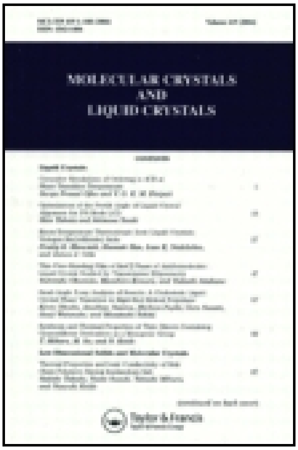

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Alkane-Like Building Blocks in the Supramolecular Structures Built of Cyanocadmate Moieties -Why Don't You, Organic Chemists, Learn More from CN-Linked Inorganic Structures?

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ALKANE-LIKE BUILDING BLOCKS IN THE SUPRAMOLECULAR STRUCTURES BUILT OF CYANOCADMATE MOIETIES
- WHY DON'T YOU, ORGANIC CHEMISTS, LEARN MORE FROM CN-LINKED INORGANIC STRUCTURES? -

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Abstract A number of $Cd_x(CN)_y$ building blocks in the multi-dimensional supramolecular structures we have developed, some of which have mineralomimetic features, have resemblance to CH_4, C_2H_6, CMe_4, $-(CH_2-)_n$ etc., due to the structural features of the $Cd_x(CN)_y$ as the entities built by linkage of the coordination tetrahedra. Better understanding of these complicated 1D, 2D and 3D supramolecular structures may be attained on the analogy of organic alkane-like structures.

INTRODUCTION

By utilising the Lewis basicity of the N-end of tetrahedral $[Cd(CN)_4]^{2-}$, a number of supramolecular structures have been constructed as polymeric condensates of the tetrahedral anions; in several cases octahedral and/or trigonal-bipyramidal Cd atoms are involved in the multi-dimensional supramolecular structures of 1D chains, 2D layers, 3D frameworks, etc.[1] Their structural features are able to be interpreted in terms of mineralomimetic chemistry that $Cd(CN)_2$ has great resemblance to SiO_2 in the AB_2 composition, A taking a tetrahedral coordination and B linking A's to build up a 3D structure. Besides cristobalite- and tridymite-like 3D structures of $Cd(CN)_2 \cdot G$ clathrates,[2] ino-silicate-mimetic pyroxene-like 1D,[3] phyllo-silicate-mimetic clay-like 2D[4] and tecto-silicate-mimetic zeolite-like 3D structures[4a,5] have been designed, prepared and characterised in our laboratories. These structures appear to be too complicated for general audience in chemistry, in particular for organic chemists, who are not always expected to have detailed knowledge in mineralogy or classic inorganic chemistry.

The authors examine to interpret the structures involving tetrahedral moieties and/or condensed tetrahedra in terms of the analogy of sp^3-C catenation in organic compounds in this presentation. The interpretation may be helpful to design supramolecular structures using aliphatic skeletons as their building blocks.

PRINCIPLES OF THE ANALOGY

First of all, the Cd atoms in octahedral coordination are discriminated as Cd^{oh} or O from tetrahedral Cd without superscript or T. Then, a Cd-CN-Cd or T-T linkage in our supramolecular structures can be approximated to a single-bond C-C in the aliphatic structure. Designating CN- that linked to another Cd (T) and CN that to Cd^{oh}, respectively, a $Cd(CN-)_4$ unit is able to be approximated to an sp^3-C, whereas a $Cd(CN)_4$ be approximated to CH_4. Let us call CH_4-approximated $Cd(CN)_4$ "methanoid", C_2H_6-approximated $Cd_2(CN)_7$ [= $(NC)_3Cd$-CN-$Cd(CN)_3$] "ethanoid", etc. Some of the representative building blocks are illustrated in Figure. 1.

DEMONSTRATIONS

Diamondoid

The clathrate $Cd(CN)_2 \cdot G$ should be the simplest in the composition among the known clathrates. As shown in Figure 2, the CN-linkages among Cd's form a diamondoid 3D framework (the space group $Fd\bar{3}m$) isostructural to H-cristobalite providing the cavity of an adamantane-like skeleton for tetrahedral or pseudo-tetrahedral guest such as $CMe_{4-n}Cl_n$ ($n = 0 - 4$);[2] the 3D host transforms to the hexagonal ($P6_3/mmc$) form isostructural to H-tridymite for the long aliphatic chain guest $Bu^n{}_2O$.[1,2d] The topology of the framework is the same to diamond (cubic) for the former and to lonsdalite (hexagonal diamond) for the latter. $Cd(CN)_2$, as well as $Zn(CN)_2$, has a double-framework self-clathrate structure of the diamondoid lattices:[2c] one lattice fills the space generated in the other.

