Mineralomimetic chemistry as a modern aspect of co-ordination chemistry

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By denoting as mineralomimetic chemistry the chemistry of the build-up of mineral-like structures using materials that never give stable minerals in nature, the multidimensional structures comprised of the linkage of co-ordination polyhedra such as those observed for natural minerals are demonstrated for the products obtained by the crystal engineering strategy based on the structural similarity between $Cd(CN)_2$ and SiO_2, and between $Cd(CN)_4$ and SiO_4. The structures of high-cristobalite, low-cristobalite, high-tridymite, stishovite, pyrosilicate, chain silicates, ring silicates, layer silicates, framework silicates, *etc.* have been mimicked by polymeric complexes of cadmium cyanide and polycyanopolycadmate(II); $[H_3(H_2O)_{14}][Cd\{Cu_2(CN)_7\}]$ has a doubly interpenetrating structure of the pyrite-mimetic $[Cd\{Cu_2(CN)_7\}]$ framework and the framework of the hydrogen-bonded water molecules has a topology approximated to that of rutile; a two-dimensional ice structure (comparable with the two-dimensional array of the water molecules in ice I_h) is built from aqua ligands and the intercalated waters in $[Cd(H_2O)_2Ni(CN)_4]\cdot 4H_2O$. As a modern aspect of co-ordination chemistry, the concept of mineralomimetic chemistry is extended more generally for the multidimensional structures built from the linkage of co-ordination polyhedra.

The co-ordination theory of Alfred Werner is closely related to the spontaneous resolution of D- and L-$NH_4[Na(CHOHCO_2)_2]\cdot 4H_2O$ crystals discovered by Pasteur and the tetrahedral bonding model for carbon proposed later by van't Hoff and Le Bel. However, octahedral co-ordination of cobalt(III) was finally verified by optical resolution of an artificially designed inorganic salt $[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]X_6$, in which the central Co^{III} is co-ordinated by three other cobalt(III) octahedra, sharing the six μ-OH groups. Thereafter, chemistry owed much in its developments to the concept that every substance has its own molecule, more specifically an Avogadro molecule. The term Avogadro molecule is used to denote a discrete chemical species, regardless of the electronic charge, comprised of definite numbers of atoms belonging to distinct elements.

Prussian blue appears to be the earliest recorded artificial co-ordination compound,[1] discovered by chance during the first decade of the eighteenth century. Following the earlier elucidation of the powder X-ray diffraction structure,[2] detailed single-crystal analysis[3] of Prussian blue clarified the three-dimensional infinite latticework built of cyanide bridges among iron atoms. The structure with the composition $Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot xH_2O$ (x = 14–16)[3] is interpreted in terms of the array of the octahedral Fe^{III} atoms on the origin and face centres (four net in total) linked by the octahedral six-handed bridging ligand $[Fe^{II}(CN)_6]^{4-}$ on the edge centres (three net in total) in the cubic $Pm\bar{3}m$ unit cell. The pseudo-face-centred primitive cubic lattice forms a cage surrounded by Fe^{III}–NC–Fe^{II}–CN–Fe^{III} edges and $Fe^{III}(NCFe^{II})_4$ faces which accommodate the water molecules; six of the water molecules co-ordinated to Fe^{III} on the face centres are hydrogen bonded to the remainder to form a cluster of water molecules inside the cage. The earliest recorded co-ordination compound was not comprised of Avogadro molecules but of co-ordination polyhedra linked three-dimensionally. A number of natural minerals such as metal oxide, hydroxide, sulfide, halide, phosphate, silicate, *etc.*, are not comprised of Avogadro molecules either but involve infinite assemblies of co-ordination polyhedra forming one-, two- or three-dimensional arrays.

Cyanometalate anions such as square planar $[Ni(CN)_4]^{2-}$, tetrahedral $[Cd(CN)_4]^{2-}$, linear $[Ag(CN)_2]^-$ *etc.*, as well as the octahedral $[Fe^{II}(CN)_6]^{4-}$ in Prussian blue, behave as linking moieties to other co-ordination centres to give a variety of multidimensional structures. Since the middle of the 1960's we have been developing one-dimensional chains, two-dimensional networks, three-dimensional frameworks, and their combinations, for a number of co-ordination compounds involving these cyanometalate anions.[4] In the course of these studies we have found some similarities in the behaviour of tetrahedral tetracyanocadmate(II), $Cd(CN)_4$, and silicate, SiO_4, and also cadmium cyanide, $Cd(CN)_2$, and silica, SiO_2, giving multidimensional structures. The term mineralomimetic chemistry was proposed to denote the chemistry of the build-up of mineral-like structures using materials that never give stable minerals in nature. Although the earliest example of cooperite (PtS)-mimetic structure, see below, was demonstrated at the beginning of the 1970's, our current interest is focused on the systems consisting of cadmium cyanide, tetracyanocadmate(II), polycyanopolycadmate(II), $Cd_y(CN)_z$, or polycyanopolycuprate(I), $Cu^I_y(CN)_z$, as the main component to mimic tetrahedral silica or silicate structures. Secondary ligands other than the primary CN group, counter ions, and/or guest molecules are also major components in the products obtained as single crystals grown under ambient conditions. In many cases the polycyanopolycadmate involves octahedral Cd_{oc} linked through CN to the tetrahedral Cd_t. Their structures are in some respects similar to those of natural minerals in general.

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Table 1 Structural features of $Cd(CN)_2$, SiO_2 and H_2O (ice)

$Cd(CN)_2$	SiO_2	H_2O (ice)	Space group
Hc-host	H-Cristobalite	I_c	$Fd\bar{3}m$
Lc-host	L-Cristobalite		$P4_1(4_3)2_12$
$[Cd\{Cd(Him)(CN)_3\}_2]$[a]	Stishovite (rutile TiO_2)		$P4_2/mnm$
Ht-host	H-Tridymite	I_h	$P6_3/mmc$
	L-Tridymite		$C222_1$ *etc.*
	H-Quartz		$P6_2(6_4)22$
	L-Quartz		$P3_1(3_2)21$
	Keatite	III, IX	$P4_1(4_3)2_12$
	Melanophlogite[b]	Clathrate hydrate I[c]	$Pm\bar{3}m$
		Clathrate hydrate II[d]	$Fd\bar{3}m$
Neat	(Cuprite Cu_2O)	VII, VIII	$Pn\bar{3}m$

[a] Him = Imidazole. [b] $46SiO_2{\cdot}8G$. [c] $46H_2O{\cdot}[6X{\cdot}2Y]$. [d] $136H_2O{\cdot}[8X{\cdot}16Y]$.

Similarities are seen in the structural principle that each of the components with simple structure is combined in simple compositions to give structural variations as complicated as those observed in natural minerals. The relevant compounds cited hereafter are denoted with the formula discriminating between the co-ordination structure [Cd_t and Cd_o] if necessary, and giving the simplest composition. Except for a few ice structures, that is, structures built of hydrogen-bonded water molecules, our mineralomimetic skeletons are combined through co-ordination and covalent bonds. A remarkable difference of our mineralomimetic compounds from natural minerals is noted for the preparative conditions. In order to copy, imitate or reproduce natural minerals or to obtain their artificial modifications by the use of compositional materials identical or similar to those of the natural minerals, syntheses are carried out in many cases under extreme conditions, such as hydrothermal atmospheres, high pressures, high temperatures, *etc.* The thermodynamically stable phase or the kinetically preferred species in a given system is theoretically predicted or empirically estimated according to the thermodynamic parameters, P, T, V and $n = \Sigma n_i$, with n_i being the amount of the i-th substance involved in the system. As well as the cases of some artificial zeolites and silica-mimetic $AlPO_4$ grown under mild conditions, it should be a matter of mere chance that our mineralomimetic compounds are grown as well developed single crystals from aqueous solutions containing relevant components with or without keeping contact with an organic phase under ambient P and T ranging from about 298 to 278 K. A rough classification of silicate structures may be given as follows: (*i*) neso-silicates with a discrete or isolated SiO_4 (orthosilicate) unit, (*ii*) soro-silicates or coupling silicates with a dimeric Si_2O_7 (pyrosilicate) or trimeric Si_3O_{10} unit, (*iii*) ino-silicates or chain silicates extending a one-dimensional $(SiO_3)_n$ (metasilicate) chain, (*iv*) cyclo-silicates or ring silicates with a ring unit of $(SiO_3)_n$, (*v*) phyllo-silicates or layer silicates extending a two-dimensional layer and (*vi*) tecto-silicates or framework silicates extending a three-dimensional framework. These silicate structures are mimicked by $Cd_t(CN)_4$, and their condensate polycyanopolycadmates, $Cd_{ty}(CN)_z$, $Cd_{ocx}Cd_{ty}(CN)_z$ *etc.* Mixed ligation of a secondary ligand L such as H_2O, NH_3, imidazole, or ethane-1,2-diamine gives structures involving CN-linked Cd_{oc} and/or Cd_t co-ordinated with L. In these polycyanopolycadmates not only the octahedral but also the tetrahedral cations found in natural silicates are sometimes mimicked by Cd_{oc}. The cyanocadmate(II) unit can be replaced by cyanocuprate(I) in some structures.

