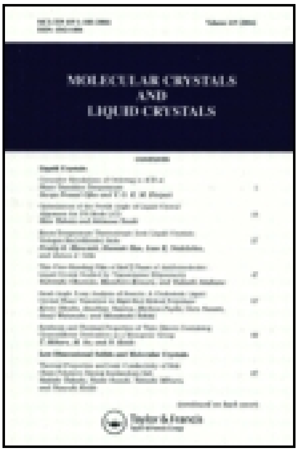

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New Type Clathrate of the 3D Metal Complex Host (N-Methyl-1,3-Diaminopropane)Cadmium(II) Tetracyanocadmate(II)

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NEW TYPE CLATHRATE OF THE 3D METAL COMPLEX HOST (*N*-METHYL-1,3-DIAMINOPROPANE)CADMIUM(II) TETRACYANOCADMATE(II)

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Abstract A new clathrate compound $Cd(mtn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$ (mtn = *N*-methyl-1,3-diaminopropane) is prepared and characterized to contain tetrahedral and octahedral Cd atoms in a ratio of 1:1, mtn chelating to the latter. A pair of 1,2-dichloroethane guest molecules are accommodated in a cavity of the host framework. The arrangement of octahedral and tetrahedral Cd atoms is different from that of the previously reported $Cd(pn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$ (pn = 1,2-diaminopropane) which has the same composition.

Introduction

The term 'mineralomimetic' was probably first coined in 1988[1,2] in order to describe the chemistry in which artificial structures similar to zeolite and clays are designed and synthesized using cadmium cyanide and polycyanopolycadmate systems.[1-7] Since tetrahedral, trigonal-bipyramidal and octahedral coordinations of cadmium can coexist, various multi-dimensional mineralomimetic structures have been synthesized.[1-13] The use of dichloromethane and benzene with mtn (= *N*-methyl-1,3-diaminopropane) provides the zeolite-like clathrate $[Cd_3(CN)_7][mtnH \cdot 2CH_2Cl_2]$ **1** [3] and the clay-like clathrate $[Cd_3(CN)_8(mtnH)_2 \cdot (C_6H_6)_2][C_6H_6]$ **2** [5] respectively, both containing tetrahedral and octahedral Cd atoms in a ratio of 2:1.

This paper describes a new clathrate $Cd(mtn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$ **3** with tetrahedral and octahedral Cd atoms in a 1:1 ratio. The host framework is built of the alternate array of the mtn-chelated octahedral Cd and tetrahedral $Cd(CN)_4$ linked at every N atoms to the former. The new clathrate **3** is not isostructural to that of the previously reported $Cd(pn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$ **4** (pn = 1,2-diaminopropane)[8], showing diamine components to be very significant on clathrate structures. Further , guest molecules have strong influence on the multi-dimensional structure in comparison with **1** and **2**.

Experimental

Preparation of Cd(mtn)Cd(CN)$_4$·CH$_2$ClCH$_2$Cl 3

An equimolar (7.75 mmol) of $CdCl_2 \cdot 2.5H_2O$ (1.77 g) and $K_2[Cd(CN)_4]$(2.26g) was dissolved in water (100 cm^3). After the pH of the aqueous solution was adjusted to 9.0 using cirtric acid and mtn, 1,2-dichloroethane(10 cm^3) was poured under the aqueous solution. Colorless crystals were obtained at the interface between the aqueous and organic phases by standing in a refrigerator at ca. 5°C for a few months. The procedure was also applied for the Cd(mtn)Ni(CN)$_4$·0.5G^{14}, replacing the square-planar $[Ni(CN)_4]^{2-}$ with the tetrahedral $[Cd(CN)_4]^{2-}$. *Anal. Found*: C, 23.36; H, 2.80; N, 16.04%. *Calcd* for $C_{10}H_{16}N_6Cl_2Cd_2$:C,23.28; H, 3.13; N, 16.29%.

