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Novel Cage-like Cavity Accommodating a Pair of Guest Molecules in the Structure of *catena*-[*dl*-1,2-Diaminopropanecadmium(II) Tetra-μ-cyanocadmate(II)]-(1,2-Dichloroethane)(1/1)

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Abstract. The title clathrate Cd(*dl*-pn)$Cd(CN)_4 \cdot CH_2ClCH_2Cl$ (pn = *dl*-1,2-diaminopropane = *dl*-propylenediamine) crystallizes in the monoclinic space group $P2_1/n$, $a = 8.278(2)$, $b = 14.904(2)$, $c = 14.477(1)$ Å, $\beta = 91.24(1)°$, $V = 1785.7(1)$ Å^3, $Z = 4$, $R = 0.068$ for 4993 independent reflections. A novel three-dimensional host is built of the alternate array of the pn-chelated octahedral Cd and the tetrahedral $Cd(CN)_4$ linked at every N atom to the former Cd to provide a cage-like cavity for a pair of 1,2-dichloroethane guest molecules.

Key words. Cadmium cyanide, cadmium tetracyanocadmate, crystal structure, dichloroethane, metal complex host, propylenediamine.

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1. Introduction

Among the series of the Hofmann-type and related inclusion compounds [1], pn-Td-type $Cd(pn)M(CN)_4 \cdot 1.5\ C_6H_6$ (pn: 1,2-diaminopropane = propylenediamine; M = Cd or Hg) clathrates [2] have been assumed to be isostructural to the en-Td-type $Cd(en)Cd(CN)_4 \cdot 2\ C_6H_6$ [3, 4] with respect to the three-dimensional host structure on the basis of the powder X-ray diffraction patterns. In the Hofmann-type analog, $Cd(pn)Ni(CN)_4 \cdot 1.5\ C_4H_5N$, the pn behaves as an ambidentate *catena*-μ-ligand to form a one-dimensional —(Cd-pn)— linkage, as the single crystal structure showed [2]. Since the methyl group of the pn is expected to increase the lipophilic character of the cavity, we examined the accommodation of aliphatic guests into the Hofmann-pn-type and the pn-Td-type hosts. As has been reported briefly [5], these inclusion compounds have host structures different from those of the Hofmann-pn-type and the pn-Td-type, respectively. This paper describes the novel host structure of $Cd(pn)Cd(CN)_4$ accommodating 1,2-dichloroethane as the guest molecule.

Since a non-stoichiometric host/guest ratio has often been observed for inclusion compounds, it might be reasonable to assume that the present 1,2-dichloroethane

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clathrate, $Cd(pn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$, is isostructural to the pn-Td-type benzene clathrate $Cd(pn)Cd(CN)_4 \cdot 1.5\,C_6H_6$. However, one cannot conclude that a chemical species is an inclusion compound nor that it is isostructural to a previously-known compound until its structure has been clarified. This paper reports a typical example of inclusion compounds which are analogous to each other in composition but different in structure.

2. Experimental

2.1. PREPARATION OF $Cd(dl\text{-}pn)Cd(CN)_4 \cdot C_2H_4Cl_2$

An aqueous solution of the host moieties was prepared by the procedure similar to that applied for the Hofmann-pn-type series [2]. After the pH of the aqueous solution was adjusted to 9.0 using citric acid, 1,2-dichloroethane was poured under the aqueous solution. Yellow plate-like crystals were obtained at the interface between the aqueous and organic phases by standing in a refrigerator for a few days. *Anal. Found*: C, 24.00; H, 2.98; N, 21.18; Cl, 8.54%. *Calcd* for $C_9H_{14}N_6Cl_2Cd_2$: C, 24.09; H, 3.03; N, 21.08; Cl, 8.89%. Attempts to prepare an *l*-pn-host clathrate of 1,2-dichloroethane have not yet succeeded.

