mtnH_2^+$ onium protons forms an intralayer hydrogen bond with the N of a CN group from the same layer, in contrast with the $dmtnH^+$ in type I.

TECTO-SILICATE-MIMETIC 3D LATTICES LIKE ZEOLITES

The T-O-T units observed in the clay-like structures construct 3D lattice structures like zeolites, too.[1a,b,d] Although the notation T-O-T usually denotes a couple of tetrahedra linked with an O^{2-} anion in zeolite chemistry, here the notation is applied in the manner used in clay chemistry, *i.e.*, to denote the linear unit of -NC-Cd(t)CN-Cd(o)-NC-Cd(t)-(CN)-. As for the 17 single crystal

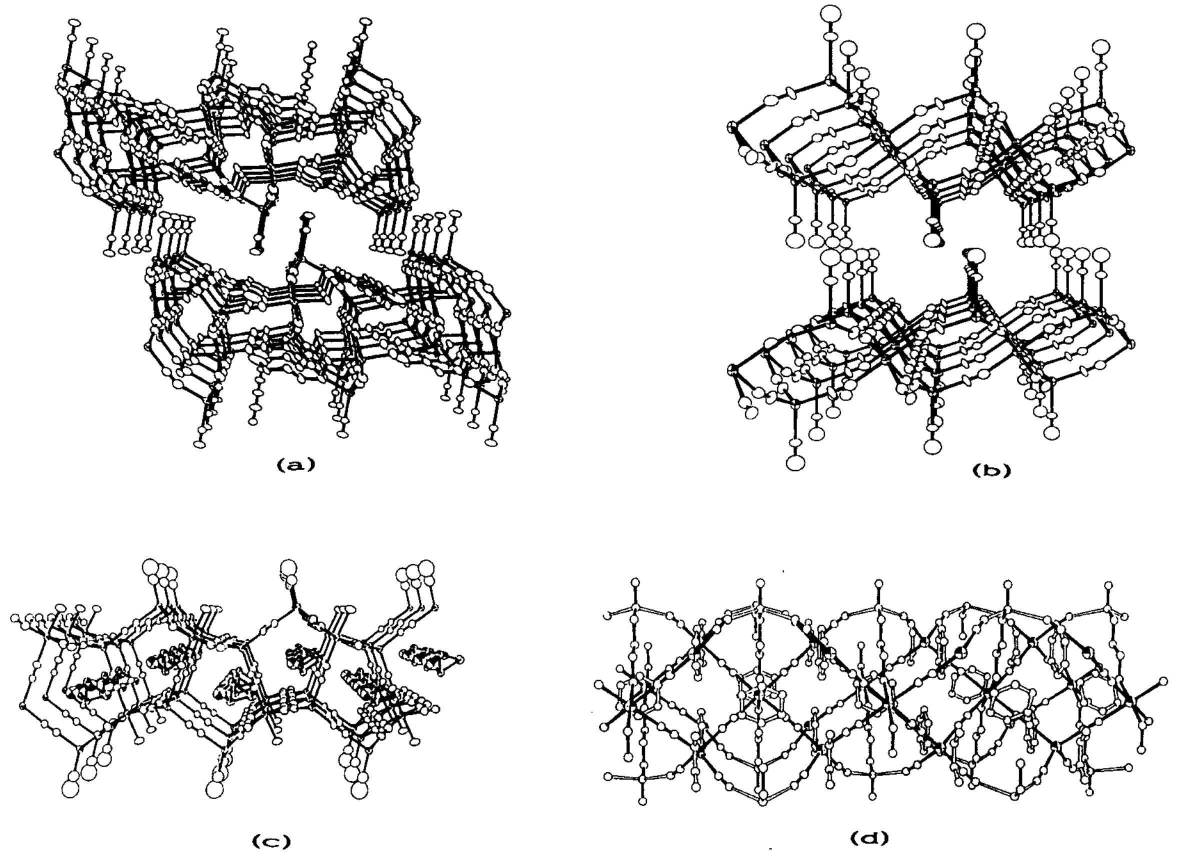

Figure 3 Structures of clay-like layers: (a) type I, (b) type II, (c) type III and (d) type III′; for the last the skeleton of the guest C_6H_6 and the hydrogen bonds from $-NH_2Me^+$ of the mtnH$^+$ to N of the CN group are shown with open lines.