Structure determination

A single crystal with 0.30 x 0.25 x 0.25 mm dimensions coated with epoxy resin was used in the intensity data collection on a Rigaku-5S diffractometer (MoKα: λ =0.71069 Å) at 295K. Three representative reflections were monitored every 150 reflections, showing no significant decay. The crystal date are: $Cd_2N_6C_{10}Cl_2H_{16}$, M = 516.00, orthorhombic, *P*bca (No. 61), a = 16.17(2), b = 15.198 (7), c = 15.070(6)Å, V = 3703 (8) Å^3, Z=8 Dm/Dx = 1.83(2)/1.85, μ(Mo Kα) =25.81 cm^{-1}, F(000) =1984. Intensities were collected by 2θ-ω scan technique with the scan width of (0.94 + 0.3tanθ) to $2\theta_{max}$ = 55°; R = 0.045, Rw = 0.047 (w = $1/\sigma^2$(Fo)) and GOF =2.39 for used unique 2265 reflections with 181 parameters.

The centrosymmetric space group *P*bca was determined from the systematic absences. The structure was solved using the TEXSAN.^{15} A Ψ-scan absorption correction was applied. Crystallographic diagrams were drawn by ORTEP program.^{16} All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not located since thermal parameters for the amine and the guest were large.

Results and Discussion

Preparation

The method of preparation for Cd(mtn)Cd(CN)$_4$·CH$_2$ClCH$_2$Cl **3** is similar to those of the zeolite-like clathrate $[Cd_3(CN)_7][mtnH \cdot 2CH_2Cl_2]$ **1** ^{3} and the clay-like clathrate $[Cd_3(CN)_8(mtnH)_2 \cdot (C_6H_6)_2][C_6H_6]$ **2** ^{5}. The clathrates of **1**, **2** and **3** were obtained from the same mother solution derived from cadmium chloride and potassium tetracyanocadmate in a 1:1 ratio. In other words, the mother solution contained Cd^{2+} and CN$^-$ ions in a 1:2 ratio. (The zeolite-like clathrate **1** were also obtained from the solution prepared by dissolving Cd^{2+} and CN$^-$ ions in a ratio of 3:7).^{3} The use of CH$_2$ClCH$_2$Cl gives the new clathrate Cd(mtn)Cd(CN)$_4$·CH$_2$ClCH$_2$Cl **3** containing tetrahedral and octahedral Cd atoms in a ratio of 1:1, while the use of CH_2Cl_2 and C_6H_6 provides the zeolite-like clathrate $[Cd_3(CN)_7][mtnH \cdot 2CH_2Cl_2]$ **1** and the clay-like clathrate $[Cd_3(CN)_8(mtnH)_2 \cdot (C_6H_6)_2][C_6H_6]$ **2** , both consisting of tetrahedral and octahedral Cd atoms in a ratio of 2:1.[3,5] These facts indicate that many kinds of polycyanopolycadmate ions and complicated equilibriums may exist in the solution containing an equimolar of $CdCl_2 \cdot 2.5H_2O$ and $K_2[Cd(CN)_4]$. Dance *et al.* recently reported that solid $Cd(CN)_2$ under laser ablation forms the compositions $[Cd_x(CN)_{2x+1}]^-$ for x up to 27 and possibly higher.[17]

The behavior of the mtn in the polycyanopolycadmate systems can be classified into three groups: (a) no-protonated mtn acting as a bidentate ligand such as **3**, (b) protonated mtn (= mtnH) acting as an onium guest in host framework such as **1**, (c) protonated mtn acting as a monodentate ligand such as **2**. The guest molecules may play a important role in protonating and no-protonating mtn in the formation of the multi-dimensional structures.

Structure of $Cd(mtn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$ 3

The final atomic parameters and the selected distances and angles are listed in Table I and II. The crystal structure and the atomic numbering scheme are illustrated in Figure 1 and 2 . A view of cavity accommodating a pair of the guest CH_2ClCH_2Cl is shown in Figure 3.