Cadmium cyanide, $Cd(CN)_2$, is comparable with silica, SiO_2, and ice, H_2O with respect to structural features: they all have the AB_2 composition, A taking a tetrahedral position linked infinitely by B to form a three-dimensional framework. Neat cadmium cyanide adopts an anti-cuprite-type doubly interpenetrating three-dimensional framework structure. Each of the interpenetrating frameworks is a diamondoid isostructural with the high-temperature phase of cristobalite (H-cristobalite) and ice I_c. The reason why $Cd(CN)_2$ adopts the doubly interpenetrating structure is due to the Cd–CN–Cd span length of about 5.5 Å, longer than the Si–O–Si span of about 3.2 Å and the O–H · · · O of about 2.8 Å. The longer span makes a more voluminous space inside the framework so that something to fill the void is necessary to stabilise the crystal structure. The self-clathrate structure like the double interpenetration in $Cd(CN)_2$ is seen in ice VII and ice VIII under high pressure, although no self-clathrate structures have been observed for silica; high pressure induces the increase in co-ordination number of Si to six and that of O to three for stishovite taking a rutile structure.

The cyanide anion is approximated to an ellipsoid with a maximum diameter of about 3.6 Å and a long axis of about 4.6 Å so that a framework surrounded by Cd–CN–Cd spans is able to imprison an oligo-atomic molecule inside the cage. In other words, the single framework of $Cd(CN)_2$ and the expanded framework structures of the polycyanopolycadmates can be stabilised by accommodating a guest or secondary ligand voluminous enough to fill up the cage. Our mineralomimetic chemistry, or mineralomimetics, the strategy of crystal engineering and how to materialise mineralomimetic structures, is thus based on the selection of the guests and secondary ligands appropriate for the stabilisation of the resulting crystal structure. In some cases one-dimensional chains or two-dimensional layers are formed with or without guests.

Silica-Mimetic Structures of $Cd(CN)_2$ Hosts in $Cd(CN)_2{\cdot}x$G (G = guest molecule) Clathrates

Structural similarities between silica and ice are well noted.[5] Table 1 compares the structural features of neat $Cd(CN)_2$ and the hosts of $Cd(CN)_2{\cdot}x$G (G = guest molecule) clathrates with those of the silica and ice polymorphs. Among the six polymorphs of silica occurring in nature, namely the high-temperature (H) and low-temperature (L) phases of quartz, tridymite and cristobalite, respectively, L-quartz is the most dense and H-cristobalite is the least. The $Cd(CN)_2$ host structures are stabilised in the form of less dense polymorphs, H-cristobalite (Hc), L-cristobalite (Lc) and H-tridymite(Ht).[6,7]

As shown in Fig. 1, the cage of an adamantane-like skeleton in the diamondoid framework of neat $Cd(CN)_2$ generates a cavity approximated to a tetrahedron cornered by the tripod vertices of the skeleton; the distance from the centre to the vertex of the tetrahedron is the same as the Cd–CN–Cd span length, about 5.5 Å in the cubic ($Pn\bar{3}m$) unit cell. In the self-clathrate structure of neat $Cd(CN)_2$ the cavity formed in one framework is occupied by the tetrahedral centre of the other framework in the orientation inverse to the former. Each Cd–CN–Cd span passes through the face centre of the cavity tetrahedron into the neighbouring cavity. The $Cd(CN)_2{\cdot}x$G clathrates of Hc- and Lc-mimetic hosts are given by the formal

Table 2 Clathrates of silica-mimetic framework hosts

Hc-host	$Fd\bar{3}m$	G
$Cd(CN)_2 \cdot G$		$CHCl_3$, $CHMeCl_2$, $CHMe_2Cl$, CCl_4, $CMeCl_3$, CMe_2Cl_2, CMe_3Cl, CMe_4, $Cl_2CHCHCl_2$, $CHMeClCH_2Cl$, $CHMe_2CH_2Cl$, $CFCl_2CF_2Cl$, CCl_3CF_3, CMe_3Et, cyclo-C_6H_{12}, cyclo-$C_6H_{11}Me$
$Cd(CN)_2 \cdot 0.5G$		$Bu^i{}_2O$, $(Pr^iCH_2CH_2)_2O$
Lc-host	$P4_1(4_3)2_12$	
$Cd(CN)_2 \cdot G$		$CHCl_2CH_2Cl$, Pr^iBr, Pr^iCN
Ht-host	$P6_3/mmc$	
$Cd(CN)_2 \cdot 0.5G$		$Bu_2O \cdot H_2O$
Hc-host	$Fd\bar{3}m$	
$[CdZn(CN)_4] \cdot 2G$		CCl_4
$[CdHg(CN)_4] \cdot 2G$		CCl_4, cyclo-C_6H_{12}
Hc-host	$F\bar{4}3m$	
$[NMe_4 \cdot G] \cdot [CdCu(CN)_4]$		CCl_4
$[NMe_4 \cdot G] \cdot [CuZn(CN)_4]$		CCl_4, none

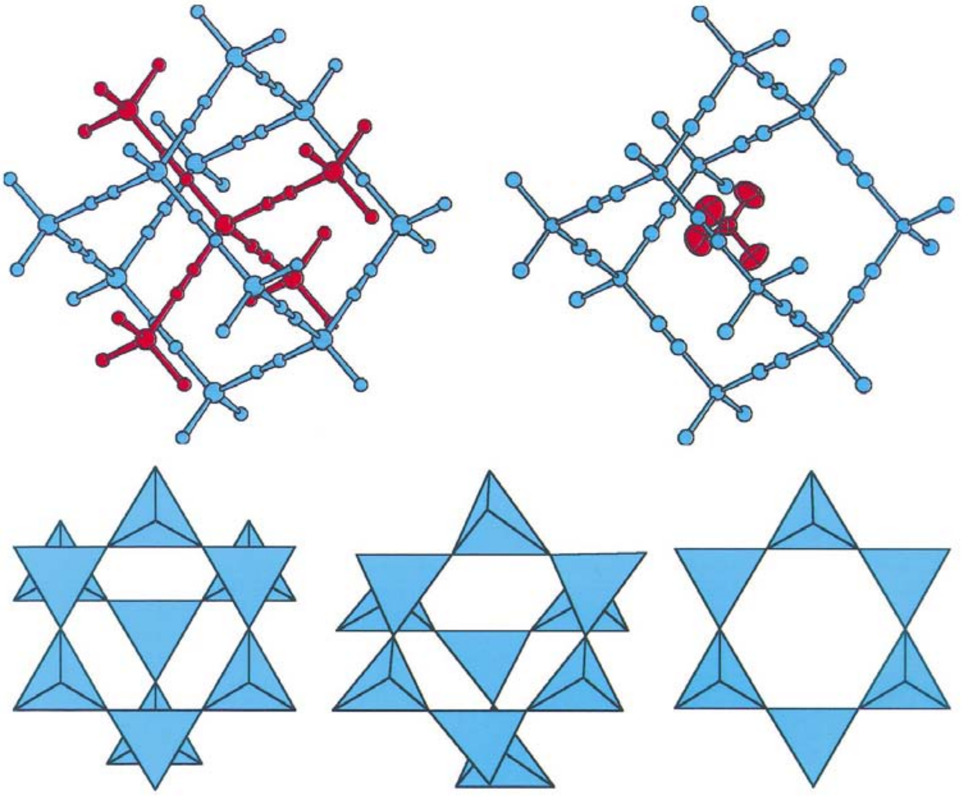

Fig. 1 Structures of neat $Cd(CN)_2$ and silica-mimetic hosts of $Cd(CN)_2 \cdot xG$ clathrates. Top left: doubly interpenetrating anticuprite structure of neat $Cd(CN)_2$; top right: Hc-host $Cd(CN)_2 \cdot CMe_4$ clathrate; bottom left: array of tetrahedra in Hc-host; bottom centre: array of tetrahedra in Lc-host; bottom right: array of tetrahedra in Ht-host

replacement of the 'guest' framework with an appropriate guest molecule. A number of the guest molecules not only with the tetrahedral or pseudo-tetrahedral symmetries but also with lower symmetries are accommodated in the cubic Hc-host (Table 2). The bulkier dumb-bell-shaped guests $Bu^i{}_2O$ and $(Pr^iCH_2CH_2)_2O$ occupy a pair of neighbouring cavities to give the $Cd(CN)_2 \cdot 0.5G$ clathrates of the Hc-host.[7] The guests $CHCl_2CH_2Cl$, Pr^iBr and Pr^iCN distort the host framework to the tetragonal Lc-host, the distortion being comparable with the thermal phase transition from H- to L-cristobalite; the deformation does not change the topology of the host framework. The hexagonal Ht-host structure is given by the guest with a longer dialkyl ether skeleton, $Bu^n{}_2O$, which is accommodated in a channel cavity generated in the host framework; another small cage cavity is occupied by a water molecule probably hydrogen bonded to the ether oxygen.[7] Thus, three of the thermally transformable silica polymorphs have been mimicked chemically by the $Cd(CN)_2$ host clathrates by selecting the guest species. The selection of the host structure by the guest is critical for the Hc- and the Lc-host: $CHMe_2CH_2Cl$ and $CHCl_2CHCl_2$ select the Hc-host but $CHCl_2CH_2Cl$ does the Lc-host.