structures so far determined and listed in Table 4, six types of structural patterns have been observed.[11] All the space groups assigned for the refined structures have mirror planes in their symmetry elements; a common feature of all the structures is that 1D chains composed of repeating -T-O-T- units run along the mirror plane. The 3D lattice structures are built by interconnections between the 1D chains on adjacent mirror planes through out-of-plane CN groups. The classification of the structures is based on the variations in the modes of bending and arrangement of these chains. Figure 4 summarises the host structures of type I to type VI.

Three fundamental modes of bending are possible for the $-(T\text{-}O\text{-}T\text{-})_\infty$ chains on a plane: E-TOT,E-TT (for types I to IV), E-TOT,Z-TT (for type V) and Z-TOT,E-TT (for type VI). The notations E and Z denote that the directions of chain-bending are the opposite and the same, respectively, to each other at both sides of the linkage -T-O-T- or -T-T-. Note that the Z-TOT,Z-TT mode cannot extend a 1D chain on a plane. The relative arrangement of these 1D chains is described as **o** (ortho) and **a** (anti): the first selected one is always defined as **o** arbitrarily, **a** being generated from **o** by an appropriate screw rotation. Since

Table 4 Zeolite-like 3D lattice structures

Type I: space group *R3m* (or *C2/m*); E-TOT,E-TT, **o-o**'	
I-1	$[Cd_3(CN)_7]\cdot[NMe_4\cdot SnMe_4]$
I-2	$[Cd_3(CN)_7]\cdot[NEt_4\cdot CH_2Cl_2]$
I-3	$[Cd_3(CN)_7]\cdot[NEt_2H(CH_2)_3NH_2\cdot CHCl_3]$
Type II: space group *Pn*2$_1$*m*; E-TOT,E-TT, **o-a**'	
II-1	$[Cd_3(CN)_7]\cdot[NMe_4\cdot E\text{-}CHCl{=}CHCl]$
II-2	$[Cd_3(CN)_7]\cdot[NMe_2H(CH_2)_3NH_2\cdot CH_2ClCH_2Cl]$
II-3	$[Cd_3(CN)_7]\cdot[NEt_2H(CH_2)_3NH_2\cdot C_6H_6]$
Type III: space group *Pnam*; E-TOT,E-TT, **o-a'-a-o**'	
III a-1	$[Cd_3(CN)_7]\cdot[SMe_3\cdot 2C_6H_6]$
III a-2	$[Cd_3(CN)_7]\cdot[NMe_4\cdot 1.5C_6H_6]$
III b-1	$[Cd_3(CN)_7]\cdot[NMe_4\cdot MeC_6H_5]$
III b-2	$[Cd_3(CN)_7]\cdot[NMe_4\cdot\frac{2}{3}\{1,3,5\text{-}Me_3C_6H_3\}]$
Type IV: space group *Pnam*;	E-TOT,E-TT, **o**(T)-**a**'(P)-**o**(P)-**a**'(T)-**a**(T)-**o**'(P)-**a**(P)-**a**'(T)
IV -I	$[\{Cd_3(CN)_7\}_2NMe_3]\cdot 2[NMe_3H\cdot CH_2ClCH_2Cl]$
Type V: space group *P*6$_3$*/mmc* (or *Bbnm*); E-TOT,Z-TT, **o-o**'	
V -1	$[Cd_3(CN)_7]\cdot[NMe_4\cdot 2CH_2ClCH_2Cl]$
V -2	$[Cd_3(CN)_7]\cdot[NMe_4\cdot 2CH_2{=}CCl_2]$
V -3	$[Cd_3(CN)_7]\cdot[NMe_4\cdot 2EtCN]$
V-4	$[Cd_3(CN)_7]\cdot[SMe_3\cdot 2CH_2ClCH_2Cl]$
V -5	$[Cd_3(CN)_7]\cdot[NMe_2H(CH_2)_3NH_2\cdot 2CH_2Cl_2]$
Type VI: space group *Pb*2$_1$*m*; Z-TOT,E-TT, **o-a**'	
VI -1.	$[Cd_3(CN)_7]\cdot[NMe_2H(CH_2)_3NMe_2\cdot CH_2\text{-}ClCH_2Cl]$
4:9-type: space group *Pnma*; $[Cd_4(CN)_9]\cdot[K\cdot 4EtCN]$	