2.2. X-RAY EXPERIMENT

A crystal of 0.75 × 0.70 × 0.10 mm dimensions was coated with acrylate resin in order to prevent spontaneous guest liberation. Refinement of lattice parameters and intensity data collection were carried out on a Rigaku AFC5R automated four-circle diffractometer equipped with a rotating molybdenum anode (MoK_α: $\lambda = 0.71059$ Å) at room temperature; 20 reflections in $19° < 2\theta < 21°$ were used to refine the lattice parameters. Crystal data are: $Cd(C_3H_{10}N_2)Cd(CN)_4 \cdot C_2H_4Cl_2$, $M_r = 502.01$, monoclinic, $P2_1/n$ (No. 14), $a = 8.278(2)$, $b = 14.904(2)$, $c = 14.477(1)$ Å, $\beta = 91.24(1)°$, $V = 1785.7(1)$ Å^3, $Z = 4$, $D_m/D_x = 1.86(1)/1.87$, $\mu(MoK_\alpha) = 26.76\ \text{cm}^{-1}$, $F(000) = 960$. Intensities were collected by the $2\theta - \omega$ scan technique with the scan width of $(1.05 + 0.3 \tan\theta)°$ to $2\theta_{max} = 70°$ in the $hk \pm l$ region. Three standard reflections (200), (040), and (002) were monitored every 200 reflections during the data collection; deviations were less than 6% from their average intensities. The Lp-corrected 4933 unique reflections with $|F_0| > 3\sigma(F_0)$ among 8506 independent reflections measured were used for structure refinement. The density was measured by the flotation technique in a carbon tetrachloride–bromoform mixture. The structure refinement was carried out on a HITAC M-680/M-682H computer system at the computer center of this University using the programs in UNICSIII [6] including ORTEP [7] and their local versions; atomic scattering factors used were those in the *International Tables* [8] including real dispersion corrections. Patterson, Fourier, and difference Fourier syntheses were successively applied; all the atoms in the host structures except hydrogens were refined anisotropically using block-diagonal least-squares procedure to minimize $\Sigma w(||F_0| - |F_c||)^2$, where $w = 0.25$ for $|F_0| < 24.17$, $w = 1$ for $24.17 \leqq |F_0| \leqq 48.33$ and $w = (48.33/F_0)^2$ for $|F_0| > 48.33$. Final $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}$, and $S = [\Sigma w(|F_0| - |F_c|)^2/$(number of reflec-

Table I. Atomic parameters with e.s.d.s for $Cd(pn)Cd(CN)_4 \cdot CH_2ClCH_2Cl$.

atom	x/a	y/b	x/c	$B_{eq}/Å^{2a}$
Cd(1)	0.82351(7)	0.39171(3)	0.75442(4)	3.59(1)
Cd(2)	0.81690(6)	0.33350(4)	0.37451(4)	3.54(1)
N(1)	1.056(1)	0.4792(5)	0.7199(6)	6.3(2)
N(2)	0.9883(8)	0.2776(5)	0.8035(5)	4.7(2)
N(3)	0.802(1)	0.3512(5)	0.6030(5)	5.2(2)
N(4)	0.6020(9)	0.3092(6)	0.8065(6)	5.7(3)
N(5)	0.651(1)	0.5197(7)	0.7336(6)	8.0(3)
N(6)	0.840(1)	0.4700(5)	0.8971(5)	5.5(2)
C(1)	1.115(1)	0.5385(6)	0.6893(6)	5.0(2)
C(2)	1.0910(9)	0.2325(5)	0.8276(5)	3.9(2)
C(3)	0.809(1)	0.3450(5)	0.5265(5)	4.1(2)
C(4)	0.5086(9)	0.2630(6)	0.8333(6)	4.5(2)
C(5)	0.666(3)	0.577(1)	0.8160(9)	13.7(7)
C(6)	0.713(2)	0.5377(9)	0.9005(9)	9.6(5)
C(7)	0.716(2)	0.5973(8)	0.9843(9)	9.8(5)
C(8)	0.360(3)	0.278(2)	0.560(2)	19(1)
C(9)	0.261(3)	0.308(2)	0.558(2)	23(2)
Cl(1)	0.2957(6)	0.1585(2)	0.6060(2)	9.6(1)
Cl(2)	0.3241(9)	0.4251(3)	0.5093(4)	15.7(2)

${}^{a}B_{eq} = 4(\Sigma_i \Sigma_j B_{ij} \mathbf{a}_i \mathbf{a}_j)/3$.

tions used – number of variables)]$^{1/2}$ for 173 parameters, were 0.068, 0.066, and 1.819, respectively. In the final cycle of the refinement, the ratios of parameter shift to e.s.d. were less than 0.2 for the cyanide atoms and 0.5 for the pn atoms, but some of those for the guest atoms exceeded 1: the largest was 2.86 for the y coordinate of Cl(2). Hence, the parameters for the guest atoms cannot be considered with much confidence. The tables of $F_0 - F_c$ and the anisotropic thermal parameters have been deposited as the supplementary material.

3. Results and Discussion

The atomic parameters refined are listed in Table I; selected bond and interatomic distances and the bond angles are in Table II. The crystal structure is shown in Figure 1 with the atomic numbering scheme; the cavity accommodating a pair of the guest molecules is illustrated in Figure 2.

