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Novel Clathrate Compound of Cadmium Cyanide Host with an Adamantane-like Cavity. Cadmium Cyanide-Carbon Tetrachloride(1/1)

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Carbon tetrachloride molecule is accommodated in the cavity formed in the three-dimensional framework of cadmium cyanide to give the title clathrate compound. The cavity has a shape of adamantane-like cage edged with -Cd-CN-Cd- linkage where the Cd atom takes a tetrahedral configuration.

Cadmium cyanide is similar to ice, OH_2, and silica, SiO_2, in the AB_2 composition, tetrahedral configuration of A, and ability to form three-dimensional network by itself; three-dimensional networks of ice and silica have been known to behave as host structures accommodating several guest molecules as exemplified by hydrate clathrates$^{1)}$ and clathrasils.$^{2)}$ Cadmium cyanide has been reported to have an anticuprite structure.$^{3)}$ The Cd atom in place of O in cuprite, Cu_2O, is a tetrahedral center, and the cyanide group in place of Cu bridges a pair of Cd atoms through -Cd-CN-Cd- linkage to form a three-dimensional framework. The framework structure resembles the diamond-type network but a cyanide group is inserted between a pair of the tetrahedral Cd atoms. With this respect the framework should be more closely related to the β-cristobalite structure. In the anticuprite structure of $Cd(CN)_2$ two identical frameworks interpenetrate to each other without any cross-connections. The cavity formed in one framework is filled by the other: the center of the assumed cavity is occupied by the Cd atom of the other framework. If one of the frameworks is replaced by appropriate guest molecules, a novel clathrate structure should be given. The idea has been materialized by the formation of the title clathrate.

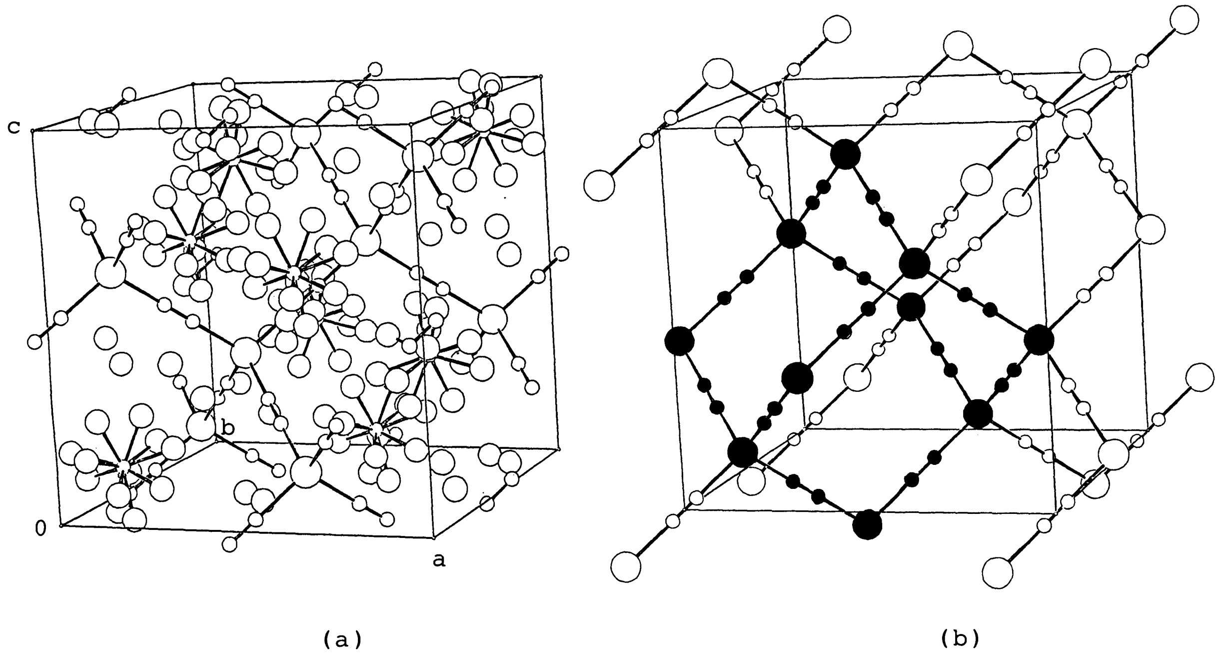
An aqueous solution containing an equimolar mixture of cadmium chloride and potassium tetracyanocadmate was placed over a neat liquid of carbon tetrachloride at room temperature. Fine colorless crystals were soon deposited at the interface between the aqueous solution and the carbon tetrachloride. The crystals were so unstable under ambient atmosphere that it was difficult to determine the chemical composition precisely by usual chemical analyses. However, the formation and the decompositon of the clathrate, $Cd(CN)_2 \cdot CCl_4$, were ascertained by IR, GC, TG, and powder X-ray diffraction techniques. On the TG analysis the clathrate liberates CCl_4 molecules with the ratio of $Cd(CN)_2:CCl_4=1:1$ to leave white powders of $Cd(CN)_2$ (Anal. Found%/calcd%: Cd, 68.13/68.35; C, 14.87/14.61; N, 17.08/17.04) whose powder X-ray diffraction pattern coincides with that observed for the anticuprite structure of cadmium cyanide. The analogous results of chemical analyses, and IR, GC, TG, and powder X-ray observations have suggested the formation of the $Cd(CN)_2{\cdot}G$-type clathrates for the guest G molecules such as $CHCl_3$, CH_3CHCl_2, CH_3CCl_3, $(CH_3)_3CCl$, $CHCl_2CH_2Cl$, $C_2H_5CHClCH_3$, $CHCl_2CHCl_2$, CCl_3CF_3, $CClF_2CCl_2F$, cyclo-C_6H_{12}, and cyclo-$C_6H_{11}CH_3$.