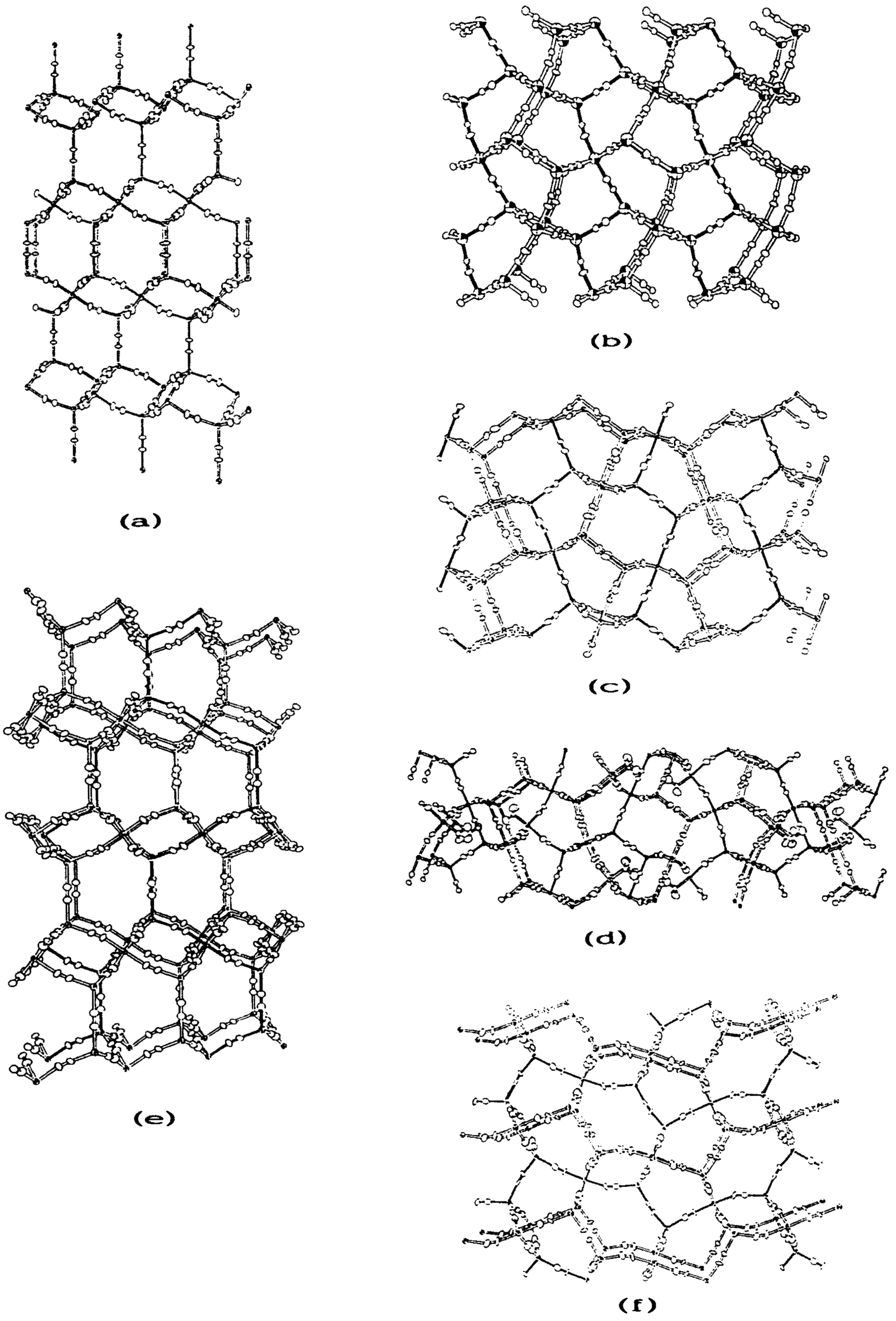

Figure 4 Structures of zeolite-like lattices; the -(T-O-T-)$_n$ chains on a mirror plane are shown with solid bonds; (a) type I: E-TOT,E-TT, o-o′; (b) type II: E-TOT,E-TT, o-a′; (c) type III: E-TOT,E-TT, o-a′-a-o′; (d) type IV: o(T)-a′(P)-o(P)-a′(T)-a(T)-o′(P)-a(P)-o′(T); (e) type V: E-TOT,Z-TT, o-o′; (f) type VI: Z-TOT,E-TT, o-a′.

the number of the relevant mirror planes in the respective unit cells is net 2, the structural patterns are denoted by the combination of the mode of bending and that of the relative arrangement, *e.g.* E-TOT,E-TT, **o-o′**; the relative arrangement on the plane adjacent to the first selected plane is further distinguished by a prime. The arrangement **o′** is given by appropriate translation of the **o** chain from the first selected plane to the adjacent plane, **a′** being by appropriate screw rotation. Accordingly, E-TOT,E-TT **o-o′** for type I to Z-TOT,E-TT **o-a′** for type VI have been denoted. In type IV, one of the four Cd(t) is additionally ligated by a unidentate NMe_3 to take a trigonal bipyramidal penta-coordination, P, so as to give two kinds of chains $-(T\text{-}O\text{-}T\text{-})_\infty$ and $-(T\text{-}O\text{-}T\text{-}P\text{-}O\text{-}T\text{-})_\infty$.

