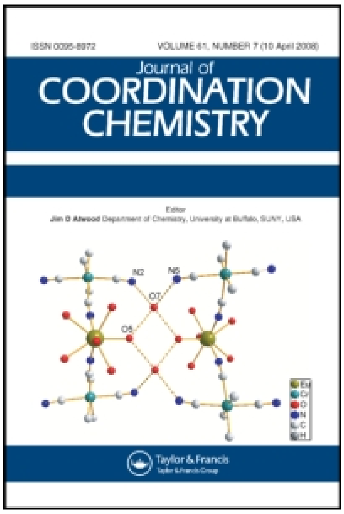

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DUAL BEHAVIOR OF ACETONITRILE IN A NEW CADMIUM CYANIDE CLATHRATE: CRYSTAL STRUCTURE OF $Cd(CH_3CN)_2Cd(CN)_4 \cdot 2CH_3CN$

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Dedicated to Professor Toschitake Iwamoto on the occasion of his 60th birthday

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We report a new crystal structure of the title clathrate containing tetrahedral and octahedral Cd atoms in a ratio of 1:1. The preparation of the compound is similar to that of the cristobalite-like clathrate $Cd(CN)_2 \cdot G$, where all Cd atoms are tetrahedral. The new inclusion compound crystallizes in the monoclinic space group $C2/c$, a = 12.337(4), b = 11.964(3), c = 13.594(3) Å, β = 108.60(2)°, Z = 4, R = 0.034 for 1631 reflections. The three-dimensional host framework is built of alternate linkages between the tetrahedral Cd atom of the tetracyanocadmate and the octahedral Cd atom similar to that of the Hofmann-Td and the en-Td types. In the new clathrate dual behavior of acetonitrile, one as a unidentate ligand in the three-dimensional host framework and the other as the guest in the cage-like cavity, has been demonstrated.

KEYWORDS: cadmium cyanide, clathrate, tetracyanocadmate(II), acetonitrile, Hofmann-Td-type clathrate, crystal structure, mineralomimetic chemistry

INTRODUCTION

The discovery of the en-Td-type clathrate $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ **1** by Iwamoto and Shriver in 1972[1] is associated with the recent development of mineralomimetic chemistry, using cadmium cyanide and polycyanopolycadmate systems.[2-11] The fact that cadmium cyanide and polycyanopolycadmate can form multi-dimensional framework structures related to cristobalite, zeolite and clays was first reported in 1988; the term 'mineralomimetic' was probably first coined by Iwamoto and colleagues in 1988.[2a,3a] Since tetrahedral, trigonal-bipyramidal and octahedral coordinations of cadmium can coexist in the cadmium cyanide and polycyanopolycadmate systems, many multi-dimensional mineralomimetic structures have been synthesized.[2-11] A number of mineralomimetic structures built of $[Cd_x(CN)_y]^{2x-y}$ moieties based on the similarity between SiO_2 and $Cd(CN)_2$ may also be generated by modifying the en-Td-type compound **1** with tetrahedral and octahedral

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Cd atoms in a 1:1 ratio. Other cadmium cyanide host frameworks containing tetrahedral and octahedral Cd atoms in a ratio of 1:1 have been reported,[5,6,9a,12,13] for example the Hofmann-Td-type $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$ **2**,[5] dual aniline clathrate $Cd(C_6H_5NH_2)_2Cd(CN)_4 \cdot 0.5C_6H_5NH_2$ **3**[5] and aqua cadmium cyanide clathare $Cd(H_2O)_2Cd(CN)_4 \cdot 2HCO(NH_3)_2$ **4**.[9a] In **2** the NH_3 coordination to octahedral Cd is *trans* similar to the bridging en coordinate in **1**, whereas the aniline coordination of **3** is *cis* similar to the aquo coordination in **4**.

We report a new clathrate $Cd(CH_3CN)_2Cd(CN)_4 \cdot 2CH_3CN$ **5** containing tetrahedral and octahedral Cd atoms in a ratio of 1:1, a pair of CH_3CN ligands coordinating to the latter in *trans* positions. Dual behavior of acetonitrile in **5**, one as the unidentate ligand in the three-dimensional host and the other as the guest in the cage-like cavity, is similar to that of aniline in **3** described by Yuge and Iwamoto.[5]

EXPERIMENTAL

Preparation of $Cd(CH_3CN)_2Cd(CN)_4 \cdot 2CH_3CN$ **5**

Neat acetonitrile (35 mL) was added into an aqueous solution (100 mL) containing 7 mmol each of $CdCl_2 \cdot 2.5H_2O$ and $K_2[Cd(CN)_4]$. The water-acetonitrile solution was kept standing in a refrigerator at *ca.* 5°C for a few days; colorless crystals were obtained.