Methanoid

The 3D host of the Td-en-type clathrate $[Cd^{oh}(en)Cd(CN)_4] \cdot 2C_6H_6$[6] involves the methanoidal $Cd(CN)_4$ moieties interlinking the two sets of $-[Cd^{oh}\text{-en-}]_\infty$ 1D chains running in parallel to one another in each set but being arrayed alternately with an about 90° inclination; the methanoid links four chains at two each Cd^{o} atoms in the two sets. Upon releasing the guests the bridging en in the clathrate host turns to a chelating ligand to the $\mathrm{Cd}^{\mathrm{oh}}$ in the residual complex $[\mathrm{Cd}^{\mathrm{oh}}(\mathrm{en})\mathrm{Cd}(\mathrm{CN})_4]$, which has a doubly interpenetrating 3D framework structur built of methanoidal $\mathrm{Cd}(\mathrm{CN})_4$ and $\mathrm{Cd}^{\mathrm{oh}}(\mathrm{en})$ behaving as a four-

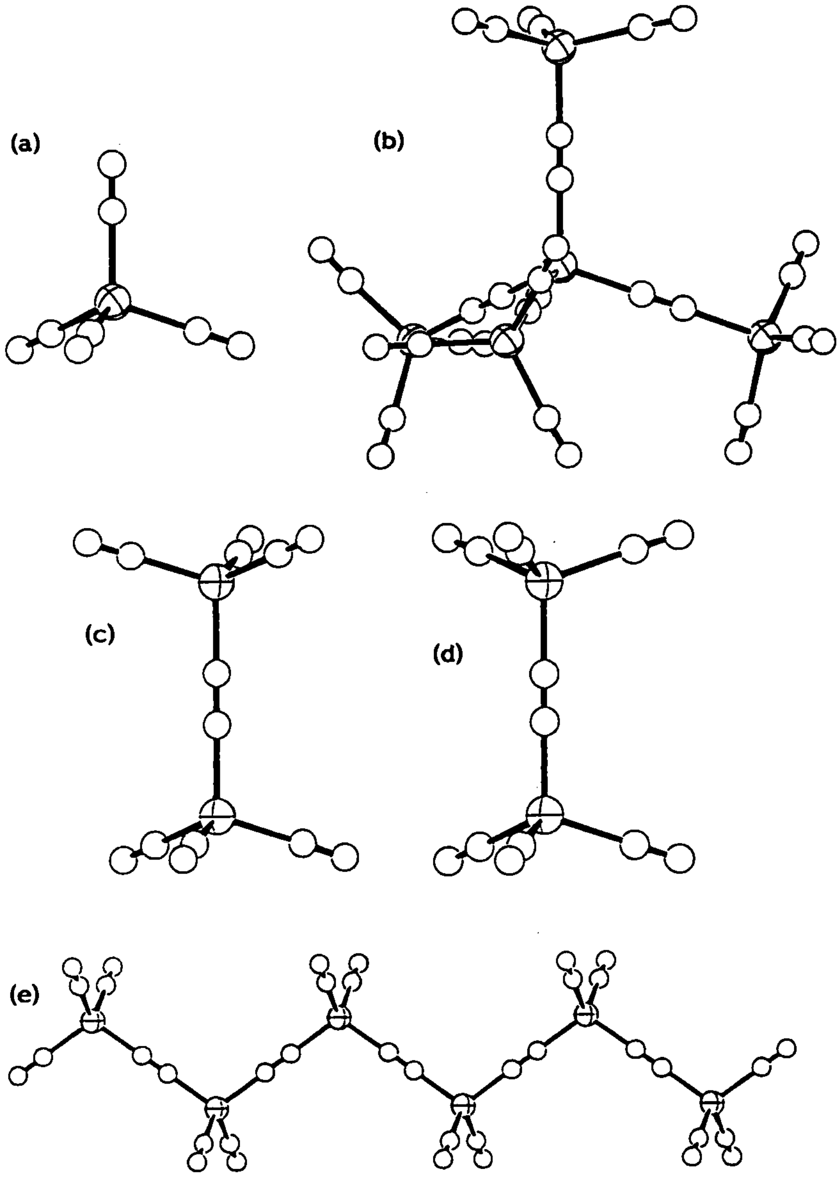


FIGURE 1 Representative $\mathrm{Cd}_x(\mathrm{CN})_y$ building blocks: (a) methanoid $\mathrm{Cd}(\mathrm{CN})_4$, (b) neopentanoid $\mathrm{Cd}\{\mathrm{CN}\text{-}\mathrm{Cd}(\mathrm{CN})_3\}_4$, (c) staggered and (d) eclipsed ethanoid $(\mathrm{NC})_3\mathrm{Cd}\text{-}\mathrm{CN}\text{-}\mathrm{Cd}(\mathrm{CN})_3$, and (e) polymethylenoid $[\mathrm{Cd}(\mathrm{CN}\text{-})(\mathrm{CN})_2]_\infty$.

hand linkage builder.[7]

Ethanoid

The pyro-silicate-mimetic discrete dimeric anion $[(NC)_3Cd\text{-}CN\text{-}Cd(CN)_3]^{3-}$ in

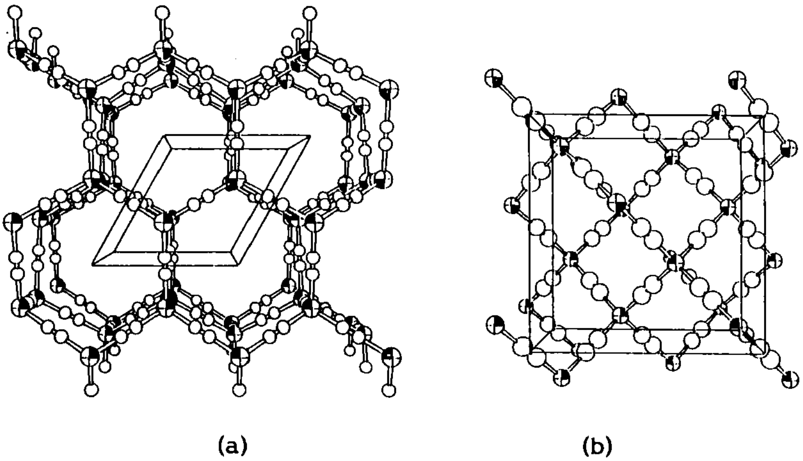

(a) (b)

FIGURE 2 (a) Diamondoid and (b) hexagonal-diamondoid $Cd(CN)_2$ host.