The three-dimensional host framework of **3** is built of the alternate linkage between the octahedral Cd(1) and tetrahedral Cd(2) atoms through the cyanide groups. The six-coordination of the octahedral Cd atom is accomplished by the six N atoms of the four cyano groups and the bidentate chelating mtn ligand. The coordination spheres around the octahedral Cd(1) and tetrahedral Cd(2) atoms are considerably distorted from the regular ones. Although the mtn ligands are chelating to octahedral Cd atoms as well as the pn ligands in $Cd(pn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$ **4** [8], the host framework of **3** is topologically different from that of **4**. The difference in the arrangement of the octahedral and tetrahedral Cd atoms is associated with the formation of the ring built of Cd atoms. A tetragonal ring, $[Cd^O\text{-}Cd^t]_2$, observed in **4** is not formed in **3**. A hexagonal ring, $[Cd^O\text{-}Cd^t]_3$ in **3** has a twist-boat conformation whereas that of **4** is a distorted chair. A octagonal ring, $[Cd^O\text{-}Cd^t]_4$ in **3** is complicated, however, that of **4** is an apparent hexagonal ring with two straight $[Cd^t\text{-}Cd^o\text{-}Cd^t]$ units.

In the new inclusion compound **3** the two CH_2ClCH_2Cl guests occupy with the cavity (Figure 2). The cavity consists of two hexagonal ring, $[Cd^O\text{-}Cd^t]_3$. One guest is trapped in the hexgonal ring. The center of the cavity is shielded by the two

Table I. Atomic parametetrs for Cd(mtn)Cd(CN)$_4$·CH$_2$ClCH$_2$Cl **3**

atom	x	y	z	B(eq)
Cd(1)	0.13928(5)	0.18823(5)	0.09419(5)	3.29(4)
Cd(2)	0.35037(5)	0.38429(5)	0.31550(5)	3.33(4)
N(1)	0.2299(7)	0.2612(8)	0.1821(7)	5.9(7)
N(2)	0.0228(6)	0.2651(7)	0.1620(7)	4.5(6)
N(3)	0.1299(6)	0.0673(6)	0.1916(7)	4.2(5)
N(4)	0.2391(8)	0.1229(8)	0.0030(7)	5.8(7)
N(5)	0.1211(8)	0.3008(8)	-0.0162(9)	7.6(8)
N(6)	0.0360(8)	0.1092(8)	0.0171(8)	7.2(8)
C(1)	0.2723(7)	0.3023(8)	0.2277(8)	4.3(7)
C(2)	-0.0313(8)	0.3083(8)	0.1685(8)	4.2(6)
C(3)	0.1342(7)	0.0077(8)	0.2369(7)	3.6(6)
C(4)	0.2797(7)	0.1127(8)	-0.0555(8)	3.8(6)
C(5)	0.080(1)	0.273(1)	-0.099(1)	10.(1)
C(6)	0.000(1)	0.230(2)	-0.083(1)	10.(1)
C(7)	0.002(1)	0.136(1)	-0.062(1)	10.(1)
C(8)	0.200(1)	0.350(1)	-0.026(1)	9.(10)
Cl(1)	0.4449(3)	0.0201(3)	0.0866(3)	10.2(3)
Cl(2)	0.3532(3)	0.0565(4)	0.3465(3)	11.7(4)
C(11)	0.387(1)	0.003(2)	0.196(2)	14.(2)
C(12)	0.399(1)	0.080(1)	0.236(2)	12.(2)

Table II. Selected distances(Å) and angles (°) for Cd(mtn)Cd(CN)$_4$·CH$_2$ClCH$_2$Cl **3**