The crystal structure of $Cd(CN)_2{\cdot}CCl_4$ has been determined by single crystal X-ray diffraction method. A 0.25×0.3×0.3 mm^3 single crystal coated with epoxy resin was subjected to the single crystal experiments on a Rigaku AFC-6A automated diffractometer using graphite-monochromated Mo $K\alpha$ radiation.[4] Crystal data are: $Cd(CN)_2{\cdot}CCl_4$, FW=318.27, cubic system, space group $Fd\bar{3}m$ (No. 227),[5] a=12.668(2) Å, U=2033(1) $Å^3$, Z=8, Dx=2.08, Dm=2.09(1) g cm^{-3}, R=0.032 for 190 independent reflections; reflection conditions for hkl: h+k,k+l,l+h=2n and for 0kl: k+l=4n. The similar single crystal data have been obtained for the clathrates of 1,1,2,2-tetrachloroethane and cyclohexane; the 1,1,2,2-tetrachloroethane clathrate: $Cd(CN)_2{\cdot}CHCl_2CHCl_2$, FW=334.33, cubic, space group $Fd\bar{3}m$, a=12.691(2) Å, U=2044(1) $Å^3$, Z=8, Dx=2.16, Dm=2.18(2) g cm^{-3}; the cyclohexane clathrate: $Cd(CN)_2{\cdot}C_6H_{12}$, FW=248.61, cubic, space group $Fd\bar{3}m$, a=12.685(2) Å, U=2041(1) $Å^3$, Z=8, Dx=1.62, Dm=1.61(3) g cm^{-3}. Their host structures are essentially the same as that of the carbon tetrachloride clathrate, although the temporary R values are still large (0.153 and 0.077) owing to the disorders observed for the orientation of guest molecules.

The structure of the carbon tetrachloride clathrate is shown in Fig. 1; the atomic parameters are listed in Table 1. The considerably large thermal parameters can be interpreted in terms of the instability of the compound and the disorders observed in the cyanide group and the guest CCl_4 molecule. According to the second choice of origin setting,[5] the Cd atoms are located at 3/8,3/8,3/8 and the equivalent positions with the $\bar{4}3m$ site symmetry; another $\bar{4}3m$ site, 1/8,1/8,1/8 (and the equivalent positions), is the center of the cavity in which the guest carbon tetrachloride molecule is accommodated. The a dimension (12.668 Å) is twice that of the anticuprite structure of cadmium cyanide (6.32 Å).[3] Discrimination between C and N atoms of the cyanide group is impossible owing to the $Fd\bar{3}m$ space group adopted from the systematic absences,[6] although discriminated coordinates were reported for the anticuprite structure of cadmium cyanide.[3] Except this, the host structure is essentially the same as the single three-dimensional framework in the anticuprite structure of cadmium cyanide. The guest CCl_4 molecules replace the other framework: the CCl_4 molecule is accommodated in the cage