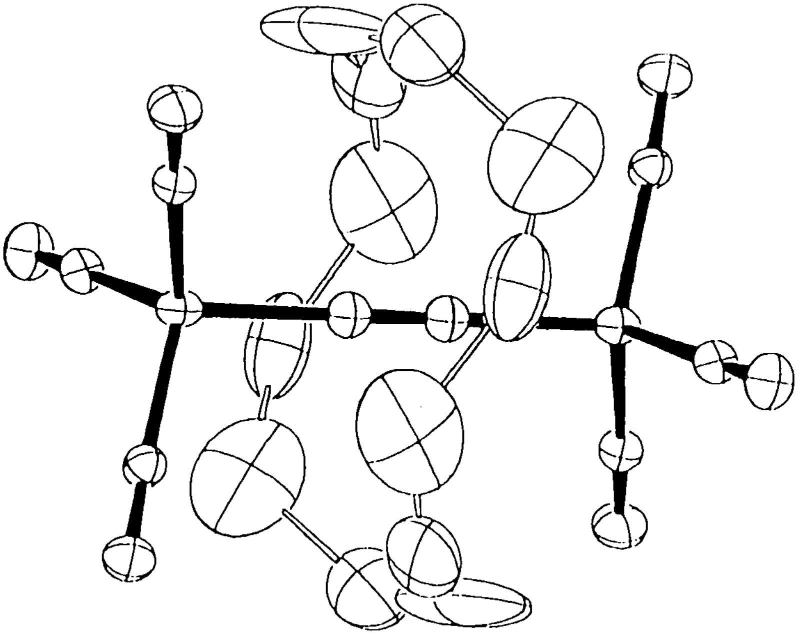
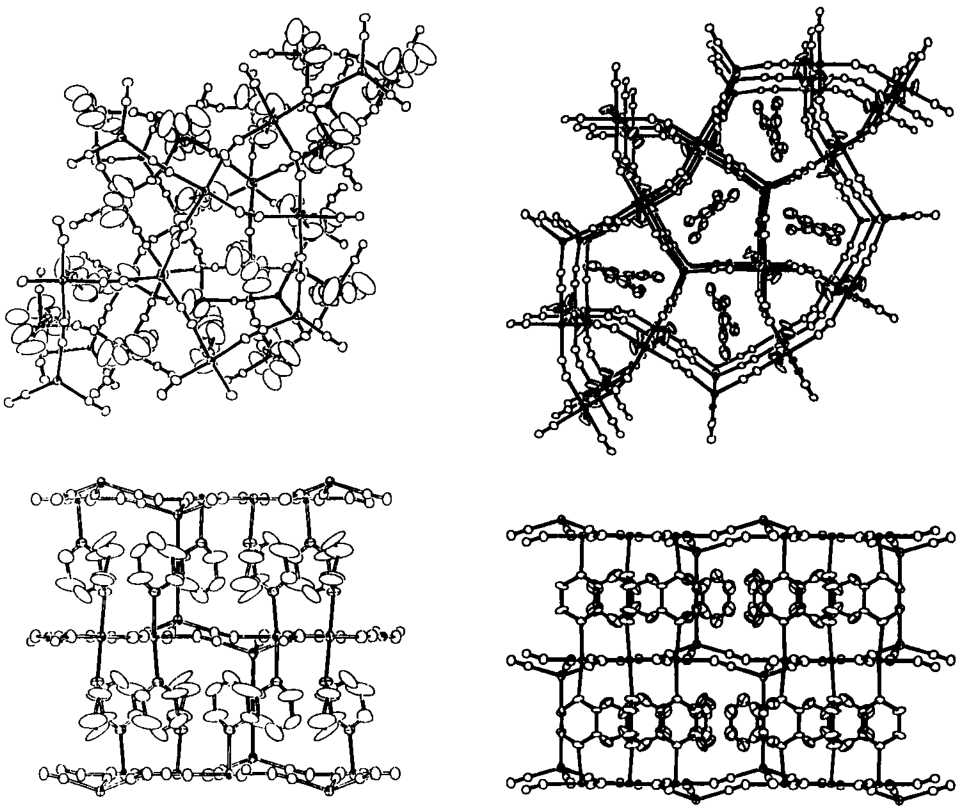


FIGURE 3 Rotaxane structure of twelve water molelcules about ethanoidal $(NC)_3Cu\text{-}CN\text{-}Cu(CN)_3$ in $[H_{31}O_{14}][Cd\{Cu_2(CN)_7\}]$.

$\mathrm{[PPh_4]_3[Cd_2(CN)_7]}$ has a staggered form as an ethanoid.[8] The isostructural ethanoid of a Cu(I) analogue $\mathrm{[Cu_2(CN)_7]^{5-}}$ is found in $\mathrm{[H_{31}O_{14}][Cd\{Cu_2(CN)_7\}]}$ with a pyrite-mimetic 3D skeletal structure, in which 12 of the 14 partly protonated water molecules form a rotaxane ring about the Cu-CN-Cu axis of the ethanoidal entity (Fig. 3).[9]

The 3D structures of a complex $\mathrm{[\{Cd^{oh}(CN)(py)_2\}_3\{Cd_2(CN)_7\}]}$[10] and a clathrate $\mathrm{[\{Cd^{oh}(CN)(den)\}_3\{Cd_2(CN)_7\}]\cdot 3\underline{o}\text{-}MeC_6H_4NH_2}$ (den = piperazine)[11] are built by the interconnection between trimeric ring unit of planar $\mathrm{[Cd^{oh}(CN)]_3}$ (cyclopropanoid) and $\mathrm{Cd_2(CN)_7}$ ethanoid. The skeletal form of the ethanoid is staggered in the former but eclipsed in the latter (Fig. 4).