Cd(1)	N(1)	2.27(1);	Cd(1)	N(2)	2.44(1);	Cd(1)	N(3)	2.36(1);
Cd(1)	N(4)	2.34(1);	Cd(1)	N(5)	2.40(1);	Cd(1)	N(6)	2.36(1);
Cd(2)	C(1)	2.21(1);	Cd(2)	C(2)^{*1}	2.25(1);	Cd(2)	C(3)^{*2}	2.23(1);
Cd(2)	C(4)^{*3}	2.26(1);	N(1)	C(1)	1.15(1);	N(2)	C(2)	1.10(1);
N(3)	C(3)	1.14(1);	N(4)	C(4)	1.11(1);	N(5)	C(5)	1.47(2);
N(5)	C(8)	1.48(2);	N(6)	C(7)	1.38(2);	C(5)	C(6)	1.46(2);
C(6)	C(7)	1.46(2);	Cl(1)	C(11)	1.91(2);	Cl(2)	C(12)	1.86(2);
C(11)	C(12)	1.33(3);	Cl(1)	Cl(1)^{*4}	3.22(1);	Cl(2)	C(8)^{*5}	3.44(2);

N(1)	Cd(1)	N(2)	91.1(4)	N(1)	Cd(1)	N(3)	93.4(4)
N(1)	Cd(1)	N(4)	96.1(4)	N(1)	Cd(1)	N(5)	97.8(5)
N(1)	Cd(1)	N(6)	173.5(4)	N(2)	Cd(1)	N(3)	93.6(3)
N(2)	Cd(1)	N(4)	168.8(4)	N(2)	Cd(1)	N(5)	81.6(4)
N(2)	Cd(1)	N(6)	84.5(4)	N(3)	Cd(1)	N(4)	94.6(4)
N(3)	Cd(1)	N(5)	167.9(4)	N(3)	Cd(1)	N(6)	82.2(4)
N(4)	Cd(1)	N(5)	88.8(4)	N(4)	Cd(1)	N(6)	89.0(4)
N(5)	Cd(1)	N(6)	86.3(5)	C(1)	Cd(2)	C(2)^{*1}	105.1(4)
C(1)	Cd(2)	C(3)^{*2}	102.7(4)	C(1)	Cd(2)	C(4)^{*3}	103.8(4)
C(2)^{*1}	Cd(2)	C(3)^{*2}	113.2(4)	C(2)^{*1}	Cd(2)	C(4)^{*3}	110.4(4)
C(3)^{*2}	Cd(2)	C(4)^{*3}	119.8(4)	Cd(1)	N(1)	C(1)	176.(1)
Cd(1)	N(2)	C(2)	160.(1)	Cd(1)	N(3)	N(3)	173.(1)
Cd(1)	N(4)	C(4)	159.(1)	Cd(1)	N(5)	C(5)	116.(1)
Cd(1)	N(5)	C(8)	109.(1)	Cd(1)	N(6)	C(7)	124.(1)
Cd(2)	C(1)	N(1)	178.(1)	Cd(2)^{*6}	C(2)	N(2)	174.(1)
Cd(2)^{*7}	C(3)	N(3)	175.(1)	Cd(2)^{*5}	C(4)	N(4)	169.(1)
C(5)	N(5)	C(8)	116.(1)	N(5)	C(5)	C(6)	113.(2)
C(5)	C(6)	C(7)	117.(2)	N(6)	C(7)	C(6)	119.(2)
Cl(1)	C(11)	C(12)	102.(2)	Cl(2)	C(12)	C(11)	101.(2)

Keys to symmetry operations. *1: 1/2+x,y,1/2-z; *2: 1/2-x,1/2+y,z;*3:x,1/2-y,1/2+z;
*4:1-x,-y,-z;*5:x,1/2-y,-1/2+z;*6:-1/2+x,y,1/2-z;*7:1/2-x,-1/2+y,z;