In the course of study concerning $[P(C_6H_5)_4]_3[Cd_2(CN)_7]$[10a] and $[Sb(C_6H_5)_4][Cd(CN)_3]$,[10b] crystals of the same acetonitrile clathrate were obtained by chance from the following procedure. An equimolar aqueous solution of $CdCl_2 \cdot 2.5H_2O$ and $K_2[Cd(CN)_4]$ was mixed with an acetonitrile solution of $Sb(C_6H_5F)_4Br$. The same clathrate was produced by keeping the solution in a refrigerator for a week.

The products lose the guest and ligand acetonitrile molecules so readily upon exposure to air that the above composition is based on the results of the X-ray structural analyses.

Structure Determination of the Acetonitrile Clathrate

A single crystal of 0.35 × 0.30 × 0.25 mm dimensions was coated with epoxy resin, and three representative reflections were monitored after 150 during the intensity data collection on a Rigaku-AFC-5S diffractometer (MoKα: λ = 0.71069 Å) at 295K; no significant decay was observed. The crystal data are: $Cd_2N_8C_{12}H_{12}$,M = 493.10, monoclinic, *C*2/*c* (No. 15), a = 12.337(4), b = 11.964(3), c = 13.594(3)Å, β = 108.60(2)°, V = 1901.5(8) Å^3, Z = 4, Dm/Dx = 1.72(2)/1.72, μ(MoKα) = 22.37 cm^{-1}, $F(000)$ = 944. Intensities were collected by the 2θ-ω scan technique with the scan width of (1.37 + 0.3tanθ) to $2\theta_{max} = 55$; $R = 0.034$, $Rw = 0.036$ ($w = 4Fo^2/\sigma^2(Fo^2)$) and GOF = 1.93, for 1631 reflections and 102 parameters used.

The centrosymmetric space group *C*2/*c* was determined from the systematic absences. The structure was solved using the TEXSAN[14] software package installed on the diffractometer system, with Ψ-scan absorption correction. Crystallographic diagrams were obtained using the ORTEP program.[15] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not located. The assignment of the orientation of cyanide group was based on the distances and bond angles.

RESULTS AND DISCUSSION

Preparation

Although the method of preparation for **5** is similar to that of the cristobalite-like clathrate $Cd(CN)_2 \cdot G$ (G = CMe_4, CCl_4, $CHCl_3$, cylo-C_6H_{12}, and so on) for which all Cd atoms are tetrahedral,[2] the host framework in **5** contains tetrahedral and octahedral Cd atoms in a 1:1 ratio. The use of CH_3CN gives the new $Cd(CH_3CN)_2Cd(CN)_4 \cdot 2CH_3CN$ **5**, while the use of CH_3CH_2CN provides the different inclusion compound $[Cd_4(CN)_9] \cdot [K \cdot 4CH_3CH_2CN]$ consisting of tetrahedral and octahedral Cd atoms in a ratio of 3:1.[10c] These facts indicate that there may be many kinds of polycyanopolycadmate ions in the solution containing equimolar $CdCl_2 \cdot 2.5H_2O$ and $K_2[Cd(CN)_4]$. The size, shape, polarity, and chemical properties of acetonitrile are associated with formation of the new inclusion compound with dual behavior of acetonitrile.

Acetonitrile was needed for preparing $[P(C_6H_5)_4]_3[Cd_2(CN)_7]$[10a] and $[Sb(C_6H_5)_4][Cd(CN)_3]$.[10b] Preparation of **5** would suggest that there may be some cadmium cyanide-acetonitrile complex intermediates in the aqueous-acetonitrile solution before the formation of the solid complexes.