The cubic Hc-host structure is possible for $[CdM(CN)_4] \cdot 2G$ (M = Hg or Zn)[6c] and $[NMe_4 \cdot G][Cu^IM(CN)_4]^-$ (M = Cd[6c] or Zn[6c,8]), although the number of solved structures is less than those for $[Cd(CN)_2]$ hosts. As for the negatively charged $[Cu^IM(CN)_4]^-$ host, half of the tetrahedral cavities are accommodated by the onium cation $NMe_4{}^+$ and the other half by the neutral guest G.

A well known problem in X-ray crystallography studies of CN-bridged structures is the discrimination between the C and N atoms of the CN group. There are two cases. One in which the selected space group forbids the discrimination theoretically due to the symmetry requirement: the presence of a two-fold axis or an inversion centre at the midpoint between C and N, or of a mirror plane bisecting the C–N axis. The other is a practical difficulty with little significant difference in electron density between C and N and/or in the M–C and M–N bond lengths. Solid-state ^{113}Cd NMR spectroscopy has given some solutions.[9] Since the ^{113}Cd signal is observed as a quintet in the

Hc-host and in neat $Cd(CN)_2$, supporting the statistical distribution of the co-ordination spheres CdC_4, CdC_3N, CdC_2N_2, CdC_3N and CdN_4, the CN group is concluded to take a random orientation. The CN group linking a pair of Cd_t takes a random orientation in many cases but that in a Cd_t–CN–Cd_{oc} linkage C is always linked to Cd_t in the more than one hundred single-crystal structures we have determined for polycyanopolycadmates. In the Hc-hosts of $[CdM(CN)_4]$ (M = Hg or Zn) the CN is disordered, whereas crystallographic discrimination is possible for the $[Cu^IM(CN)_4]^-$ host in which the $Cu^I(CN)_4$ keeps its structural integrity with C co-ordinating to Cu;[6c,8] the solid-state NMR supported this conclusion.[9e] Table 2 lists the clathrates with the silica-mimetic host frameworks.

When a considerably strong Lewis base occupies the cavity in the cristobalite-like $Cd(CN)_2$ host, it ligates to the Cd from the inside of the cavity. The structure of $[Cd(CN)_2]_2$·4,4′-bpy (4,4′-bpy = 4,4′-bipyridine)[10,11] is analogous to $[Cd(CN)_2]$·0.5G [G = Bu^i_2O or $(Pr^iCH_2CH_2)_2O$][7] with respect to the accommodation of the dumb-bell-shaped ligand as a guest in a pair of neighbouring cavities. Each Cd atom adopts a distorted trigonal bipyramidal five-co-ordinate geometry with the additional ligation of N from the 4,4′-bpy in the cavity. Another example of additional ligation is found in $[\{Cd(H_2O)(CN)_2\}_4\{Cd(CN)_2\}]$·4cyclo-$C_6H_{11}OH$ [= $5Cd(CN)_2$·$4H_2O$·4cyclo-$C_6H_{11}OH$] in which four of the five Cd atoms are bonded by an aqua ligand.[9c] The four aqua ligands are accommodated in a cavity to form a tetrahedral hydrogen-bonded cluster, to which the OH groups of the cyclo-$C_6H_{11}OH$ guests are hydrogen bonded; these guests are accommodated in the four neighbouring cavities (Fig. 2).

The three-dimensional framework of $Cd(CN)_2$ in $Cd(CN)_2L$ complexes [L = pyrazine, quinoxaline or 1,4-bis(4-pyridyl)-butadiyne] have a different topology to the silica-mimetic hosts.[11]

Clathrate hydrate I $46H_2O$·(6X·2Y) and II $136H_2O$·(8X·16Y) (where X and Y are guest molecules in the larger and smaller cavities respectively), and melanophlogite $46SiO_2$·8G, formulated as the limiting compositions respectively, are the clathrate minerals occurring in nature. However, the corresponding $Cd(CN)_2$ hosts are unknown. Owing to the longer span length of Cd–CN–Cd, bulkier guests may be necessary to stabilise the clathrate hydrate-like host structures.

Isolated Silicate-like Structure

The composition of potassium tetracyanocadmate $K_2[Cd(CN)_4]$ is formulated as A_2BX_4 similar to that of spinel Al_2MgO_4; Ziegler and Babel[12] interpreted the crystal structure in terms of cyanospinel. The array of Cd on the tetrahedral site and K on the octahedral site surrounded by N atoms of six $Cd(CN)_4$ moieties is similar to that of Mg and Al located on the tetrahedral and octahedral sites among the face-centred cubic packing of O^{2-} anions in spinel, although there is no discrete MgO_4 unit in spinel.

Neso-, Ino- and Cyclo-silicate-like Structures

Fig. 3 shows the structures of cyanocadmates mimicking silicate structures. As is mentioned later, these structures are similar to the aliphatic skeletons of C atoms when a Cd_t–CN–Cd_t linkage is approximated to a C–C bond.

Pyrosilicate-like $Cd_2(CN)_7$

A discrete heptacyanodicadmate anion $[Cd_2(CN)_7]^{3-}$ is found in the crystal structure of $[PPh_4]_3[Cd_2(CN)_7]$.[13] The dimeric anion has a staggered form with a linear Cd_t–CN–Cd_t array [Fig. 3(*b*)]; in pyrosilicate minerals the central Si–O–Si often bends with the angle varying from 180 to 133° dependent on the counter cation. Generally, the Si–O–Si linkage bends from 180° to a greater or less extent in silicate minerals.

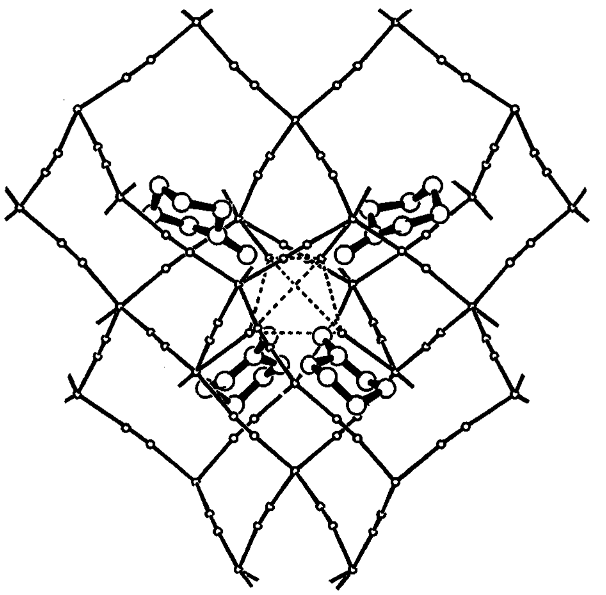

Fig. 2 Hydrogen bonded cluster of $(H_2O)_4$·$4C_6H_{11}OH$ in five neighbouring cavities of $[\{Cd(H_2O)(CN)_2\}_4\{Cd(CN)_2\}]$·4cyclo-$C_6H_{11}OH$; the $(H_2O)_4$ tetrahedron is shown with dotted lines