The zeolite-mimetic 3D hosts of $\mathrm{[Cd_3(CN)_7]\cdot[onium\cdot xG]}$ clathrates are grouped into six types according to the structural features of the 1D chains $\mathrm{-(NC\text{-}Cd\text{-}CN\text{-}Cd^{oh}\text{-}NC\text{-}Cd\text{-})_\infty}$ [= $\mathrm{-(T\text{-}O\text{-}T\text{-})_\infty}$] running on the mirror planes in the respective single crystal structures;[5] the 3D structures are formed by



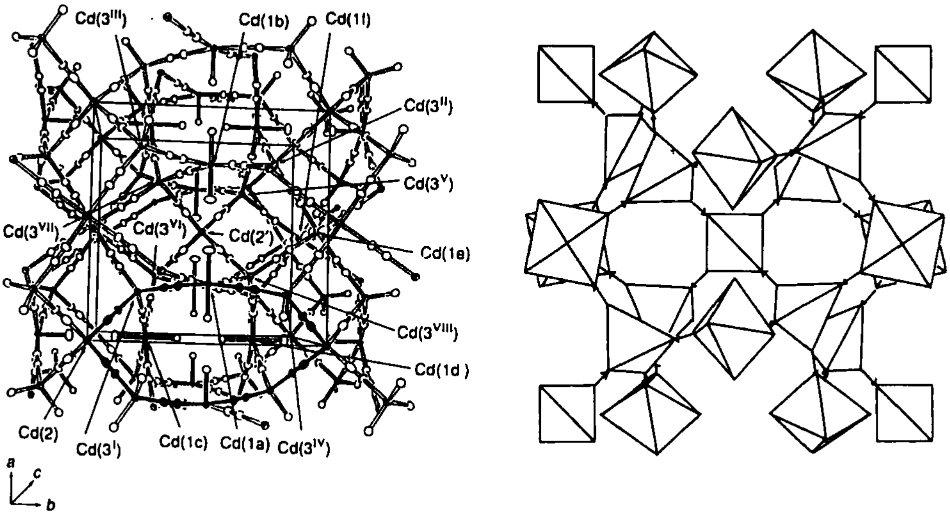
(a) (b)

FIGURE 4 $\mathrm{(NC)_3Cd\text{-}CN\text{-}Cd(CN)_3}$ ethanoid staggered in (a) $\mathrm{[\{Cd(CN)(py)_2\}_3\{Cd_2(CN)_7\}]}$ and eclipsed in (b) $\mathrm{[\{Cd(CN)(den)\}_3\{Cd_2(CN)_7\}]\cdot 3\underline{o}\text{-}MeC_6H_4NH_2}$.

interconnection of the 1D chains through out-of-plane CN groups: Cd-CN-$\mathrm{Cd^{oh}}$ and $\mathrm{Cd^{oh}}$-NC-Cd. These structures may be understood as the assemblies of the ethanoidal -T-T- unit on the mirror plane interconnected by the O moieties in the same and two adjacent mirror planes. Eclipsed ethanoids are involved in type V, whereas staggered ones are in types I -IV and VI.

Neopentanoid

The clathrates $[\{\mathrm{Cd^{oh}(H_2O)_2}\}_3(\mathrm{Cd\{CN\text{-}Cd(CN)_3\}_4})]\cdot 6G$ (G = $\mathrm{Et_2O}$, $\mathrm{Pr^i{}_2O}$) have a $\mathrm{Cd^{oh}}$:Cd ratio of 3:5 in their isostructural 3D hosts.[12] The five tetrahedral Cd atoms are linked by four CN groups to take a neopentanoid structure: the central Cd is coordinated with four $\mathrm{Cd(CN)_4}$ tetrahedrally. The origin and the body-centre of the cubic $P\bar{4}3n$ unit cell are occupied by the central Cd atoms which extend four each $\mathrm{\text{-}CN\text{-}Cd(CN)_3}$; the terminal $\mathrm{Cd(CN)_3}$ is linked to three $\mathrm{Cd^{oh}}$ each of which is to three other terminals to build up the 3D host (Fig. 5).

