

Novel Series of Clathrate Compounds of the Three-Dimensional Metal Complex Hosts (*N*-Methyl-1,3-diaminopropane)cadmium(II) Tetracyanonickelate(II), (*N,N*-Dimethyl-1,3-diaminopropane)cadmium(II) Tetracyanonickelate(II), and (2-Hydroxyethylmethylamine)cadmium(II) Tetracyanonickelate(II)

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Abstract. The clathrate compounds of the title three-dimensional metal complex hosts have been prepared with various aliphatic, alicyclic, and aromatic guest molecules. The typical structure has been demonstrated for a cyclohexane clathrate (*N*-methyl-1,3-diaminopropane)cadmium(II) tetracyanonickelate(II)-cyclohexane(2/1) by X-ray single crystal analysis. The powder X-ray diffraction data were assigned for the other clathrates to the tetragonal systems isostructural to the cyclohexane clathrate in which the box-like cavity with the approximate dimensions of $7 \times 7 \times 5 \text{ \AA}^3$ accommodates the guest molecule.

Key words. Alicyclic guest, aliphatic guest, aromatic guest, cadmium, crystal structure, cyclohexane, 2-hydroxyethylmethylamine, *N,N*-dimethyl-1,3-diaminopropane, *N*-methyl-1,3-diaminopropane, tetracyanonickelate(II).

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1. Introduction

As we have previously reported [1–6], the α,ω -diaminoalkanes behave as bridging ligands to build up the three-dimensional host structures of the Hofmann-diam-type clathrates: the ligands span adjacent layers of a two-dimensional *catena*-[cadmium(II) tetra- μ -cyanonickelate(II)] network to form *catena*-[*catena*- μ -(α,ω -diaminoalkane)cadmium tetra- μ -cyanonickelate(II)]-organic guest clathrates.

A novel three-dimensional host structure has been derived in the attempt to use *N*-substituted α,ω -diaminoalkane in place of the non-substituted α,ω -diaminoalkane in the Hofmann-diam-type. As has been reported briefly [7], the *N*-methyl-1,3-diaminopropane (mtn) behaves as a chelating ligand in the crystal structure of (*N*-methyl-1,3-diaminopropane)cadmium(II) tetracyanonickelate(II)-cyclohexane(2/1). The three-dimensional host framework is built up of the linkage

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of the square-planar tetracyanonickelate(II) moieties and the mtn-chelated cadmium(II) atoms; the cavity formed in the host structure has the shape of a box with the approximate inner dimensions of $7 \times 7 \times 5 \text{ \AA}^3$. A variety of aromatic, aliphatic and alicyclic molecules are accommodated in the novel host. The fact that the *N*-methyl-1,3-diaminopropane behaves as a chelating ligand to the cadmium(II) is the most distinct feature of the novel host structure and differentiates it from those of the Hofmann-diam-type series. Using *N*-substituted diamines or amines such as *N,N*-dimethyl-1,3-diaminopropane (dmtn), 2-hydroxyethylmethylamine (*N*-methylethanolamine:mmea), the clathrates of the similar three-dimensional hosts have been prepared. This paper reports the syntheses of clathrates built of the metal complex hosts (*N*-methyl-1,3-diaminopropane)cadmium(II) tetracyanonickelate(II), (*N,N*-dimethyl-1,3-diaminopropane)cadmium(II) tetracyanonickelate(II), and (2-hydroxyethylmethylamine)cadmium(II) tetracyanonickelate(II). The crystal structure of (*N*-methyl-1,3-diaminopropane)cadmium(II) tetracyanonickelate(II)-cyclohexane(2/1) is described in detail.

2. Experimental

2.1. SYNTHESSES

2.1.1. *mtn-Series*

Into 80 mL of water 1.82 g of cadmium chloride–water(2/5), 2.08 g of potassium tetracyanonickelate(II)–water(1/1), and 2.15 g of citric acid were dissolved successively while stirring. *N*-methyl-1,3-diaminopropane (mtn) was gradually added with stirring until the pH of the solution became 8.6 (ca. 5 mL). After filtration through a plastic membrane (Millipore, pore size $0.5 \mu\text{m}$), the aqueous solution was covered with the neat liquid of the guest species and allowed to stand at 5°C in a refrigerator for a week. Products, grown as fine crystals at the interface between the aqueous and the organic phases, were filtered on a sintered glass and washed with small amounts of water, ethanol, and acetone, successively.