The 3D $[Cd_3(CN)_7^-]_\infty$ host thus formed by the interconnection of 1D chains provides cavities for the guests, both organic onium cations, neutralising the negative charge of the host, and neutral aromatic and aliphatic guests. The cavities are approximated to polyhedra cornered by Cd(t) and Cd(o) atoms, T (including P) and O, the faces of which are also approximated to polygons such as tetragon, pentagon, hexagon, octagon, although these polygons are more or less distorted from a coplanar arrangement of the Cd corners and -CN- edges. The opening becomes wider as the order of the polygon increases from tetragon to octagon. For example, as shown in Figure 5, in type III a-2 benzene clathrate $[Cd_3(CN)_7]\cdot[NMe_4\cdot 1.5C_6H_6]$, the benzene molecules are accommodated in cavities III A ($4^35^26^1$) and III B (6^28^1) with $\frac{2}{3}$ probability each and NMe_4^+ in III C (5^26^1), whereas in type III b-1 toluene clathrate $[Cd_3(CN)_7]\cdot[NMe_4\cdot MeC_6H_5]$ the toluene occupies cavities III B and III C, and NMe_4^+ III A.

Another structural variation has been demonstrated for $[Cd_4(CN)_9]\cdot[K\cdot 4EtCN]$ whose 3D host is constructed by the interconnection of $-(T\text{-}T\text{-}T\text{-}O\text{-})_\infty$ chains;[12] the ratio of Cd(o) to Cd(t) is 1:3. In place of the organic onium cation K^+ is accommodated in the cavity.