Structure

The refined atomic parameters are listed in Table 1; the selected distances and angles are listed in Table 2. The crystal structure is illustrated in Fig. 1. The structure of **5** has the base-centered monoclinic unit cell with space group *C*2/*c* similar to that of **2**, whereas the crystal system of **1** is tetragonal. The monoclinic β angle of **5** is larger by *ca.*7.6° than that of **2**. There are two kinds of Cd atoms, Cd(1) with *trans* $CdN_2(CH_3C\mathit{N})N_4(C\mathit{N})$ geometry and Cd(2) with $CdC_4(CN)$ geometry, in the host lattice. Order in the orientation of the cyanide groups in **1** has

Table 1 Final atomic coordinates and equivalent thermal parameters *B*eq for $Cd(CH_3CN)_2$ $Cd(CN)_4 \cdot 2CH_3CN$**5**

atom	*x*	*y*	*z*	Beq/Å^{2a}
Cd(1)	1/4	1/4	0	2.67(2)
Cd(2)	0	0.40139(5)	1/4	2.70(2)
N(1)	0.1668(5)	0.2890(5)	0.1279(4)	3.9(2)
N(2)	0.1620(5)	0.5940(5)	0.4116(4)	3.9(2)
C(1)	0.1104(5)	0.3196(5)	0.1723(5)	3.3(3)
C(2)	0.1119(5)	0.5234(5)	0.3624(5)	3.2(3)
N(3)	0.4181(5)	0.3586(5)	0.0898(4)	4.6(3)
C(3)	0.4992(6)	0.4110(6)	0.1187(5)	4.1(3)
C(4)	0.6037(6)	0.4780(7)	0.1560(6)	6.0(4)
N(4)	0.1425(7)	0.1511(8)	0.4114(7)	8.8(5)
C(5)	0.2320(9)	0.1460(7)	0.4035(6)	5.9(4)
C(6)	0.3461(7)	0.1346(8)	0.3942(7)	6.9(5)

[a] $Beq = 8\pi^2[\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j]/3$

Table 2 Selected bond distances and angles for **5**.

distance/Å					
Cd(1)	N(1)	2.332(5)	Cd(1)	N(2)*^{1}	2.297(5)
Cd(1)	N(3)	2.421(6)	Cd(2)	(1)	2.201(6)
Cd(2)	C(2)	2.242(6)	N(1)	(1)	1.118(7)
N(2)	C(2)	1.131(7)	N(3)	C(3)	1.140(8)
C(3)	C(4)	1.464(9)	N(4)	C(5)	1.14(1)
C(5)	C(6)	1.46(1)			

angle/°							
N(1)	Cd(1)	N(1)*^{2}	180.0	N(1)	Cd(1)	N(2)*^{1}	91.1(2)
N(1)	Cd(1)	N(2)^{3}	88.9(2)	N(1)	Cd(1)	N(3)	91.6(2)
N(1)	Cd(1)	N(3)*^{2}	88.4(2)	N(2)*^{1}	Cd(1)	N(2)*^{3}	180.0
N(2)*^{3}	Cd(1)	N(3)	90.8(2)	N(2)*^{1}	Cd(1)	N(3)	89.2(2)
N(3)	Cd(1)	N(3)*^{2}	180.0	C(1)	Cd(2)	C(1)*^{4}	127.2(3)
C(1)	Cd(2)	C(2)	106.0(2)	C(1)	Cd(2)	C(2)*^{4}	107.7(2)
C(2)	Cd(2)	C(2)*^{4}	98.7(3)	Cd(1)	N(1)	C(1)	165.0(5)
Cd(1)*^{5}	N(2)	C(2)	173.9(5)	Cd(2)	C(1)	N(1)	172.4(6)
Cd(2)	C(2)	N(2)	172.3(6)	Cd(1)	N(3)	C(3)	170.4(6)
N(3)	C(3)	C(4)	179.8(8)	N(4)	C(5)	C(6)	178(1)

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

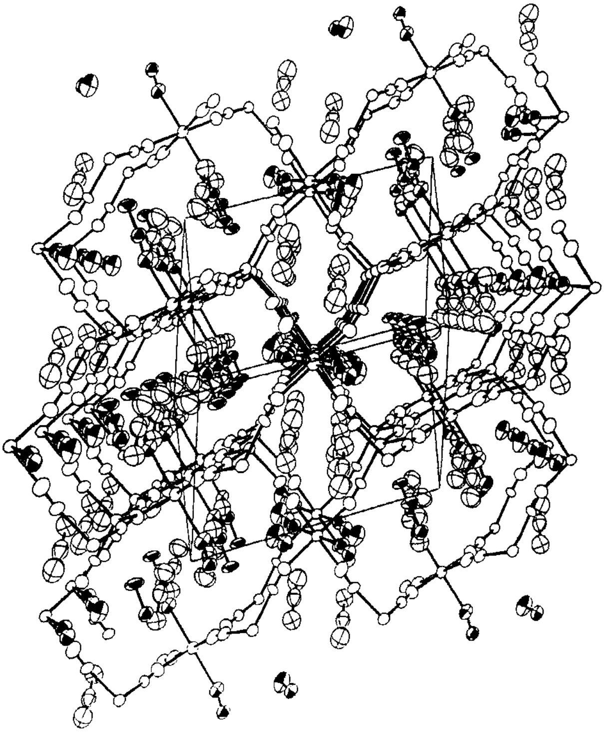

Figure 1 A perspective view of $Cd(CH_3CN)_2Cd(CN)_4 \cdot 2CH_3CN$ **5**: projection on [1i0]. Anisotropic sections and peripheries are shown for the acetonitrile ligands and guests respectively.

