Tetrahedral Guest in a Tetrahedral Cavity: a Neopentane Molecule Encaged in a Three-dimensional Cadmium Cyanide Framework

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The mineralomimetic three-dimensional framework of cadmium cyanide, like cristobalite or cubic ice, enchlathrates a neopentane (2,2-dimethylpropane) molecule with an orientation such that the respective C–Me bonds direct toward the tetrahedral corners of the adamantane-like cage cavity, whereas carbon tetrachloride encaged in the same host distributes the C–Cl bonds statistically about the threefold axis of the cubic crystal.

We have been developing a number of mineralomimetic inclusion structures similar to cristobalite, clays and zeolites, using cadmium cyanide and polycyanopolycadmate systems.[1–5] The simplest in composition and structure among them is the series of $Cd(CN)_2{\cdot}G$ clathrates (G = CCl_4, $MeCCl_3$, Me_3CCl, cyclo-C_6H_{12}, *etc.*).[1,3,5] Cadmium cyanide, $Cd(CN)_2$, has a resemblance in structural features with silica (SiO_2) and ice (H_2O): they all have the AB_2 composition, A takes a tetrahedral configuration, B forms an A–B–A linkage and the linkages frame a three-dimensional cage with con-

Table 1 Atomic parameters for Cd(CN)$_2$·CMe$_4$

Atom	x	y	z	B_{eq}/Å^{2a}
Cd	0.125	0.125	0.125	4.04(4)
CN^b	0.0257(2)	$=x$	$=x$	4.32(8)
CG1	0.375	0.375	0.375	5.77(4)
CG2	0.3068(5)	$=x$	$=x$	14.9(2)

^{a} $B_{eq} = 4(\Sigma_i\Sigma_j\beta_{ij}a_ia_j)/3$. ^{b} The atom has been refined as 50% each occupancy of C and N atoms at the coordinates. It is impossible to discriminate between the C and N atoms of the cyanide in the $Fd\bar{3}m$ space group. The disorder in the orientation of the cyanide group has been supported from the data of solid state ^{113}Cd NMR for the Cd(CN)$_2$ host,[8] although the discrimination was attempted by the other workers applying other space groups for Cd(CN)$_2$[9,10]

siderable void space. The differences between Cd(CN)$_2$ and silica and ice are that no Cd(CN)$_2$ minerals have occurred in nature and that the Cd–CN–Cd span length of *ca.* 5.5 Å is longer by *ca.* 2.5 Å than those of Si–O–Si (*ca.* 3.3 Å) and O–H···O (*ca.* 2.8 Å). The longer span makes it possible to accommodate an oligoatomic molecule inside the cage formed in the most compact framework of Cd(CN)$_2$ as has been exemplified in the Cd(CN)$_2$·G clathrates.[1,3,5]

The cavity formed in the Cd(CN)$_2$ framework has a shape similar to the skeleton of an adamantane molecule C$_{10}$H$_{16}$. Although the centre of the cavity has a site symmetry of $\bar{4}3m$ (T_d), the CCl$_4$ guest with the T_d molecular symmetry shows disorder of the Cl atoms distributed about the crystal threefold axis of the $Fd\bar{3}m$ space group [a = 12.668(2) Å, Z = 8].[1] Hence, we attempted to accommodate another T_d molecule CMe$_4$ in the Cd(CN)$_2$ host in order to synthesise a highly symmetric structure without disorder.

Single crystals of Cd(CN)$_2$·CMe$_4$ were obtained by leaving an aqueous solution of cadmium chloride and potassium tetracyanocadmate in a 1 : 1 molar ratio in contact with neopentane at 6 °C. The single crystal structure was determined using the intensity data collected on a four-circle X-ray diffractometer. All the non-hydrogen atoms were refined anisotropically; the atomic parameters refined are listed in Table 1.†

As shown in Figs. 1 and 2, the three-dimensional framework built of Cd–CN–Cd linkages provides the cavity edged by twelve Cd–CN–Cd linkages and capped by ten Cd atoms. The cavity can be seen to the first approximation as a tetrahedron cornered by the four 'tripod' Cd atoms, although all the ten Cd atoms involved with the cage are crystallographically equivalent. The guest CMe$_4$ molecule encaged in the cavity is compared with the statistically distributed CCl$_4$ in Fig. 2. The neopentane molecule takes an orientation such that the respective C–Me bonds direct toward the tripod corners; in other words the methyl group is encapped by the Cd(–CN–Cd–)$_3$ tripod. Thus, the guest molecule with the tetrahedral skeleton is just fitted inside the tetrahedral cavity as if it behaves as a tetrapod to support the adamantane-like host framework on the inside without any direct chemical bonds. The distance of 5.524(3) Å ($= a\sqrt{3}/4$) between the cavity centre and the Cd atom at the tripod corner is appropriate to accommodate the C–Me moiety with a van der Waals contact. Since the directions toward the face-centres of the approximate tetrahedral cavity are left vacant, considerable void space still remains in the crystal structure. In the isomorphous Cd(CN)$_2$·G series for G = CCl$_4$, MeCCl$_3$, Me$_2$CCl$_2$, Me$_3$CCl and CMe$_4$, the a dimension increases from 12.714(1) for CCl$_4$‡ through 12.717(1), 12.731(1) and 12.743(2) to 12.757(2) Å for CMe$_4$. Hence the void space left unoccupied decreases successively by replacing Me by Cl in the neopentane molecule if the effective volume of the guest is unchanged upon replacement. The reason why the neopentane molecule takes the definite orientation in the cavity with considerable space left vacant can be interpreted in terms of a weak hydrogen bond and/or the steric hindrance between the methyl hydrogens and the π-electron-rich cyanide groups, although no experimental evidence has been obtained for the hydrogen-bond formation.