2.1.2. *dmtn-Series*

The aqueous solution was prepared as described above but 1.8 g of citric acid, 8.0 mL of 2-aminoethanol, and 5 mL of *N,N*-dimethyl-1,3-diaminopropane (dmtn) were added to keep the pH at 9.5.

2.1.3. *mmea-Series*

The aqueous solution was prepared as described above but 3.0 g of citric acid and 4.5 mL of 2-hydroxyethylmethylamine (mmea) were added to keep the pH at 9.5.

2.1.4 *Analyses*

Chemical compositions were determined by common microanalytical methods. Accommodation of the guest molecules was ascertained by infrared, gas-chromato-

graphic and thermogravimetric techniques. Powder X-ray diffraction patterns were recorded on a JEOL DX-GO-F diffractometer using a nickel-filtered $\text{CuK}\alpha$ radiation and a GM counter. The patterns were assigned to tetragonal systems by taking the refined structure of the cyclohexane clathrate into account. The lattice parameters were refined by the program RSLC-3 in the library of the Computation Center of this University[8]: readings of 2θ values less than ca. 40° were used to refine the parameters through the least-squares calculations with the weight of $1/[\sin 2\theta \cdot \sigma(\theta)]^2$ (applied $\sigma(\theta) = 0.1$) for each 2θ value.

2.2. STRUCTURE DETERMINATION OF THE CYCLOHEXANE CLATHRATE

The crystal data are: $\text{Cd}[\text{CH}_3\text{NH}(\text{CH}_2)_3\text{NH}_2]\text{Ni}(\text{CN})_4 \cdot 0.5 \text{C}_6\text{H}_{12}$; F.W. = 405.40; tetragonal, space group $P4/mbm$, $a = b = 14.209(2) \text{ \AA}$, $c = 7.876(1) \text{ \AA}$, $V = 1590.2(5) \text{ \AA}^3$, $Z = 4$; $d_0 = 1.68(1) \text{ g/cm}^3$ (flotation method in bromoform-xylene mixture), $d_x = 1.69 \text{ g/cm}^3$; $\mu(\text{MoK}\alpha) = 25.02 \text{ cm}^{-1}$; Rigaku AFC-6A automated four-circle diffractometer, $\text{MoK}\alpha$ (graphite-monochromated, $\lambda = 0.70926 \text{ \AA}$; $2\theta - \omega$ scan technique with $1.30 + 0.50 \tan \theta$ scan width, $2\theta = 2 - 60^\circ$, $h = 0 - 20$, $k = 0 - 20$, $l = 0 - 11$; reflection conditions for $h0l$, $h = 2n$; $0.20 \times 0.20 \times 0.18 \text{ mm}$ crystal; 2751 reflections observed, 961 independent ones ($|F_0| > 3\sigma(F_0)$) used; L_p and absorption corrections [9].

The structure solution and the refinement of the parameters were achieved by the ordinary heavy-atom method, successive Fourier syntheses, and block-diagonal least-squares processes on the HITAC M-280 system of the Computation Center of this University using the programs in UNICSII and III [10] including ORTEP [11] and their local versions. Atomic scattering factors including those for real and imaginary dispersion corrections were taken from the International Tables [12]. The Laue group $4/mmm$ was ascertained by checking the distribution of intensities for the 616 reflections of all octants in the region of $2\theta = 20 - 24^\circ$; the $P4/mbm$ space group was uniquely adopted because of the negative thermal parameters given in the refinement processes applying the $P\bar{4}b2$ and $P4bm$ space groups which are possible from the observed systematic absences.