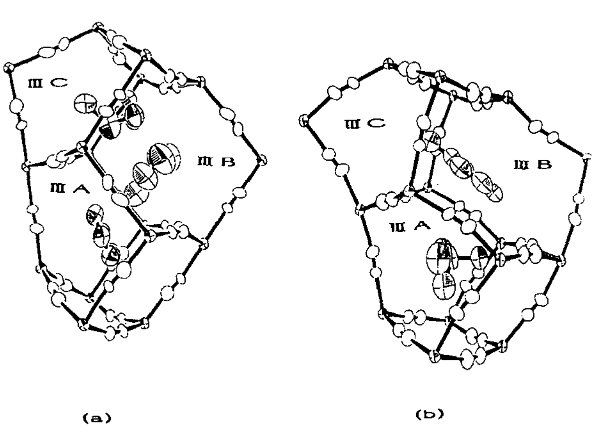

Figure 5 Inclusion structures of type III benzene and toluene clathrates. (a) Type III a-2 $[Cd_3(CN)_7]\cdot[NMe_4\cdot 1.5C_6H_6]$: C_6H_6 in cavities III A ($4^35^26^1$) and III B (6^28^1) with $\frac{2}{3}$ probability each and NMe_4^+ in III C (5^26^1). (b) Type III b-1 $[Cd_3(CN)_7]\cdot[NMe_4\cdot MeC_6H_5]$: MeC_6H_5 in cavities III B + III C (45^26^3), and NMe_4^+ in III A.

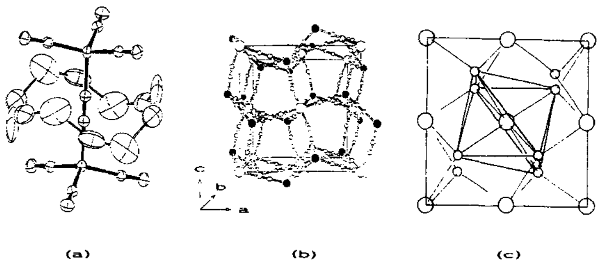

Figure 6 Structure of heptacyanodicuprato(I)cadmic(II) acid tetradecahydrate; (a) the rotaxane structure of 12 waters about $(NC)_3Cu(CN)Cu(CN)_3$; (b) the pyrite-like 3D lattice of the host: Cd, large open ball; Cu, solid ball; (c) the hydrogen-bond network of H_2O molecules in the unit cell; moiety A, the 12 H_2O ring, is approximated to a large circle, moiety B, the H_2O hydrogen-bonded to three A rings, to a small circle; the A ring is coordinated octahedrally with six B H_2O.

PYRITE-LIKE $[H_{31}O_{14}][Cd\{Cu_2(CN)_7\}]$

As for heteropolycyanopolymetallates $[M_xM'_y(CN)_z]$, the acid hydrate of heptacyanodicuprato(I)cadmate(II), $[H_3(H_2O)_{14}][Cd\{Cu_2(CN)_7\}]$ gives a 3D lattice like pyrite FeS_2 with the cubic structure of space group $Pa\bar{3}$ [a = 12.9401(9) Å].[13] Cd^{2+} is at the position of Fe^{2+} and $[Cu_2(CN)_7]^{5-}$ at that of S_2^{2-} (Fig. 6). The pyrosilicate-like dimeric heptacyanodicuprate(I) anion, taking a staggered conformation, is linked to six Cd^{2+} at the respective N ends of the terminal CN groups; the octahedral Cd^{2+} is coordinated with the N ends from the six dimeric anions.

The partly protonated 14 water molecules are divided into two moieties A and B with the ratio of 12:2, *i.e.*, $[(H_2O)_{12}](H_2O)_2 = AB_2$, when the acid protons are omitted. Moiety A makes a hydrogen-bonded ring of twelve water molecules encircling the bridging CN group of the dimeric anion to give a rotaxane-like structure. Ring A is hydrogen-bonded to six water molecules of moiety B, while each moiety B is hydrogen-bonded to three A rings. The linking relationship between A and B is similar to that in rutile TiO_2 with six-coordinate Ti^{4+} and three-coordinate O^{2-}.

CONCLUSION

The mineralomimetic cyanometallate compounds discussed above have rather simple chemical compositions but their crystal structures show a great variety. Although it appears to be possible to interpret their structural variations in terms of their similarity with real minerals, the available information is still too little to fully understand these multi-dimensional structures systematically. Much has been left to be explored in the field of polymeric coordination compounds.

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