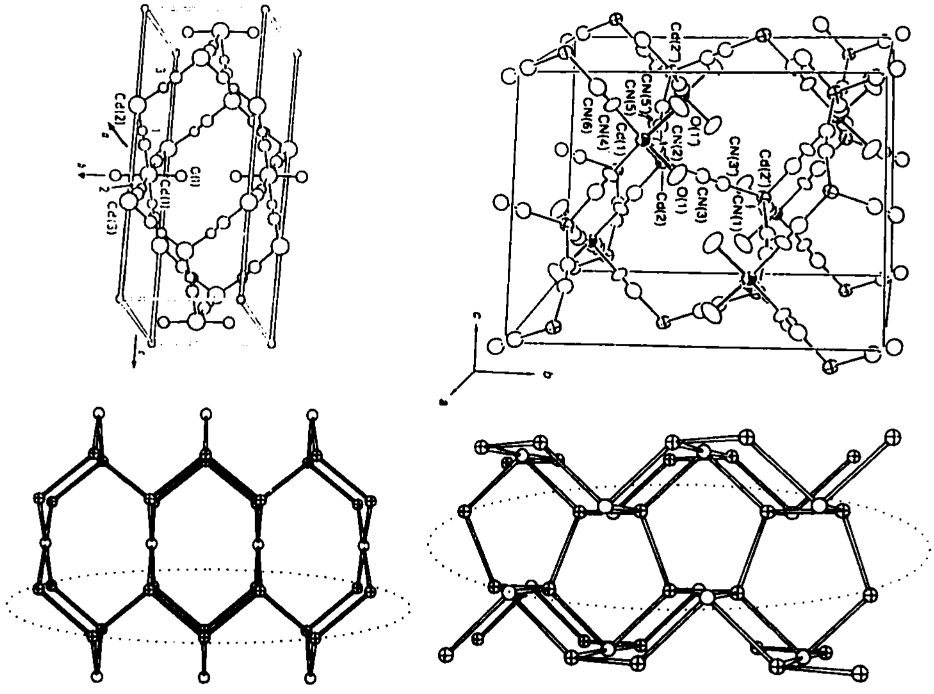


(a) (b)

FIGURE 5 Neopentanoidal array of the tetrahedral moieties in $[\{\mathrm{Cd(H_2O)_2}\}_3(\mathrm{Cd\{CN\text{-}Cd(CN)_3\}_4})]\cdot 6\mathrm{Et_2O}$. (a) Ball-and-stick illustration of the unit cell; (b) linkages of the coordination polyhedra.

Polymethylenoid

The 1D chain of $\mathrm{\text{-}[Cd(CN\text{-})(CN)_2]_\infty}$ in $\mathrm{[SbPh_4]_2[Cd(CN)_3]_2}$, the formula denoting the presence of two kinds each of the crystallographically independent cations and anions in the monoclinic $P2_1/c$ unit cell,[3] consists of the linear array of tetrahedral $\mathrm{Cd(CN)_4}$ sharing the vertex cyanides like a polymethylene chain in



(a) (b)

FIGURE 6 Polymethylenoid chains in (a) all-trans configuration in $[Cd^o(H_2O)_2\{Cd(CN)_3\}_2]\cdot 3Bu^tOH$[13] and (b) cis-trans configuration in $[Cd^o(H_2O)_2\{Cd(CN)_3\}_2]\cdot 2Pr^iOH$.[14] From the unit cell structures shown above the polymethylenoid chains connecting Cd atoms (shown with cross) are found.

all-trans conformation of the skeleton. One of the two CN groups out of the skeletal extension appears to have weak interaction with the $SbPh_4^+$ in the distances of 3.20(2) and 3.43(3) Å to the central Sb leading to a trigonal-bipyramidal coordination of the Sb^{5+}; the CN groups directed toward Sb are arranged in the trans positions within the chain.

Two kinds of polymethylenoid chains are found in the complicated 3D host structures of alcohol-guest clathrates developed by other groups: $Cd(CN)_2\cdot{}^2/_3H_2O\cdot Bu^tOH$[13] ≡ $[Cd^{oh}(H_2O)_2\{Cd(CN)_3\}_2]\cdot 3Bu^tOH$ and $Cd(CN)_2\cdot{}^2/_3H_2O\cdot{}^2/_3Pr^iOH$[14] ≡ $[Cd^{oh}(H_2O)_2\{Cd(CN)_3\}_2]\cdot 2Pr^iOH$ (Fig. 6). The channel cavity in the former with a hexagonal cross section is walled by the equatorial planes of the trans-$Cd^{oh}(H_2O)_2$ moieties linked successively with the all-trans polymethylenoid chains of $-[Cd(CN-)(CN)_2]_-$. The polymethylenoid chain takes a cis-trans conformation in the latter, as well as one of our clathrates $[\{cis\text{-}Cd^{oh}(H_2O)_2\}\{Cd(CN)_3\}_2]\cdot 2Pr^n{}_2O$,[12] owing to the cis-ligation at Cd^{oh}.