The parameters refined were the positional and anisotropic thermal ones for the eleven host atoms and two guest atoms in an asymmetric unit; all the hydrogen atoms were not included in the calculations. The applied $P4/mbm$ space group enforced disorder to the mtm chelate ring and the guest cyclohexane molecule. The skeleton of the chelate ring was distributed statistically in relation to the mirror planes $\{220\}$ and $\{001\}$. The cyclohexane molecule is unable to correlate with the $4/m$ site symmetry of the center of cavity at $1/2, 1/2, 1/2$ (and $0, 0, 1/2$); the guest molecule was seen as a torus of 1.48 \AA radius distributed on $\{002\}$ in the difference-Fourier map obtained after the host structure alone had been refined anisotropically to $R = 0.065$. Two peaks with the electron densities 1.8 e/\AA^3 and 1.6 e/\AA^3 were found in the torus with the average electron density of 1.5 e/\AA^3 . The two peaks were read as the carbon atoms of the guest molecule statistically distributed about the fourfold axis passing through the center of the cavity, and included in the final refinement procedure. The final difference Fourier map showed residual electron densities of $1.3, 0.6, 0.9$ and 0.3 e/\AA^3 at the positions of Cd, Ni(1), Ni(2), and around the torus. The R -indices, $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$,

$R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma (F_0)^2]^{1/2}$ ($w = 75/F_0^2$ for $|F_0| \geq 75$, $w = 1$ for $75 > |F_0| \geq 32$, and $w = 0.25$ for $|F_0| \leq 32$), and $S = [\Sigma w(|F_0| - |F_c|)^2 / (\text{number of used reflections} - \text{number of parameters})]^{1/2}$, were 0.043, 0.034, and 1.16 at the final stage of refinement, and 0.055, 0.086, and 2.81 at the stage of the refinement including the host atoms only. Tables of anisotropic thermal parameters and structure factors have been deposited.

3. Results and Discussion

3.1. STRUCTURE DESCRIPTION OF THE CYCLOHEXANE CLATHRATE

The structure is illustrated in Figures 1 and 2, and selected bond distances and angles are shown in Figure 3; the atomic parameters are listed in Table I. There are two kinds of $\text{Ni}(\text{CN})_4$ moieties in the host structure. One, centered at Ni(1), participates in the two-dimensional metal complex network of *catena*-[cadmium(II) tetra- μ -cyanonickelate(II)] extended on $\{001\}$, and the other, centered at Ni(2), forms a belt-like extension involving the Cd-mtn chelate rings on $\{220\}$. The Cd atom is coordinated with two N-terminals of Ni(1)(CN) $_4$ on $\{001\}$ and of Ni(2)(CN) $_4$ on $\{220\}$, and a bidentate mtn ligand on $\{220\}$. The cavity centered at $1/2, 1/2, 1/2$ (and $0, 0, 1/2$) has the shape of a box topped and bottomed by Ni(1)(CN-Cd $_{1/4}$) $_4$ moieties, and walled at each side by a couple of each half of the mtn chelate rings from the top and bottom Cd atoms and by a half of the Ni(2)(CN-Cd $_{1/4}$) $_4$ moiety. The effective inner dimensions are approximated as $7 \times 7 \times 5 \text{ \AA}^3$.

The Ni(1)(CN) $_4$ group is little distorted from the square-planar structure, but the Ni(1)—C(1)—N(1)—Cd linkage bends at N(1) by $22.2(5)^\circ$. Such a bending at the joint between the square-planar Ni(CN) $_4$ moiety and the six-coordinate Cd has

Table I. Atomic parameters for Cd(mtn)Ni(CN) $_4 \cdot 0.5 \text{ C}_6\text{H}_{12}$ ^a

atom	G^b	x/a	y/b	z/c	$M_{\text{eq}}/\text{\AA}^2 \text{ c}^c$
Cd	0.250	0.17754(3)	0.32246(3)	0	2.36(1)
Ni(1)	0.125	0	0	0	2.74(3)
Ni(2)	0.125	0	0.5	0.5	2.34(3)
C(1)	0.500	0.0431(4)	0.1239(5)	0	3.2(3)
C(2)	0.500	0.0649(3)	0.4351(3)	0.3294(7)	2.8(1)
C(3)	0.500	0.3553(7)	0.1917(9)	0.163(2)	7.1(7)
C(4)	0.250	0.3617(5)	0.1383(5)	0	7.9(6)
C(5)	0.250	0.259(1)	0.241(1)	0.330(4)	15(1)
C(6)	0.375	0.470(2)	0.403(2)	0.5	14(2)
C(7)	0.375	0.413(2)	0.457(1)	0.5	14(2)
N(1)	0.500	0.0690(4)	0.1988(4)	0	4.5(3)
N(2)	0.500	0.1022(3)	0.3978(3)	0.2235(7)	3.7(1)
N(3)	0.500	0.2651(3)	0.2349(3)	0.1994(9)	7.0(2)

^amtn = $\text{CH}_3\text{NH}(\text{CH}_2)_3\text{NH}_2$.