As shown in Figures 1 and 2, the three-dimensional host framework is built of the infinite metal complex *catena*-[propylenediaminecadmium tetra-μ-cyanocadmate] in which the tetrahedral $Cd(CN)_4$ moieties and the octahedral Cd atoms are alternately interconnected at the N atoms of the tetracyanocadmate. The six-coordination of the octahedral Cd atom is accomplished by the four N atoms of the cyano groups and the bidentate chelating pn ligand. The chelation of pn is the remarkable difference of this host from the previous pn-Td-type one in which the pn behaves as an ambidentate bridging ligand.

Table II. Selected bond/interatomic distances, l, and angles, δ.

Distance, l/Å[a]

Cd(1)—N(1)	2.38(1);	Cd(1)—N(2)	2.28(1);	Cd(1)—N(3)	2.28(1);
Cd(1)—N(4)	2.35(1);	Cd(1)—N(5)	2.40(1);	Cd(1)—N(6)	2.37(1);
Cd(2)—C(1)^{*1}	2.20(1);	Cd(2)—C(2)^{*2}	2.21(1);	Cd(2)—C(3)	2.21(1);
Cd(2)—C(4)^{*3}	2.23(1);	N(1)—C(1)	1.11(1);	N(2)—C(2)	1.13(1);
N(3)—C(3)	1.11(1);	N(4)—C(4)	1.11(1);	N(5)—C(5)	1.47(3);
C(5)—C(6)	1.41(2);	C(6)—C(7)	1.50(2);	C(6)—N(6)	1.46(2);
Cl(1)—C(8)	1.97(3);	C(8)—C(9)	0.94(3);	C(9)—Cl(2)	1.96(3);
Cl(1)—C(1)^{*6}	3.52(1);	Cl(2)—C(1)^{*5}	3.58(1);	Cl(1)—N(5)^{*2}	3.61(1);
Cl(1)—N(6)^{*2}	3.62(1);	Cl(2)—N(5)^{*4}	3.62(1);	Cl(2)—C(3)^{*4}	3.63(1);
Cl(2)—Cl(2)^{*4}	3.68(1);	Cl(1)—C(2)^{*5}	3.82(1);	Cl(2)—N(3)^{*4}	3.84(1);
Cl(1)—N(1)^{*6}	3.86(1);	Cl(1)—Cd(2)^{*7}	3.89(1);	Cl(2)—N(1)^{*5}	3.90(1).

Angle, δ/°

N(1)—Cd(1)—N(2)	89.7(3);	N(1)—Cd(1)—N(3)	89.4(3);
N(1)—Cd(1)—N(5)	91.2(3);	N(1)—Cd(1)—N(6)	83.3(3);
N(2)—Cd(1)—N(3)	97.9(3);	N(2)—Cd(1)—N(4)	88.6(3);
N(2)—Cd(1)—N(6)	94.2(3);	N(3)—Cd(1)—N(4)	97.2(3);
N(3)—Cd(1)—N(5)	93.1(3);	N(4)—Cd(1)—N(5)	89.3(3);
N(4)—Cd(1)—N(6)	90.5(3);	N(5)—Cd(1)—N(6)	75.0(3);
N(1)—Cd(1)—N(4)	173.4(3);	N(2)—Cd(1)—N(5)	169.0(3);
N(3)—Cd(1)—N(6)	165.9(3);	C(1)^{*1}—Cd(2)—C(2)^{*2}	118.7(3);
C(1)^{*1}—Cd(2)—C(3)	111.4(3);	C(1)^{*1}—Cd(2)—C(4)^{*3}	104.9(3);
C(2)^{*2}—Cd(2)—C(3)	107.3(3);	C(2)^{*2}—Cd(2)—C(4)^{*3}	103.5(3);
C(3)—Cd(2)—C(4)^{*3}	110.7(3);	Cd(1)—N(1)—C(1)	152.6(8);
Cd(1)—N(2)—C(2)	167.6(6);	Cd(1)—N(3)—C(3)	167.0(7);
Cd(1)—N(4)—C(4)	172.5(7);	Cd(2)—C(1)^{*1}—N(1)^{*1}	168.3(8);
Cd(2)—C(2)^{*2}—N(2)^{*2}	169.9(7);	Cd(2)—C(3)—N(3)	178.8(7);
Cd(2)—C(4)^{*3}—N(4)^{*3}	175.1(8);	Cd(1)—N(5)—C(5)	108.6(9);
N(5)—C(5)—C(6)	119(1);	C(5)—C(6)—N(6)	116(1);
C(5)—C(6)—C(7)	117(1);	N(6)—C(6)—C(7)	116(1);
Cl(1)—C(8)—C(9)	102(3);	C(8)—C(9)—Cl(2)	102(3).