In the polymeric structure of $[\{Cd_{oc}(CN)(py)_2\}_3][Cd_{t2}(CN)_7]$ (py = pyridine) [= $5Cd(CN)_2$·6py] involving Cd_{oc},[14] the $Cd_2(CN)_7$ unit is in a staggered form and plays the role of a network builder, together with the trimeric rings of $[Cd_{oc}(CN)]_3$ at the terminal CN groups, and the role of the pillar supporting the networks to construct a three-dimensional structure. The trimeric ring is linked to six dimeric anions and the dimeric anion is linked to three trimeric rings in the puckered network. The pillar in the staggered configuration rotates the array of the adjacent network by 120° so as to make the interlayer space for the py ligands co-ordinating to Cd_{oc} at the *trans* positions. Using the doubly unidentate piperazine (den) in place of the unidentate py, the clathrate $[Cd_{oc}(CN)(den)]_3[Cd_{t2}(CN)_7]$·$3PhNH_2$ [= $5Cd(CN)_2$·3den·$3PhNH_2$] is obtained. The three-dimensional host has pillars of den and $Cd_2(CN)_7$ in an eclipsed form [Fig. 3(*c*)]; the guest is accommodated in the interlayer cavity capped at the top and bottom by the faces of the tetrahedra at the terminals of the dimeric units in the eclipsed form. Structures with staggered and eclipsed $Cd_2(CN)_7$ are compared in Fig. 4. This clathrate structure resembles that of hemimorphite $[Zn_4(OH)_2][Si_2O_7]$·H_2O with respect to the Si_2O_7 moiety in an eclipsed form playing the role of pillar and network builder together with the oligomeric assembly of co-ordination polyhedra, which is the tetrameric assembly of the tetrahedra, $Zn_4(OH)_2$, in hemimorphite.[15]

Chain Structure of $[Cd(CN)_3]_n$

In contrast with $[PPh_4]_3[Cd_2(CN)_7]$, involving the pyrosilicate-like dimeric anion, the tetraphenylstibonium salt $[SbPh_4][Cd(CN)_3]$ involves a one-dimensional polymeric chain of $[Cd(CN)_3]_n$ with a dimeric repeating unit in a staggered configuration[16] (like ino-silicate chains in pyroxenes) [Fig. 3(*d*)]. There are two types of crystallographically independent cation and anionic chains in the unit cell, similar to some pyroxene structures. The cation $SbPh_4^+$ appears to interact with a terminal N of unbridged CN in the chain with Sb–N distances of 3.20(2) and 3.43(3) Å for the two independent structural units, respectively. Thus, the difference in structure between the PPh_4^+ and the $SbPh_4^+$ salt may be associated not only with the larger size of the cation but also with the weak Sb–N interaction in the latter. As for the formulation of this compound, $[SbPh_4]_2[Cd(CN)_3]_2$ was used in the original ref. 16 in order to denote

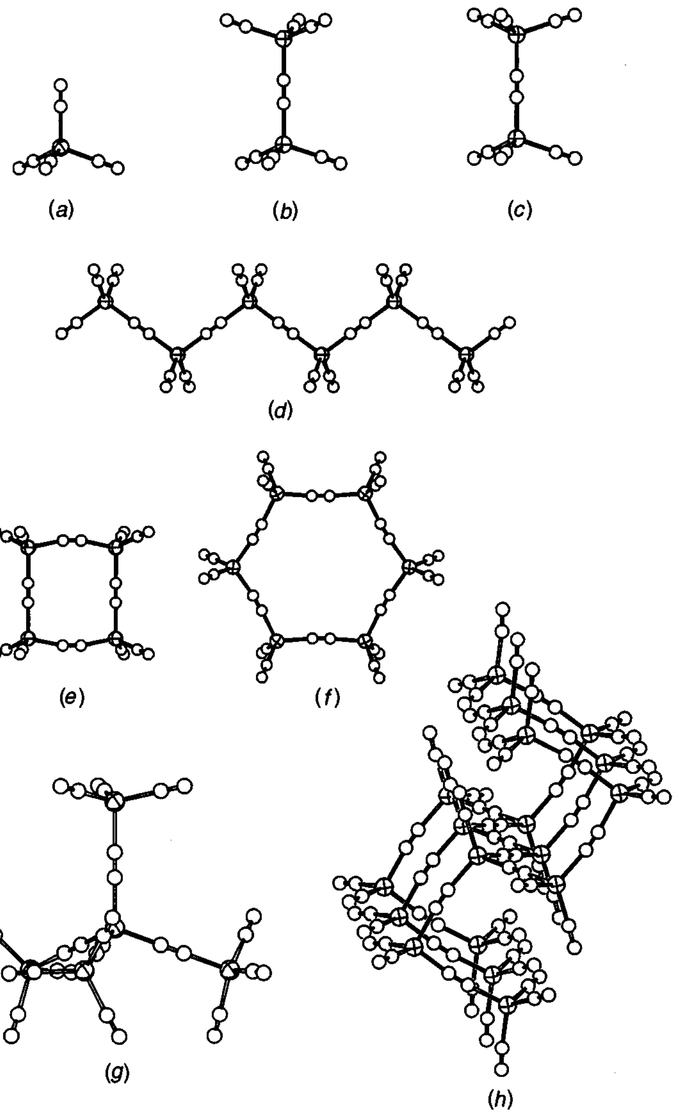

Fig. 3 Structural units of polycyanopolycadmates mimicking silicate structures; all the Cd atoms are tetrahedral. (*a*) Discrete $Cd(CN)_4$, like isolated SiO_4 (methanoid); (*b*) dimeric staggered $Cd_2(CN)_7$, like pyrosilicate Si_2O_7 (ethanoid); (*c*) eclipsed $Cd_2(CN)_7$; (*d*) polymeric $[Cd(CN)_3]_n$, like ino-silicate $(SiO_3)_n$ (polymethylenoid); (*e*) tetrameric $[Cd(CN)_3]_4$, like ring silicate $(SiO_3)_4$ (cyclobutanoid); (*f*) hexameric $[Cd(CN)_3]_6$, like ring silicate $(SiO_3)_6$ (cyclohexanoid); (*g*) pentameric cluster of $[Cd\{(CN)Cd(CN)_3\}_4]$, like $Si(OSiO_3)_4$ (neopentanoid); (*h*) polymeric $[Cd(CN)\{Cd_2(CN)_5\}(CN)]_n$, with no counterpart of silicate but like $(CHEt)_n$. Analogous aliphatic skeletons are shown in parentheses; ionic charges have been neglected.

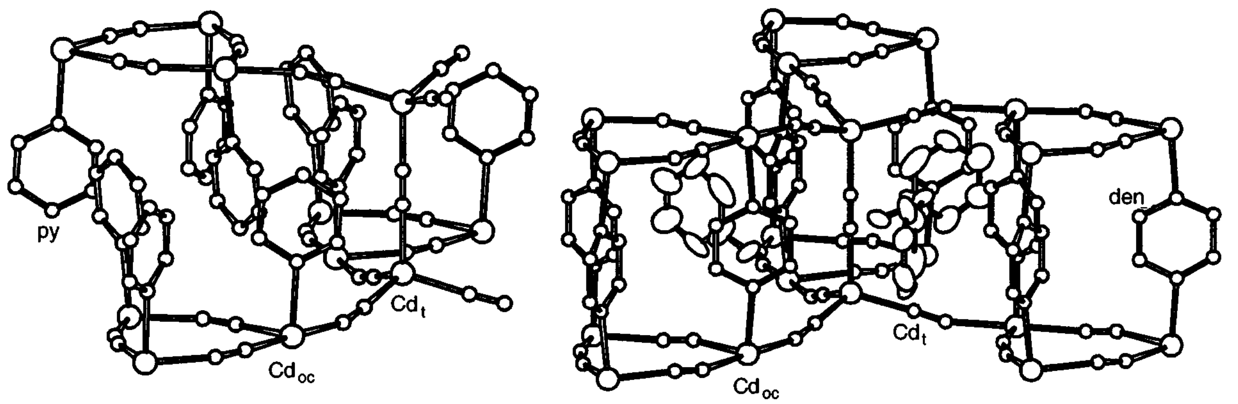

Fig. 4 Parts of the layer structures pillared with staggered $Cd_2(CN)_7$ in $[\{Cd_{oc}(CN)(py)_2\}_3][Cd_{t2}(CN)_7]$ (left) and eclipsed $Cd_2(CN)_7$ in $[Cd_{oc}(CN)(den)]_3[Cd_{t2}(CN)_7]\cdot 3PhNH_2$ (right)

the presence of two crystallographically independent species. In pyroxene chemistry those compounds involving a dimeric repeating unit of ino-silicate are often formulated as $M^{II}_2(Si_2O_6)$.