^b G : multiplicity

^c $B_{\text{eq}} = 4(\Sigma_i \Sigma_j B_{ij} a_i a_j) / 3$.

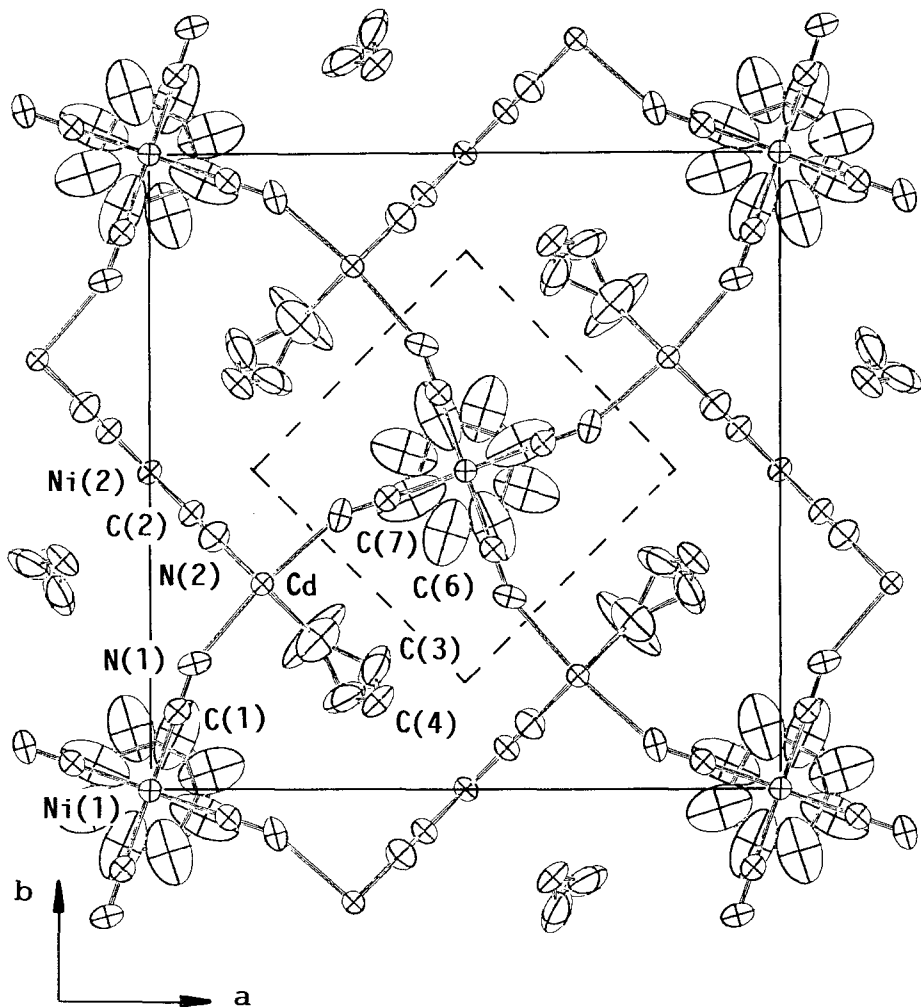


Fig. 1. Structure of $\text{Cd}[\text{CH}_3\text{NH}(\text{CH}_2)_3\text{NH}_2]\text{Ni}(\text{CN})_4 \cdot 0.5\text{C}_6\text{H}_{12}$; 50% probability ellipsoids: projection along the c -axis. The inner dimensions of the cavity centered at $1/2, 1/2, 1/2$ are shown with broken lines. Cd, Ni(1), C(1), N(1), and C(4) are at $z = 1$; C(2), N(2), and C(3) are at the positions produced by the symmetry operation $x, y, 1-z$ from the coordinates given in Table I.

been observed for the two-dimensionally extended *catena*-[cadmium(II) tetra- μ -cyanonickelate(II)] layer of the Hofmann-diam-type host structures. The linkage in the present structure, however, becomes three-dimensional at the Cd atom owing to the *cis*-coordination of the bidentate mtn ligand. The Cd atom plays a role of junction between Ni(2)(CN)₄ moieties to build up the belt-like extension along the crystal c -axis, the extension in which the Ni(2)(CN)₄ moiety, slightly elongated along the c -axis, is an 'X-shaped' member of the meshed belt.