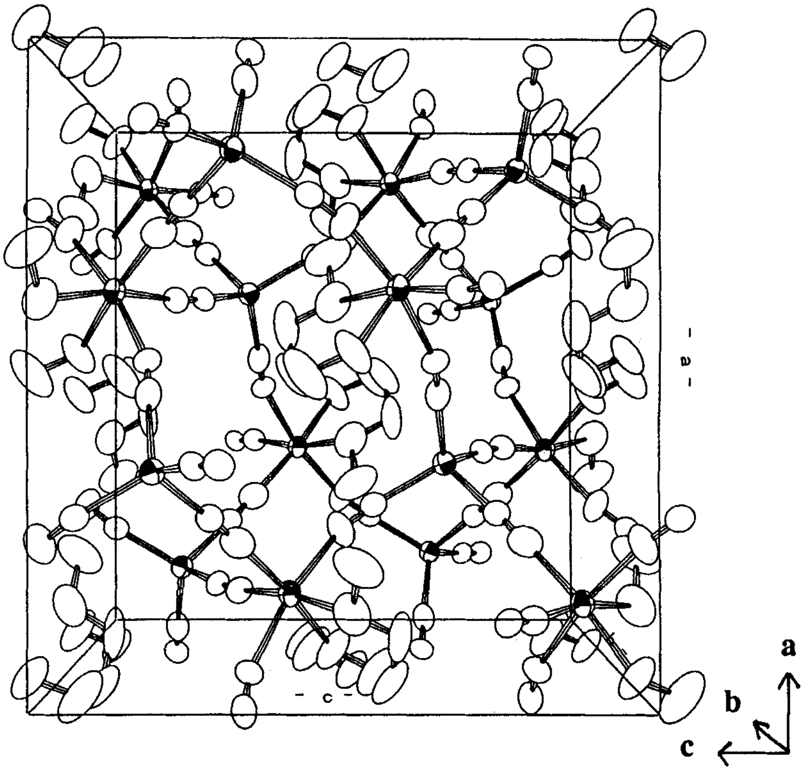

Fig. 1. Perspective view of the host framework Cd(mtn)Cd$(CN)_4$ of compound **3**. Anisotropic sections are shown for the Cd atoms.

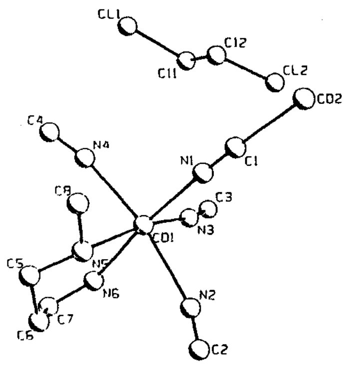

Fig.2 Atomic numbering scheme in the asymmetric unit.

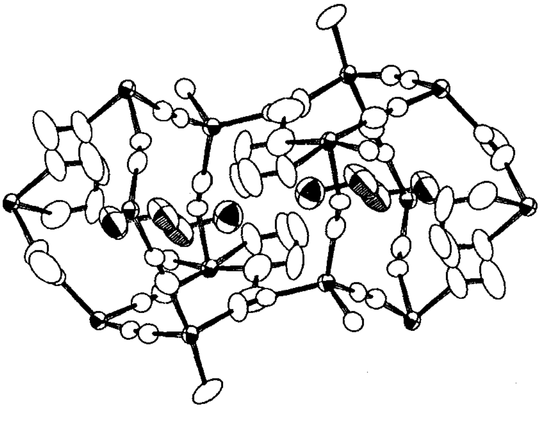

Fig. 3. Perspective view of the cavity. The Anisotropic sections are shown for the CH_2ClCH_2Cl and the Cd atoms.

chelating mtn ligands. The cavity of **3** is different from that of **4** due to the arrangement of Cd atoms. The size, shape and conformation of both mtn and CH_2ClH_2Cl are suitable to forming the cavity of **3**. The two guest 1,2-dichloroethane molecules in the cavity are related by a cetrosymmetry. The intermolecular contact between Cl(1) and Cl(1)* atoms is 3.22(1) Å, being slightly shorter than the sum of van der Waals radii of two chlorine atoms probably due to the large thermal motion.

Supplementary Material

Full lists of anisotropic temperature factors, bond distances and angles, and calculated and observed structure factors are available on request from the author.

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