The 3D host of another zeolite-like clathrate [Cd$_4$(CN)$_9$]·[K·4EtCN][15] with a Cd$^{\mathrm{oh}}$:Cd ratio of 1:3 has -(O-T-T-T-)$_\infty$ chains, similar to -(T-O-T-)$_\infty$ in types I - VI with the Cd$^{\mathrm{oh}}$:Cd ratio of 1:2, running on the mirror planes of the Pnma unit cell (Fig. 7). The -O-T-T-$\underline{\mathrm{T}}$- unit in the chain, underlined for the T at one end of the unit, is successively linked by $\underline{\mathrm{T}}$-$\underline{\mathrm{T}}$ connection between the mirror planes to give another set of -{$\underline{\mathrm{T}}$-(T-T-O)}$_\infty$ chains running across the mirror planes with the ethanoidal branch, which may be formulated as an ethanoid-substituted -[Cd(CN-)(CN){Cd(CN)$_2$CNCd(CN)$_3$}]$_\infty$ like -(CHEt-)$_\infty$. The -$\underline{\mathrm{T}}$-$\underline{\mathrm{T}}$- sequence has an all-*trans* conformation; each of the (CN) groups in the ethanoidal moiety and at $\underline{\mathrm{T}}$ is linked to Cd$^{\mathrm{oh}}$.

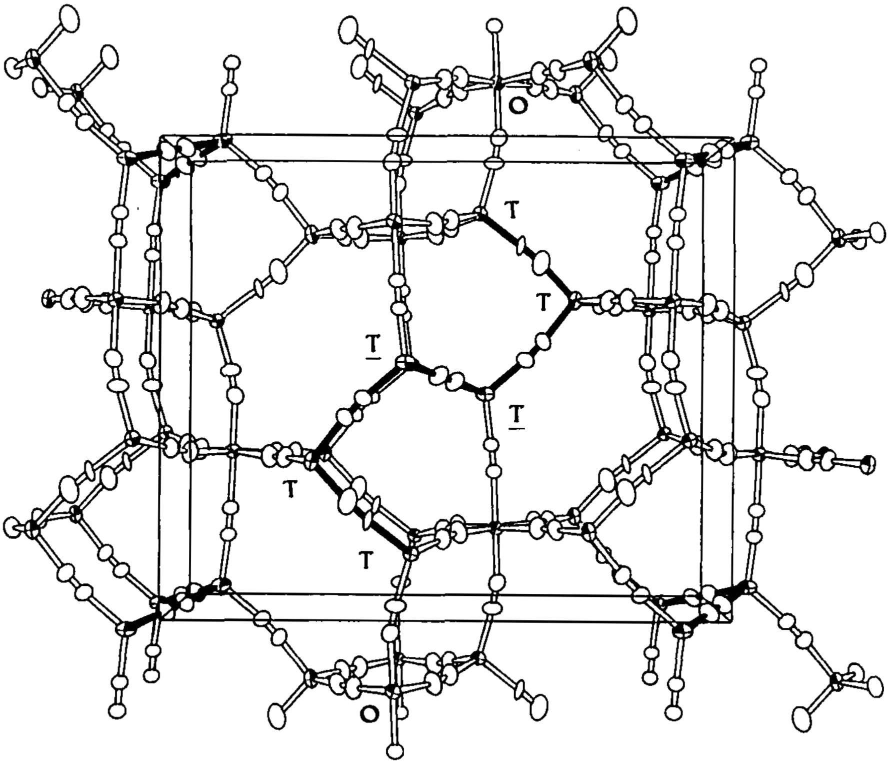


FIGURE 7 Ethanoid-substituted polymethylenoid in the 3D host of [Cd°{Cd(CN)$_3$}$_3$]·[K·4EtCN]. Polymethylenoid chains run along the direction vertical to the page at the centre and every corner of the unit cell, as shown with solid bonds; the ethanoidal substitutes are exemplified only in the chain at the centre with solid bonds.

CONCLUDING REMARKS

Construction of supramolecular structures by means of crystal engineering has recently been paid much attention. With this respect we have lots of precedented models in nature, both in biosphere and lithosphere, where the most elemental building blocks are tetrahedral, viz., sp^3-C and Si^{4+}. It is the common sense of chemists that compositional similarity never means structural similarity in organic compounds. The sense may be extended to the field of inorganic and coordination chemistry with the inversion that completely different composition never means structural dissimilarity.

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