A variation of the one-dimensional chain structure is observed for $[Cd(CN)_2(dmen)]_n$ (dmen = *N*,*N*-dimethylethane-1,2-diamine) in which the Cd atom adopts trigonal bipyramidal five-co-ordination with the chelating dmen and an unbridged CN equatorial and two bridging CN ligands extending the chain;[17] the chain structure is apparently obtained by the replacement of an unbridged CN in the pyroxene-mimetic chain with the bidentate chelating ligand dmen. The singlet

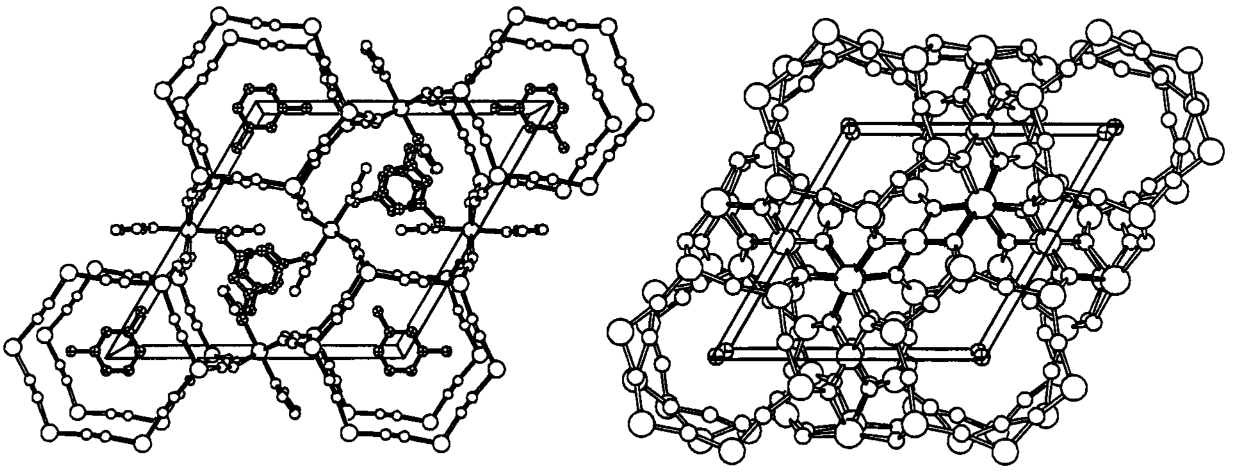

Fig. 5 Structures of $[Cd_{oc}(Him)_2\{Cd_t(CN)_3\}_2]\cdot m\text{-}C_6H_4Me_2$ clathrate with the beryl-mimetic host skeleton (left) and beryl, $Al_2Be_3(SiO_3)_6$ (right)

observed in the ^{113}Cd NMR spectrum supports the fact that the repeating unit $-[Cd(dmen)CN]-CN-$ is monomeric in the non-centrosymmetric space group $Pna2_1$ with both orientations of bridged and unbridged CN groups ordered, as estimated from the results of the crystal-structure determination.

A number of one-dimensional chains of polycyanopolycadmate have been found in other two- or three-dimensional structures, as building blocks for networks or frameworks. These are mentioned later with the relevant multidimensional structures.

Ring Structures of $[Cd(CN)_3]_n$

The host skeleton of $[Cd_{oc}(Him)_2\{Cd_t(CN)_3\}_2]\cdot m\text{-}C_6H_4Me_2$ [$= 3Cd(CN)_2\cdot 2Him\cdot m\text{-}C_6H_4Me_2$] clathrate has a beryl-like structure involving a hexameric ring [Fig. 3(*f*)] of $[Cd(CN)_3]_6$, as shown in Fig. 5.[18] In beryl, $Al_2Be_3(SiO_3)_6$, the hexameric rings of $(SiO)_6$ are stacked along the *c* axis of the $P6/mcc$ unit cell at $z = 0$ and 0.5 (on the mirror planes) with a twist angle of 30° about the *c* axis due to the *c* glide plane.[19] The rings in the mutually twisted array are linked through the out-of-ring O atoms to the tetrahedral Be^{2+} at $z = 0.25$ and 0.75. The role of the tetrahedral Be^{2+} is played by the octahedral Cd_{oc} ligated with two Him at *trans* positions: the Cd_{oc} behaves as a square-planar linkage builder owing to the blocking at the axial positions by the Him ligands. Hence, the hexameric rings are connected by the Cd_{oc} through the out-of-ring CN groups without twisting the $P6/m$ unit cell; the position of Al^{3+} in beryl is occupied by the Him ligand and the guest *m*-xylene.

A tetrameric ring unit of $[Cd(CN)_3]_4$ [Fig. 3(*e*)] like the Si_4O_{12} ring in tetramellite, $Ba_2(Fe,Ti,Mg)_2(OH)_2(Si_4O_{12})$, is involved in the three-dimensional host structures of $[\{Cd_{oc}(den)\}_2\{Cd_t(CN)_3\}_4]\cdot 4PhOMe$[20] [$= 6Cd(CN)_2\cdot 2den\cdot 4PhOMe$] and $[K\cdot 6CH_2{=}CHCN]\cdot[Cd_{oc}\{Cd_t(CN)_3\}_3]$[21] [$= 4Cd(CN)_2\cdot KCN\cdot 6CH_2{=}CHCN$] clathrates, respectively. The former host structure is analogous to $[Cd_{oc}(CN)(den)]_3[Cd_{t2}(CN)_7]\cdot 3PhNH_2$ with respect to the polycyanopolycadmate condensate pillar supporting the layer involving Cd_{oc};the pillar is the dimeric bar in the $PhNH_2$ clathrate but the tetrameric square plate in the PhOMe clathrate.

Layer Structures

Clay-mimetic layer structures are formed by the CN-linkages among Cd_t and Cd_{oc}. In typical clays such as talc, mica, montmorillonite, the layer is composed of T-O-T units, namely the array of tetrahedral, octahedral and tetrahedral co-ordination polyhedra sharing the oxide anions for linking. The $Cd_t{-}CN{-}Cd_{oc}{-}NC{-}Cd_t$ linkage mimics the T-O-T unit in clay structures. A remarkable difference of the clay-mimetic structures from natural clays is observed for the surface layer. In natural clays the surface layer is covered by the faces of co-ordination polyhedra, whereas that of the clay-mimetic layer is covered by the vertices of co-ordination polyhedra. Hence, the surface is almost flat for the former layers but rather puckered for the latter ones. Typical examples of the artificial layers are shown in Fig. 6.

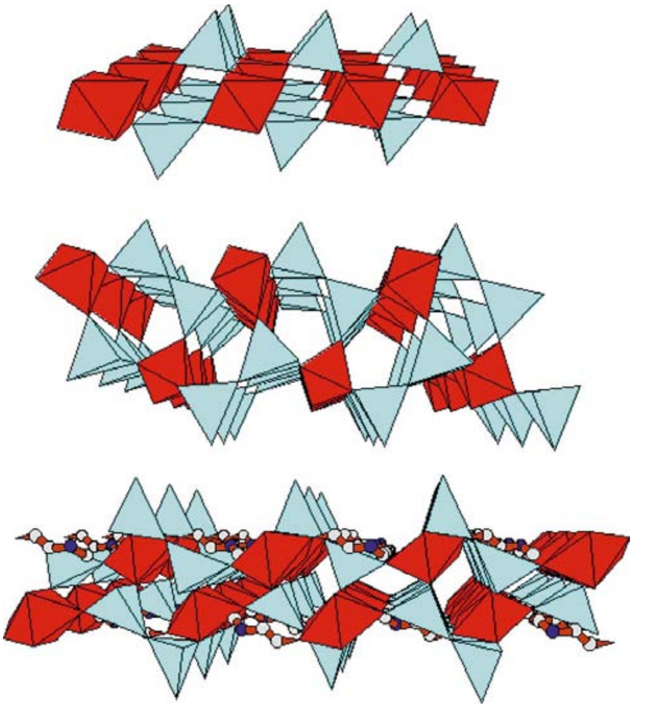

Fig. 6 Clay-mimetic layer structures of polycyanopolycadmates. Top: anionic $[Cd_{oc}\{Cd_t(CN)_4\}_2]$ layer with T-O-T repeating unit typical for clays; middle: cationic $[Cd_{oc}(H_2O)\{Cd_{t2}(CN)_7\}]$ layer with intralayer cavity; bottom: neutral $[Cd_{oc}(Hdmtn)\{Cd_{t2}(CN)_7\}]$ layer

The octacyanotricadmate $[Cd_3(CN)_8]^{2-}$, actually $[Cd_{oc}\{Cd_t(CN)_4\}_2]^{2-}$, gives a typical T-O-T layer structure. All the Cd_{oc} octahedra are respectively linked to six Cd_t tetrahedra each of which leaves a CN group unbridged. The negative charge of the layer is neutralised by the onium cations accommodated in the interlayer space along with the neutral guest molecule in the intercalation compounds $[2NMe_4\cdot Cl_2C{=}CCl_2]\cdot[Cd_3(CN)_8]$ [$=3Cd(CN)_2\cdot 2NMe_4CN\cdot Cl_2C{=}CCl_2$] and $[2NHMe_3\cdot C_6H_6]\cdot[Cd_3(CN)_8]$ [$= 3Cd(CN)_2\cdot 2NHMe_3CN\cdot C_6H_6$] prepared from NMe_4Cl and NMe_3 as the respective onium sources. When NMe_4I was used as the onium source, $[2NMe_4\cdot Cl_2C{=}CCl_2]\cdot[Cd_3(CN)_{(6+x)}I_{(2-x)}]$ ($x = ca.$ 0.29) was obtained in which the vertex of the tetrahedron at the surface of the layer structure was substituted in part with I^- at random.[22]