The methyl group of the mtn chelate ring is distributed statistically in relation to the mirror plane $\{002\}$ with 50% probability each in the positions shown in Figure 1; C(3) is also distributed statistically in relation to the mirror plane $\{220\}$, with

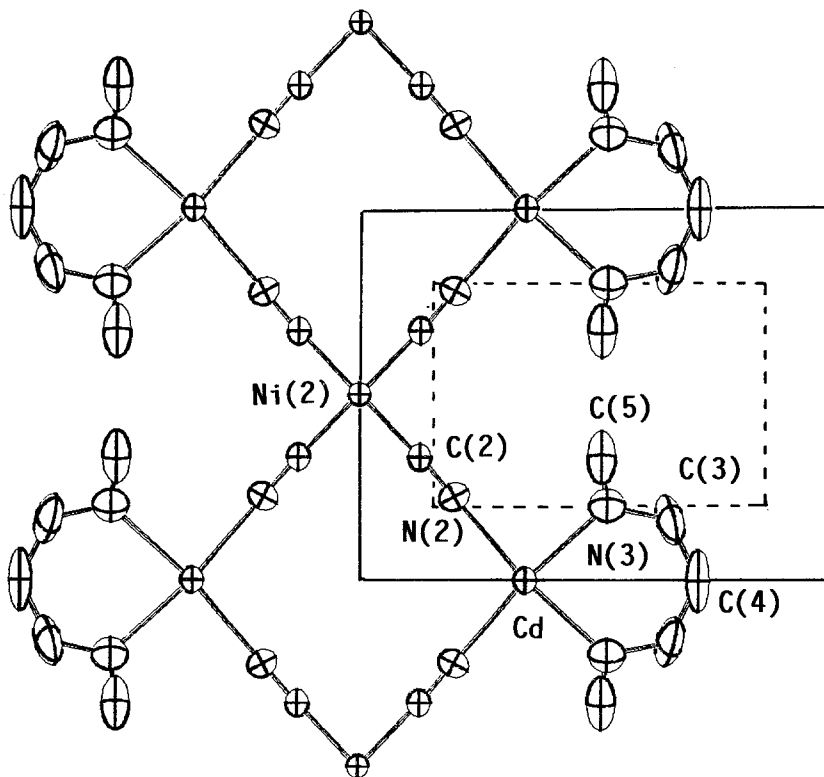


Fig. 2. Section of the unit cell along the $\{220\}$ plane. The section is shown with solid lines; the inner dimensions of the cavity centered at $1/2, 1/2, 1/2$ are shown with broken lines.

50% probability each. Both the skew form and the boat form of the six-membered Cd-mtn chelate ring can be depicted with the statistically distributed positions of the methyl group and C(3) atom.

3.2. RESULTS OF SYNTHESSES

The clathrates characterized are listed in Table II along with the analytical results and tetragonal lattice parameters [13]. Since the powder X-ray diffraction patterns were similar to one another and to that of the cyclohexane clathrate, the lattice parameters a and c were assigned to the tetragonal systems with acceptable e.s.d.s [14]. The stoichiometry between the host metal complex and the guest is about 2:1 for almost all of the products. The 2:1 ratio supports the full occupancy of the guest in the cavity formed in the host structure, similar to that of the cyclohexane clathrate.

3.2.1 *mtn*-Series

The largest guest molecule accommodated, in view of the number of skeletal atoms, C, N, O, and/or halogen, is *o*-nitrotoluene, $C_7H_7NO_2$, among the aromatic guests,