been found by solid-state ^{113}Cd NMR spectroscopy.[16] The three-dimensional host framework is built by alternate linkage between octahedral Cd(1) atoms and tetrahedral Cd(2) atoms through the cyanide groups. There are two kinds of CH_3CN molecules, one is ligand coordinating to octahedral Cd atom in *trans*(N(3),C(3),C(4)), the other is a guest in a cage-like cavity(N(4),C(5),C(6)). The host framework of **5**, $Cd(CH_3CN)_2Cd(CN)_4$, is generated by substituting the two *trans* CH_3CN ligands for the two *trans* NH_3 ligands in **2**, $Cd(NH_3)_2Cd(CN)_4$. The Cd-N(acetonitrile) distance of 2.421(6) Å is considerably greater than those of Cd-N(CN) (2.332(5) Å, 2.297(5)Å).

Two kinds of cavities, α and β, are formed in **5**, almost identical with those of **1** and **2**. The α and β cavities have been discussed in detail by Yuge and Iwamoto.[5,6] The α cavity is approximated as a rectangular box, the β activity as a biprismatic cage. In **1** and **2**, benzene molecules are accommodated in both cavities; there are two crystallographically different kinds of benzene molecules. In the new inclusion compound **5** two CH_3CN guests occupy the α cavity, while only one C_6H_6 guest is accommodated in the α cavity of **1** and **2**. Though one C_6H_6 guest is included in the β cavity of **1** and **2**, the two CH_3CN ligands of **5** are located in the β cavity (Fig. 2). The CH_3CN ligands act as "guest-ligand" in the β cavity. The larger volume of the CH_3CN ligand in **5** than that of the NH_3 ligand in **2** is responsible for the lack of room in the β cavity for a guest. From the viewpoint of the *trans* or *cis*

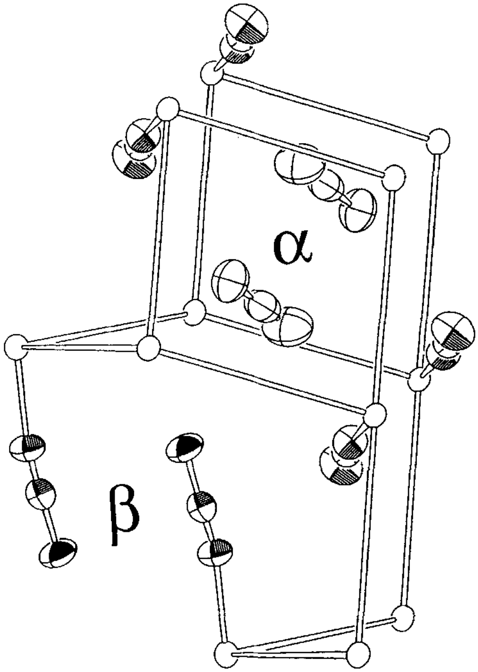

Figure 2 A Perspective view of the CH_3CN molecules in the α and β cavities. Only the cadmium atoms and the acetonitrile molecules are shown. Two CH_3CN guest molecules are accommodated in the α cavity. A pair of CH_3CN ligands protrude into the β cavity. Anisotropic sections and peripheries are shown for acetonitrile ligands and guests respectively.

configuration in the octahedral Cd atom and the host-guest ratio, the dual behavior of acetonitrile in **5** is different from that of aniline in **3**. A different behavior for acetonitrile in metal cyanide host-guest systems has also been found in $Cd(H_2O)_3Cu(CN)_3 \cdot CH_3CN$ by Nishikiori and Iwamoto, in which the guest acetonitrile molecule is hydrogen-bonded to a water molecule.[17]

The present work has also demonstrated the remarkable flexibility of multidimensional cadmium cyanide host-guest systems. The dual behavior of acetonitrile molecules in the new compound **5** may have potential utility in the fields of molecular sieves, catalysts, optical materials, *etc.*

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SUPPLEMENTARY MATERIAL

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

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