Use of SMe_3Cl or SMe_3I as the onium source gave a layered zeolite structure with an intralayer cavity accommodating SMe_3^+, $SMe_3{\cdot}[Cd_{oc}(H_2O)\{Cd_{t2}(CN)_7\}]$ [$=3Cd(CN)_2{\cdot}SMe_3CN{\cdot}H_2O$] and $SMe_3{\cdot}[Cd_{oc}(H_2O)\{Cd_{t2}(CN)_{(6+x)}I_{(1-x)}\}]$ ($x = ca.$ 0.49).[22] The cavity is analogous to that formed in the three-dimensional tecto-silicate-mimetic structures to be reviewed in the following section. The Cd_{oc} at the surface of the layer is co-ordinated with a unidentate aqua ligand; the unidentate CN at the Cd_t on the surface is substituted in part, at random, with I^- when SMe_3I was used. Apart from natural clay, this type of layer structure, as well as the following structure, cannot be generated by the parallel translation of the T-O-T unit along the layer plane; a pair of T-O-T units correlated with an inversion centre is the repeating unit of the layer structures.

The electronically neutral host layer of $[Cd_{oc}(Hdmtn)\{Cd_{t2}(CN)_7\}]{\cdot}G$ [$=3Cd(CN)_2{\cdot}HdmtnCN{\cdot}G$; $G = C_6H_6$, C_6H_5F, CCl_4 or Me_2CHCH_2OH] involves a cationic ligand Hdmtn, $NH_2(CH_2)_3NMe_2H^+$, co-ordinating to Cd_{oc}.[22,23a] The Hdmtn skeleton protruding from Cd_{oc} lies on the surface of the layer and the dimethylammonium group is hydrogen bonded to the unidentate CN protruding from Cd_t in an adjacent layer. The neutral guest molecule is accommodated in the interlayer cavity divided by the hydrogen-bonded pillars.

There is an infinite chain of $[Cd_{t2}(CN)_6]_n$, similar to that in $[SbPh_4][Cd(CN)_3]$, running perpendicular to the layer section in the layers composed of $Cd_{oc}L\{Cd_{t2}(CN)_7\}$. Three of the four out-of-chain CN groups in the dimeric repeating unit are linked to three different Cd_{oc}'s; the remaining one is unbridged at the surface of the layer.

Tecto-silicate-mimetic Three-dimensional Frameworks of Polycyanopolycadmates

A series of negatively charged three-dimensional framework structures are formed in $[onium{\cdot}xG]{\cdot}[Cd_{oc}\{Cd_{t2}(CN)_7\}]$ [$=3Cd(CN)_2{\cdot}oniumCN{\cdot}xG$] clathrates accommodating a number of neutral aliphatic and aromatic guest molecules G and aliphatic onium cations.[23,24] In their single-crystal structures a one-dimensional bent chain with a T-O-T repeating unit, namely a linear $-NC-Cd_t-CN-Cd_{oc}-CN-Cd_t-$ unit, is found in common, which runs along a mirror plane of the trigonal, orthorhombic or hexagonal unit cell; an exception to this found in the monoclinically distorted structure of $[SMe_3{\cdot}p\text{-}C_6H_4Me_2]{\cdot}[Cd_{oc}\{Cd_{t2}(CN)_7\}]$ with the chain running along a pseudo-mirror plane.[24] The three-dimensional frameworks are built up by the interconnection of the bent chains through out-of-plane CN groups between Cd_t and Cd_{oc}. The framework structures are classified into six types based on the features observed for the bending mode of the chain and the orientation of the bent chains.[23b] Depending on the bending mode and orientation of the chains, the interconnection between them generates polyhedral cavities framed by Cd–CN–Cd edges and faced by polygons such as tetragon, pentagon, hexagon or octagon, which are generally puckered.

The term 'zeolite-mimetic' is given to such structures due to the polyhedral feature of the cavity surrounded by the closer and wider polygonal openings and cornered by co-ordination polyhedra; the difference from natural zeolites is the involvement of octahedra in addition to tetrahedra in the zeolite-mimetic structures. The cavity structures surrounded by co-ordination polyhedra are shown in Fig. 7. A comment should be added that the notation T-O-T or TOT means a pair of tetrahedral centres coupled by an oxide anion in zeolite chemistry; the notation used here is the same as that used in clay chemistry.

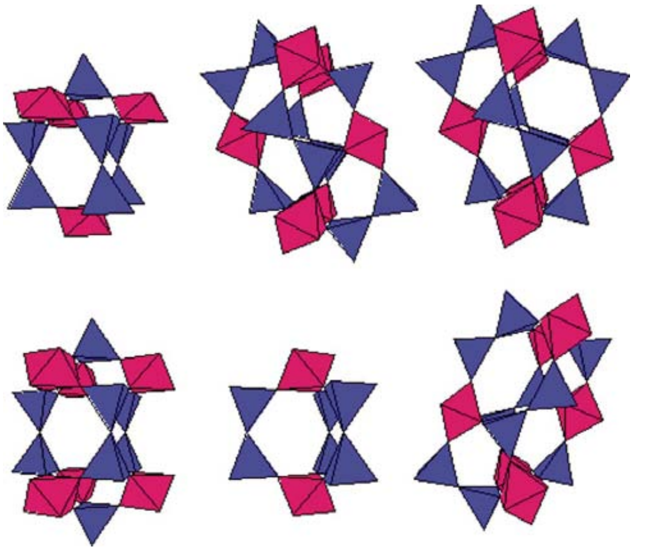

Fig. 7 Cavities in zeolite-mimetic $[Cd_{oc}\{Cd_{t2}(CN)_7\}]$ hosts. Top left: IA $[4^36^3]$ (polyhedron faced with three tetragons and three hexagons) with 4O-7T (surrounded by four octahedra and seven tetrahedra); top centre: IIA $[4^15^46^1]$ with 4O-7T and IIB $[4^15^46^1]$ with 4O-7T; top right: IIIA $[4^35^26^1]$ with 4O-6T, IIIB $[6^28^1]$ with 3O-4T and IIIC $[5^26^1]$ with 3O-4T; bottom left: VB $[4^66^3]$ with 6O-8T; bottom centre: VA $[6^3]$ with 2O-6T; bottom right: VIA $[4^15^46^1]$ with 4O-7T and VIB $[4^36^3]$ with 4O-7T

The chain in $[K{\cdot}4EtCN]{\cdot}[Cd_{oc}\{Cd_{t3}(CN)_9\}]$ [$= 4Cd(CN)_2{\cdot}KCN{\cdot}4EtCN$] has a T-O-T-T repeating unit.[25] Owing to the increase in the number of T in the unit on the mirror plane, the Cd_t–CN–Cd_t linkage is involved with the interconnection of the chains on adjacent mirror planes, which extends a pyroxene-mimetic one-dimensional chain of $[Cd_t(CN)\{Cd_{t2}(CN)_5\}(CN)]_n$ perpendicular to the mirror plane with a T-T branch at every Cd_t in the chain [Fig. 3(*h*)]. The orientation disorder of the CN groups bridged between the Cd_t atoms was verified by solid-state ^{113}Cd NMR spectroscopy for this compound, too.[25]

Inclusion selectivity was examined for benzene (B), toluene (T), *o*- (O), *m*- (M) and *p*- (P) isomers of xylene and ethylbenzene (E) in fractional enclathration-crystallisation processes to give mixed-guest clathrates of the zeolite-mimetic hosts $[NMe_4{\cdot}xG]{\cdot}[Cd_{oc}\{Cd_{t2}(CN)_7\}]$ (N-host) and $[SMe_3{\cdot}xG]{\cdot}[Cd_{oc}\{Cd_{t2}(CN)_7\}]$ (S-host), respectively, by feeding their binary to quinary mixtures.[26] The order of preference in N-host is $T > B > P \gg M > O$ and $E > P \gg M > O$; in S-host $P > T > B \gg M > O$ and $P > E \gg M > O$. The onium guest appears to influence the selectivity for the aromatic guest. The host structure of B, T, O, M and E clathrates belongs to orthorhombic (*Pnam*) type III and that of P to hexagonal ($P6_3/mmc$) type V; that of each of the mixed-guest clathrates was assignable to the type which the single guest clathrate of the most enriched guest belongs to.