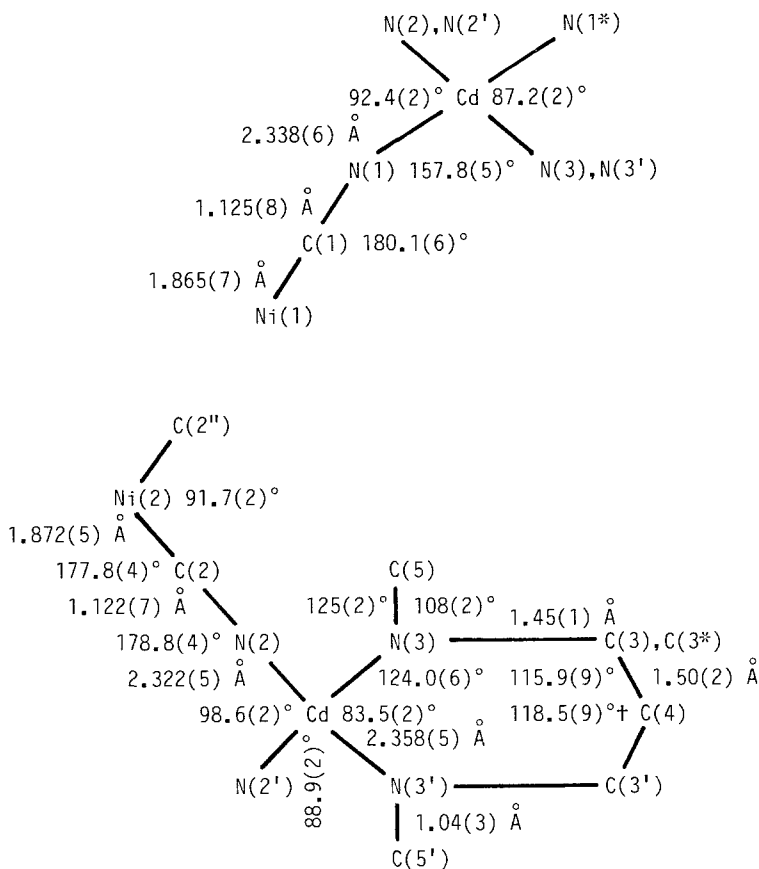


Fig. 3. Selected bond distances and angles. Symmetry operations: $x, y, -z$ for C(2), C(3), C(4), C(5), N(2'), and N(3'); $x, y, 1-z$ for C(2''); $1/2-y, 1/2-x, z$ for C(3*) and N(1*). †Angle C(3*)–C(4)–C(3') = 132.6(9)°.

1-hexanol, $C_6H_{13}OH$, among the normal aliphatic guests, and 4-methylpentane-2-one (methyl isobutyl ketone) among the branched aliphatic guests. The smallest guest is dichloromethane. 1-Butanol is the smallest and 1-hexanol is the largest among the *n*-aliphatic alcohols; the largest haloalkane in Table II is 1,3- or 1,2-dichloropropane [13].

The values of the *a* and *c* dimensions, and of the unit cell volume, ranging from 14.12 to 14.33 Å, from 7.69 to 7.85 Å, and from 1535 to 1614 Å³, respectively, appear not to be related directly to the size and/or shape of the respective guest molecules. We conclude that the host structure does not change substantially in spite of the variety of accommodated aliphatic, aromatic, or alicyclic guest molecules. The twisted Ni(1)—CN—Cd linkage and the X-membered belt may be responsible for the flexibility of the host structure within the range of variation in the *a* and *c* dimensions.

The composition of the ethylbenzene clathrate seems curious. The analytical results support $n = 0.25$, which means a half number of total cavities are occupied

Table II. Lattice parameters and analytical results (found/calc^a)