Table 1. Atomic parameters for $Cd(CN)_2{\cdot}CCl_4$

Atom	Multiplicity	Site symmetry[5]	x	y	z	$B_{eq}/Å^2$
Cd	8	$\bar{4}3m$	0.375	=x	=x	6.1(0)
C or N of CN	32	.3m	0.473(1)	=x	=x	6.5(2)
C of CCl4	8	$\bar{4}3m$	0.125	=x	=x	9.1(8)
Cl	96/3	..m	0.1665(8)	=x	0.2478(7)	15.2(4)



(a) (b)

Fig. 1. Structure of $Cd(CN)_2 \cdot CCl_4$. (a) With the guest molecules in disorder. (b) Host structure only; the origin is shifted by -1/4 each along the a, b, and c directions. The atoms comprising an adamantane-like cage are shown as solid circles. Large circle: Cd; medium circle: Cl; small circle: C or N.

built of the linear -Cd-CN-Cd- linkages. Each of the Cd atoms takes a tetrahedral configuration to be shared with four linkages. The cage is similar in shape to the skeleton of an adamantane molecule: four hexagons, each of which is edged with Cd-CN-Cd linkages and puckered to a chair-form, are combined to form a cage. Each Cl atom of the guest CCl_4 molecule is distributed statistically about the three-fold axis of crystal. The orientation that each Cl atom is directed to the center of the hexagon makes the repulsions from the guests in neighboring cavities too much, although the site symmetry coincides with the $\bar{4}3m$ molecular symmetry in this orientation. The van der Waals radius of CCl_4 molecule estimated as 3.52 Å is longer by ca. 0.78 Å than the 2.743 Å distance between the centers of the cavity and the hexagon face. In other words the Cd-CN-Cd span length 5.485 Å is not long enough to keep the orientation of the CCl_4 molecule giving the coincidece of the molecular symmetry with the site symmetry.$^{7)}$ Zinc cyanide, being isostructural to cadmium cyanide with the estimated Zn-CN-Zn span length of 5.12 Å,$^{8)}$ has never given any clathrates similar to those of the cadmium cyanide host under the similar experimental conditions. Obviously the span length is an important factor to make the size of the cage appropriate to accommodating the guest molecules of a certain range of dimensions.

From the view-point of cage dimensions cadmium cyanide is much different from ice and silica: the span length of O-H-O is ca. 2.8 Å, that of Si-O-Si being ca. 3.4 Å. Therefore, the adamantane-like cavity in, e.g., the cubic (Fd3m) phase of ice is too small to accommodate even a neon atom, and that in β-cristobalite is barely large enough to accommodate an alkali or alkaline earth cation; polyatomic guest molecules in hydrate clathrates and clathrasils are accommodated in polyhedral cavities such as 12-, 14-, 16-hedra. A variety of similar polyhedral cage structures have been observed for so-called alkyl-onium salt hydrates1) and lots of aluminosilicate minerals such as zeolites. As has been previously reported,9) clay-like and zeolite-like host structures have been materialized for various kinds of guest molecules by the combination of tetrahedral and octahedral coordination spheres of Cd atoms bridged by cyanide groups in the presence of 3-(dimethylammonio)propylamine (=dmtnH$^+$, a protonated form of N,N-dimethyl-1,3-diaminopropane at the dimethylated N atom); the composition of the host is dmtnH$^+$Cd$_3$(CN)$_7{}^-$ for the clay-like one and Cd$_3$(CN)$_7{}^-$ for the zeolite-like one. These observations, including that for the present results, suggest that Cd$_x$(CN)$_y$ systems (charge is omitted) serve as two- and three-dimensional host builders like the Si$_x$(Al)$_y$O$_z$ systems of the silicate or aluminosilicate minerals which are known to accommodate guest molecules. Such inclusion structures in minerals may be mimicked by the cadmium cyanide, and cyanocadmate or cyanocadmium complex systems. The Cd-CN-Cd span, being longer than that of Si-O-Si(Al), may endow the mineralomimetic host structures with ability to accommodate guest molecules full of variety more than those in the natural minerals.

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6) The atomic scattering factors of N atom have been applied to the atom at x,x,x (and the equivalent positions) in the structure refinement.
7) The refinements with the space groups of the symmetries lower than that of $Fd\bar{3}m$, i.e., the attempts to hold the CCl$_4$ molecule at any definite orientations and/or to discriminate C and N atoms of the cyanide, have never yielded better results.
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