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

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[a] Values less than 4.0 Å have been listed.

The coordination sphere is considerably distorted from the regular one about both the octahedral Cd(1) and tetrahedral Cd(2). Cd(1)—N bond distances range from 2.28(1) Å of Cd—N(3) to 2.40(1) Å of Cd—N(5); N—Cd(1)—N angles from 75.0(3)° of N(5)—Cd(1)—N(6) to 97.9(3)° of N(2)—Cd(1)—N(3). Cd(2)—C bond distances range from 2.20(1) Å of Cd(2)—C(1) to 2.23(1) Å of Cd(2)—C(4) with less deviation than those for Cd(1)—N, but C—Cd(2)—C angles from 103.5(3)° of C(2)—Cd(2)—C(4) to 118.7(3)° of C(1)—Cd(2)—C(2). As for the pn-chelate ring, C(5) and C(6) are shifted respectively by 0.14 Å below, and by 0.30 Å above, the plane defined by Cd(1), N(5), and N(6); the pn-methyl group takes an equatorial position with respect to the chelate ring.

The cage-like cavity formed in the framework can be approximated to a distorted hexagonal box; the tetrahedral Cd(t) and the octahedral Cd(o) atoms occupy the alternate vertices, the ambidentate cyano group being seen as an edge between Cd(t) and Cd(o) vertices. The top hexagon is cornered by three each Cd(t) and Cd(o) atoms, the bottom being generated by the inversion of the top about the crystallographic inversion center at 1/2,1/2,1/2, which is also the center of the cavity. The top is supported by four Cd(t)—CN—Cd(o) columns, but the side edges at the right and the left in Figure 2(a) are broken. Instead of the Cd(t)—CN—Cd(o) column, the pn-chelate rings of Cd(t)—CN—Cd(o) < pn and Cd(o) < pn moieties (Cd(o) < pn denotes the moiety of pn-chelated Cd(o)) shield the guests inside the cavity, as shown in Figure 2(b). As for the Cd(t)—CN—Cd(o) < pn moiety, the chelate ring is inclined towards the neighboring cavity so that a cavity is shielded approximately by two-halves of the moieties.

A pair of the guest 1,2-dichloroethane molecules, related by the inversion center, are accommodated in the cavity. Cl(1) of the guest is separated from the pn in the

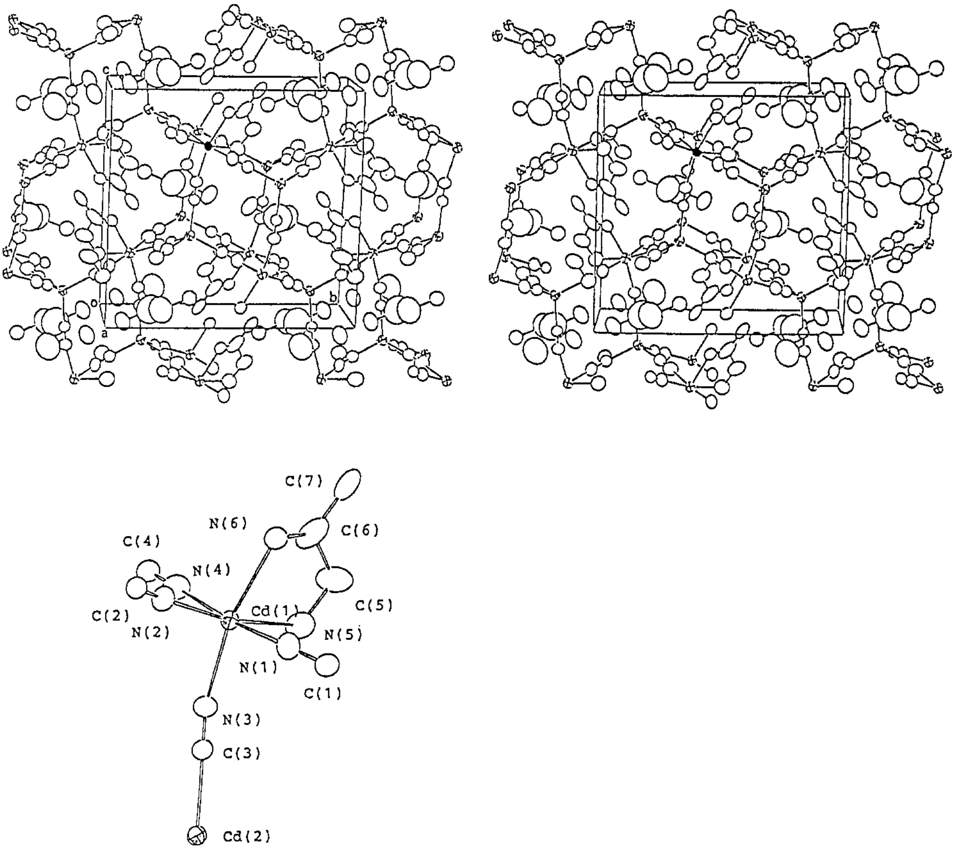
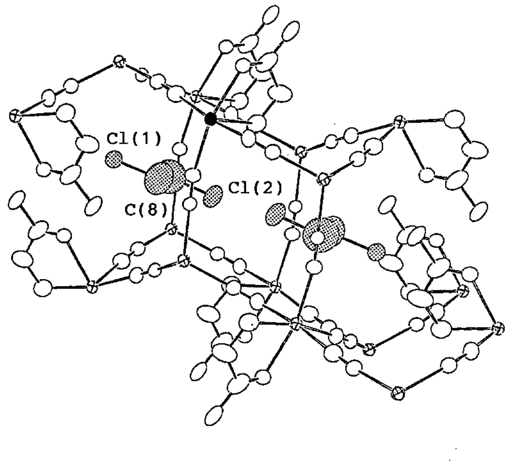