The three-dimensional host framework of $[\{Cd_{oc}(H_2O)_2\}_3\{Cd_{t5}(CN)_{16}\}]{\cdot}6G$ [$= 8Cd(CN)_2{\cdot}6H_2O{\cdot}6G$; $G = Et_2O$ or $Pr^i{}_2O$][27] contains a pentameric unit of $Cd\{(CN)Cd(CN)_3\}_4$ [Fig. 3(*g*)] similar to the $Si(OSiO_3)_4$ entity in zunyite, $Al_{12}(AlO_4)Cl(OH,F)_{18}(Si_5O_{16})$.

Other Mineralomimetic Structures

Cooperite (PtS)-like skeleton

Our earliest mineralomimetic structure of the cooperite (PtS)-like skeleton was obtained as the three-dimensional host of Hofmann-Td-type $[Cd(NH_3)_2Hg(CN)_4]{\cdot}2C_6H_6$[28] and en-Td-type $[Cd(en)Cd(CN)_4]{\cdot}2C_6H_6$[29] (en = ethane-1,2-diamine) clathrates derived from the Hofmann-type $[Cd(NH_3)_2Ni(CN)_4]{\cdot}2C_6H_6$[4,30] through the crystal engineering process, replacing the square planar $Ni(CN)_4$ moiety with the tetrahedral moieties, respectively; for the latter the pair of ammine ligands were further replaced by the doubly unidentate en bridge. The CN-linked host framework has the topology of cooperite (PtS) in which a square-planar Pt is linked to four tetrahedral S and

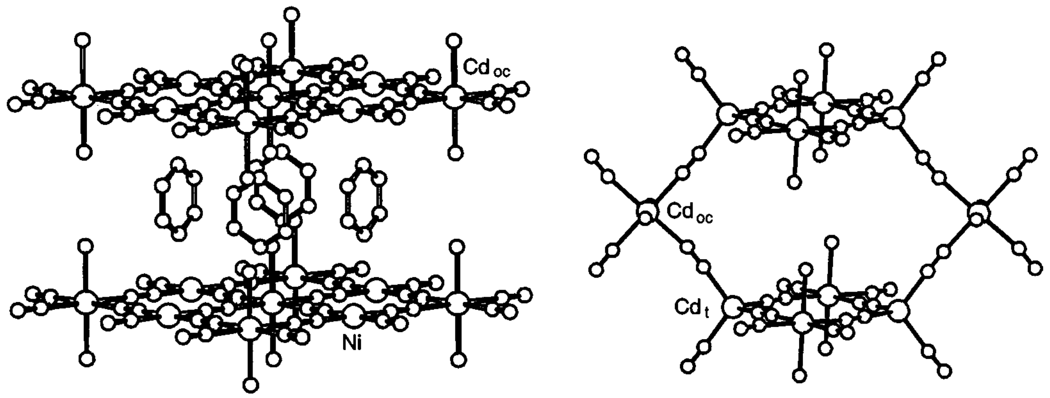

Fig. 8 Structures of the Hofmann-type $[Cd(NH_3)_2Ni(CN)_4]\cdot2C_6H_6$ clathrate (left) and cooperite (PtS)-mimetic host skeleton of the Hofmann-Td-type $[Cd_{oc}(NH_3)_2Cd_t(CN)_4]\cdot2C_6H_6$; only four guest benzene molecules for the former and no guests for the latter have been shown for the sake of clarity

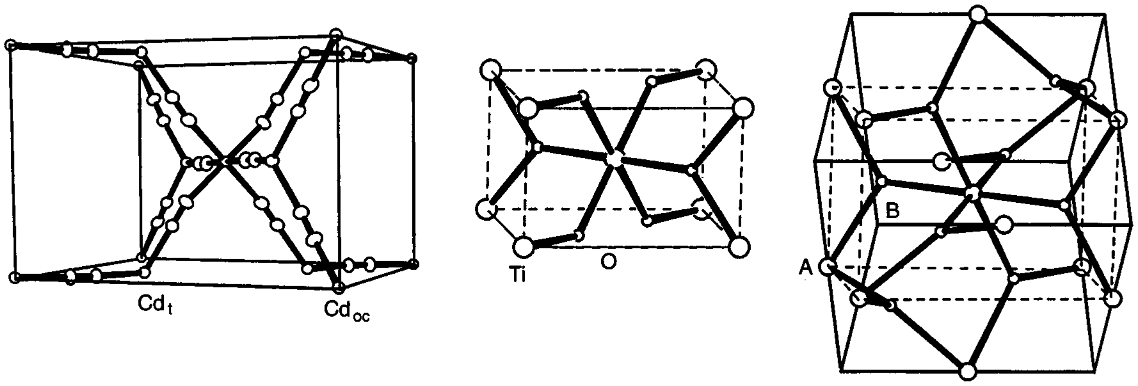

Fig. 9 Structures of rutile-mimetic host of $[Cd_{oc}\{Cd_t(CN)_3(Him)\}_2]\cdot$*p*-$C_6H_4Me_2$ (left), rutile (TiO_2) (centre) and rutile-mimetic array of hydrogen-bonded water molecules in $[H_3(H_2O)_{14}]\cdot[Cd_{oc}\{Cu_2(CN)_7\}]$ (right: the ring of twelve water molecules is depicted as the octahedral centre A)

the S to four Pt, as shown in Fig. 8. In the PtS-mimetic hosts, the square-planar site is occupied by the octahedral Cd whose *trans* positions are blocked by the secondary ligand NH_3 or en so as to make the Cd behave as a square-planar co-ordination centre for CN-linking; the tetrahedral site is occupied by Hg or Cd.

Rutile (TiO_2)-mimetic structure

The site of the electronegative component in the mineral is replaced by cyanometalate in several mineralomimetic structures. The host in $[Cd_{oc}\{Cd_t(CN)_3(Him)\}_2]\cdot$*p*-$C_6H_4Me_2$ [=3Cd-$(CN)_2\cdot$2Him$\cdot$*p*-$C_6H_4Me_2$] has the same topology as that of stishovite, SiO_2 involving octahedral Si^{4+} and trigonal O^{2-}, is isomorphous to rutile TiO_2, as shown in Fig. 9.[24] The tetrahedral Cd_t is blocked at one co-ordination site by the unidentate Him, this acts as a trigonal site in the rutile-mimetic framework, in which cavity the secondary ligand Him and the neutral guest *p*-$C_6H_4Me_2$ are accommodated.

Pyrite (FeS_2)-mimetic skeleton and rutile-like array of H_2O

The solid acid $[H_3(H_2O)_{14}]\cdot[Cd_{oc}\{Cu_2(CN)_7\}]$ [=3HCN$\cdot$Cd-$(CN)_2\cdot$2CuCN$\cdot$14H_2O] has a doubly interpenetrating hetero-framework structure: one framework of $CdCu_2(CN)_7$ is pyrite (FeS_2)-mimetic, the other being a hydrogen-bonded framework comprising of a ring of twelve water molecules and two waters connecting the rings in a rutile-mimetic topology.[31] In pyrite the Fe is octahedrally surrounded by six S atoms and one S of the S_2 entity is on a tetrahedral centre co-ordinating to the other S and three Fe atoms. The $Cu_2(CN)_7$ entity with a staggered configuration co-ordinates to three Cd_{oc} atoms and the Cd_{oc} accomplish its octahedral co-ordination with six N from six $Cu_2(CN)_7$, as shown in Fig. 10. The void generated in the pyrite-mimetic framework is filled by partly protonated water molecules. By neglecting the three acid protons, 14H_2O in the formula are classified into two groups A (12H_2O) and B (H_2O) with a composition AB_2. The twelve water molecules form a rotaxane structure of the puckered hydrogen-bonded ring A surrounding the central CN group of the $Cu_2(CN)_7$ entity. Six water molecules in each A ring are further hydrogen bonded to six other water molecules belonging to B; the water molecule B is linked to three A rings. Thus, a three-dimensional hydrogen-bonded framework of water molecules interpenetrates into the pyrite-mimetic framework of $[Cd_{oc}\{Cu_2(CN)_7\}]$. Assuming ring A has an octahedral centre extending hydrogen bonds to six B, the water framework has a rutile-mimetic topology, as is illustrated in Fig. 9 (right). Order–disorder transition in the rutile-mimetic water framework has recently been studied in detail by calorimetry and dielectric measurements.[32]

Two-dimensional ice

A two-dimensional ice mimicking a part of ice I_h structure is found in $[Cd(H_2O)_2Ni(CN)_4]\cdot4H_2O$,[33] as shown in Fig. 11. The host complex has a Hofmann-H_2O-type structure, in which the NH_3 in the Hofmann-type host is replaced by H_2O. A hydrogen-bonded network of water molecules is formed in the interlayer space between the puckered two-dimensional metal-complex networks with the aqua ligands protruding from the metal-complex networks and the guest water molecules intercalated between the networks. The hydrogen-bonded water network is meshed with boat-form hexagons similar to the two-dimensional array of water molecules cut away from the ice I_h structure along the [100] plane. The six water molecules in the formula, involving twelve H atoms and lone-pairs in total, provide two lone-pairs for co-ordination to Cd and nine H atoms and lone-pairs for the hexagonal network formation; three H atoms and one lone-pair are outside the network.