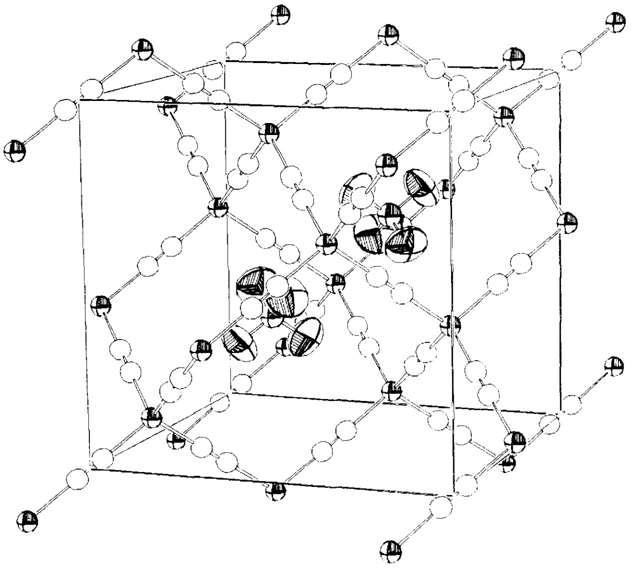

Fig. 1 The host framework of Cd(CN)$_2$ and the selected guest CMe$_4$ molecules at 3/8, 3/8, 3/8 and 5/8, 5/8, 5/8 in the $Fd\bar{3}m$ unit cell. Anisotropic sections are shown for the Cd and guest-C atoms.

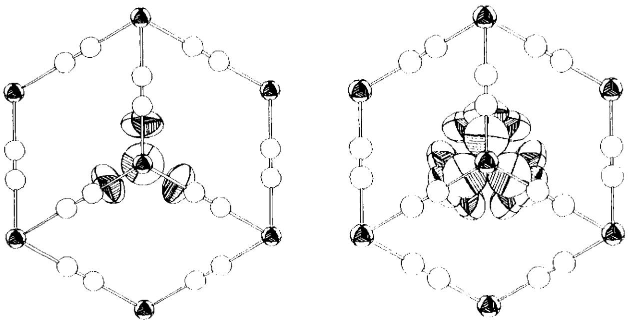

Fig. 2 Views of the tetrahedrally-oriented neopentane (left) and the statistically-distributed carbon tetrachloride (right) molecules in the respective cavities along the crystal threefold axis. The thermal ellipsoids are shown with 50% each probability; the anisotropic section are shown for the Cd atoms and the guest C and Cl atoms. The central C atoms of the guest molecules are not seen.

The C–Me bond distance of 1.507(11) Å, being shorter by *ca.* 0.02 Å than that of 1.539(2) Å in the gaseous state,[6] is apparently contracted due to the thermal oscillation of the methyl group, whose carbon atom CG2 is given a large thermal parameter, of 14.9(2) Å^2 in the equivalent isotropic value. As far as the authors' knowledge extends, the solid state structure of neat neopentane is highly disordered at low temperatures and can be approximated to a sphere.[7] The present Cd(CN)$_2$·CMe$_4$ is the first example of the neopentane molecule taking a definite orientation in the solid state, the

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† *Crystal data*: Cd(CN)$_2$·CMe$_4$, M = 236.60; cubic system, $Fd\bar{3}m$ (No. 227), a = 12.757(2) Å, U = 2076(2) Å^3, Z = 8, D_m = 1.53(2), D_x = 1.51 g cm^{-3}; μ(Mo-Kα) = 20.21 cm^{-1}; 196 reflections observed, 134 used; 9 parameters refined; R = 0.028. Thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ The unit cell parameter a has been revised from the previous value of 12.668(2) Å in ref. 1.

rigid orientation arising due to the geometrical fit and the symmetrical coincidence between the orientation-labile guest molecule and the host lattice.

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