Fig. 1. A stereoview of the unit cell along the *a*-axis; Cd(1) is shown as a solid ellipsoid. Atomic numbering scheme is given for the selected asymmetric unit.

Cd(o) < pn moiety by 3.61(1) Å from the amino nitrogen N(5), 4.12(1) Å from the methine carbon C(6), and 4.25(1) Å from the methyl carbon C(7). As for the Cd(t)—CN—Cd(o) < pn moieties, the distances are 4.37(2) and 4.50(2) Å for C(7) and C(7′), 4.45(2) and 4.58(2) Å for C(6) and C(6′), and 4.73(2) and 4.19(2) Å) for C(5) and C(5′), respectively, where the atoms with primed number are those from the framework of the neighboring cavity. The intermolecular contact between Cl(2) atoms is 3.68(1) Å, the value being approximately equal to twice the van der Waals radius of a chlorine atom.

Thermal parameters of the pn and the guest molecule are large. As for the pn, the methylene carbon C(5) gives the largest ($B_{eq} = 13.7(7)$ Å^2); the value of 8.0(3) Å^2 for the Cd(1)-coordinated N(5) is also unusually large. Thermal motion of the guest 1,2-dichloroethane appears to be vigorous with the short C(8)—C(9) distance of 0.94(4) Å and B_{eq} of ca. 20 Å^2, although the molecule takes apparently the *s-trans* conformation of the rotational isomers with the dihedral angle of 1.3° between the C—C—Cl bond planes. The imbalance of the B_{eq} values in the respective guest atoms, in particular between Cl(1) and Cl(2), can be interpreted in terms of the flexibility of the cage-like cavity. In the middle part of the cavity, surrounded by the four Cd(t)—CN—Cd(o) columns, the framework is so rigid as to make the B_{eq} values larger for the Cl(2) end of the guest. At both sides of the cavity the thermal motions are shared by the host moieties shielding the cavity and the Cl(1) end of the guest. In other words, the guest is shielded by the host tightly in the more flexible regions, and is accommodated more loosely in the more rigid regions to give the less-defined atomic coordinates and the greater B_{eq} value for Cl(2).

In our work on the Hofmann-type and related inclusion compounds since 1967 [9], we have been developing several isostructural or topologically similar series of



(a) (b)

Fig. 2. Perspective views of the cage-like cavity. (a) A view approximately along the *a*-axis; the guest atoms are dotted and with the atomic numbering, except for C(9) which is behind C(8). (b) A view approximately along the *b*-axis; the pn-chelate rings shielding the cavity at the front side are hatched. Cd(1) in each view is shown as a solid ellipsoid.

the multi-dimensional cyanometal-complex hosts accommodating various guest molecules [10]. However, the novel Cd(pn)Cd(CN)$_4$ host appears unable to accommodate guests other than 1,2-dichloroethane; any clathrates either of the isostructural host or of different structure and/or composition have not yet been obtained for prospective guests such as dichloromethane, chloroform, carbon tetrachloride, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,1,2,-trichloroethylene, and 1,1,2,2-tetrachloroethylene. Although the present host framework appears to be flexible with respect to the broken edge of the cavity, the crystal structure appears to be selective only for the particular combination of the host with 1,2-dichloroethane as the guest.

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