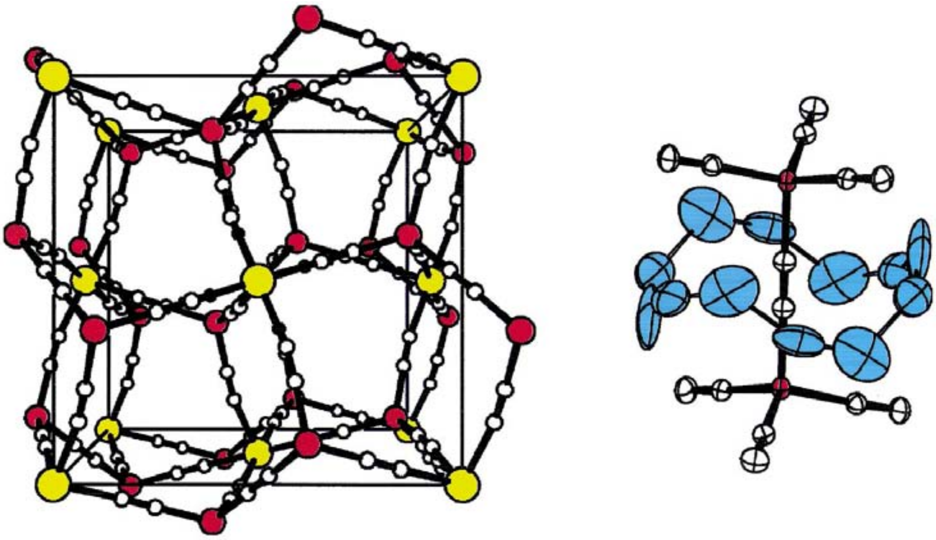

Fig. 10 Structure of $[H_3(H_2O)_{14}][Cd\{Cu_2(CN)_7\}]$. Right: pyrite (FeS)-mimetic host framework; left: the hydrogen-bonded ring of twelve water molecules about the pyrosilicate-mimetic $Cu_2(CN)_7$ entity

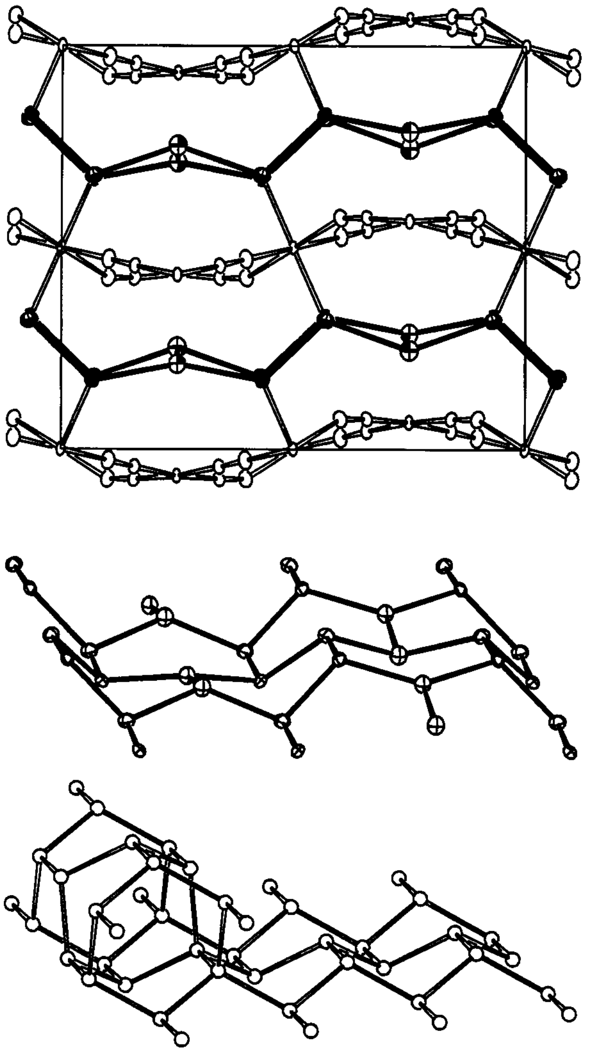

Fig. 11 Structure of $[Cd(H_2O)_2Ni(CN)_4]\cdot 4H_2O$. Top: the layers of the metal complex host and the hydrogen bonded water molecules (with solid bonds); middle: the hydrogen-bonded network of the aqua and intercalated water molecules; bottom: the two-dimensional array of the water molecules along the [100] plane in ice I_h

Mineralomimetics and Co-ordination Chemistry

Examples are given in recent review articles[34,35] and a comprehensive treatise.[36] So-called supramolecular assemblies, self-organised molecular systems, functional nanostructures with microporous frameworks, *etc*., are much-cited keywords in current works of solid-state chemistry both organic and inorganic. Molecular science-oriented supramolecular co-ordination chemistry uses the central metal as a designed joint around which functional ligand molecules can be arranged in a desired order, the applied co-ordination chemistry may be said to be the chemistry of ligands perturbed or modulated by the central metals. Biomimetic chemistry appears to mimic functions of bio-molecules or bio-substances with artificially designed and organised molecular systems using non-biotic or semi-biotic organic materials. The mineralomimetic chemistry described here is far more oriented towards co-ordination chemistry itself.

Werner's co-ordination theory was interpreted in terms of the relationship between the central atom at the origin and the ligating atoms on three-dimensional coordinates, that is, the relationship between point (atom) and point (atom). Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$, discovered in 1827, exemplified the extension of the concept of co-ordination to the relationship between point (atom) and line (linear π-bond) about 130 years later; this was also exemplified by ferrocene, to that of point (atom) and plane (ring π-bond). A new aspect of the mineralomimetic chemistry is the co-ordination relationship among solids (co-ordination polyhedra including bars and plates). There are prototypes of such structures in natural minerals. However, the scope of the mineralomimetic chemistry should not be limited only to mimicking mineral structures but should be extended to explore much about unknown multidimensional structures comprised of assemblies of co-ordination polyhedra. As is exemplified for the systems involving linear $Ag(CN)_2$, square planar $Ni(CN)_4$ and tetrahedral $Cd(CN)_4$,[4] we have various multidimensional structures, but it is difficult to compare them with those of natural minerals.

A new scientific term is not always proposed on the basis of a completely unprecedented scientific concept. Even within our mineralomimetic chemistry, the prototype can be traced back to the attempt to replace the square planar $Ni(CN)_4$ entity in the Hofmann-type $[Cd(NH_3)_2Ni(CN)_4]$ host by the tetrahedral $Cd(CN)_4$ in 1972;[29] a H-quartz-mimetic lattice but with a six-fold interpenetration of $[Co\{Au(CN)_2\}_2]$ was found in 1982;[37] the single framework of $K[Co\{Au(CN)_2\}_3]$ in the triply interpenetrating trigonally distorted three-dimensional lattice[38] reported in 1980 has a topology similar to the structure of $K_2Fe^{II}[Fe^{II}(CN)_6]$, assumed by Keggin and Miles[2] in 1936 to have K^+ accommodated in the cage; the varieties in the catenation behaviour of the diaminoalkanes depending on the methylene chain length in the recently reported $[Cd(diam)_2$-

$Ni(CN)_4]$ [diam = $NH_2(CH_2)_nNH_2$; $n = 2$–7 and 9][39] and [Cd($NH_2CH_2CH_2OH$)(diam)$Ni(CN)_4$] ($n = 5$ or 6)[40] have prototypes of the form $[Cu\{NC(CH_2)_nCN\}_2]NO_3$ ($n = 2$–4)[41] reported in 1959 including a quartz-mimetic four-fold interpenetrating lattice for $n = 4$, although the variation in the catenation behaviour of the $Ni(CN)_4$ in the multidimensional structures was newly found.

Finally it should be commented upon that the catenation of tetrahedra in inorganic polymeric structures has a similarity to aliphatic skeletons, if Cd_t–CN–Cd_t or Si–O–Si is replaced by C–C,[42] as is exemplified in the caption of Fig. 3. Hence, we might find already known prototypes for apparently unprecedented structures with careful surveys of the old literature.

A few proceedings have briefly described parts of this work.[43] A comprehensive review of cyanometal complexes has recently been published.[44]

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