No.	G	n	a/Å	c/Å	C	H	N	
			Cd[(CH ₃ NH(CH ₂) ₃ NH ₂)] ₄ [Ni(CN) ₄ · nH ₂ O]					
01	<i>cyclo</i> -C ₆ H ₁₂	0.5	14.23(1)	7.890(9)	32.56/32.59	4.46/4.48	20.80/20.73	
02	CH ₃ C ₆ H ₅	0.5	14.28(1)	7.85(2)	33.65/33.74	3.93/3.94	20.99/20.53	
03	<i>p</i> -(CH ₃) ₂ C ₆ H ₄	0.5	14.33(2)	7.82(2)	33.85/34.61	4.07/4.12	20.39/20.18	
		0.45			33.89	4.05	20.44	
04	<i>o</i> -(CH ₃) ₂ C ₆ H ₄	0.5	14.24(1)	7.79(3)	33.99/34.61	4.07/4.12	20.50/20.18	
		0.45			33.89	4.05	20.44	
05	C ₂ H ₅ C ₆ H ₅	0.25	14.273(7)	7.831(6)	30.84/30.81	3.75/3.75	21.81/21.56	
06	C ₆ H ₅ CH ₂ OH	0.5	14.283(8)	7.718(9)	32.91/33.09	3.57/3.86	20.04/20.14	
07	C ₆ H ₅ COCH ₃	0.5	14.30(2)	7.78(2)	33.38/34.02	3.55/3.81	20.01/19.85	
08	<i>dl</i> -CH ₃ CH(C ₆ H ₅)OH	0.5?	14.28(1)	7.81(1)	30.70/33.96	3.58/4.04	17.90/19.80	
09	C ₆ H ₅ NO ₂	0.5	14.22(3)	7.83(4)	30.83/31.10	3.38/3.44	21.42/21.43	
10	<i>o</i> -NO ₂ C ₆ H ₄ CH ₃	0.5	14.238(7)	7.767(7)	31.48/31.98	3.58/3.62	21.25/21.08	
11	CH ₃ (CH ₂) ₃ OH	0.5	14.28(1)	7.73(2)	29.78/30.00	4.02/4.28	20.85/20.99	
12	(CH ₃) ₂ CHCH ₂ OH	0.5	14.29(1)	7.795(9)	29.95/30.00	4.25/4.28	21.03/20.99	
13	C ₂ H ₅ CH(OH)CH ₃	0.5	14.30(1)	7.77(1)	29.90/30.00	4.36/4.28	20.99/20.99	
14	CH ₃ (CH ₂) ₄ OH	0.5	14.26(6)	7.71(6)	30.75/30.96	4.34/4.45	20.85/20.63	
15	(CH ₃) ₂ CH(CH ₂) ₂ OH	0.5	14.30(6)	7.83(6)	30.90/30.96	4.33/4.45	20.88/20.63	
16	CH ₃ (CH ₂) ₅ OH	0.5	14.31(2)	7.81(2)	31.58/31.88	4.46/4.62	20.56/20.28	
17	CH ₃ O(CH ₂) ₂ OH	0.5	14.31(3)	7.75(3)	28.41/28.43	3.99/4.02	20.05/20.94	
18	C ₂ H ₅ COC ₂ H ₅	0.5	14.277(8)	7.73(1)	30.51/31.03	4.17/4.22	20.50/20.68	

19	$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$	0.5	14.32(6)	7.87(6)	31.57/31.96	4.29/4.39	20.40/20.33
20	CH_2Cl_2	0.5	14.275(8)	7.694(9)	24.67/25.16	3.26/3.22	20.08/20.71
21	CHCl_3	0.65			/24.83	/3.20	/20.08
22	CHBr_3	0.5	14.277(9)	7.754(9)	24.10/24.14	2.97/2.98	19.83/19.87
23	$\text{CH}_2\text{ClCH}_2\text{Cl}$	0.5	14.24(2)	7.74(2)	21.03/20.85	2.54/2.57	17.31/17.16
24	$\text{CH}_2\text{BrCH}_2\text{Br}$	0.5	14.28(1)	7.73(1)	26.27/26.19	3.47/3.42	20.42/20.36
25	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{Cl}$	0.5	14.20(1)	7.73(1)	23.51/23.64	2.97/3.09	18.32/18.38
26	$\text{CH}_3\text{CHClCH}_2\text{Cl}$	0.5	14.18(1)	7.77(1)	27.45/27.18	3.63/3.60	20.29/20.02
27	$\text{C}_2\text{H}_5\text{CHClCH}_3$	0.5	14.336(8)	7.837(7)	27.22/27.18	3.59/3.60	20.18/20.02
			14.12(3)	7.70(4)	29.18/29.32	3.88/4.06	20.66/20.52
$\text{Cd}\{(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{NH}_2\}_n\text{Ni}(\text{CN})_4 \cdot n\text{G}$							
28	CH_2Cl_2	0.5	14.19(1)	7.58(1)	26.99/27.17	3.59/3.60	20.14/20.01
29	CHCl_3	0.5	14.18(1)	7.60(1)	25.84/26.11	3.31/3.34	19.23/19.23
30	CHBr_3	0.5	14.18(2)	7.60(2)	22.33/22.65	2.83/2.90	16.57/16.68
31	$\text{CH}_2\text{ClCH}_2\text{Cl}$	0.5	14.33(5)	7.74(5)	27.50/28.14	3.63/3.75	19.56/19.69
$\text{Cd}\{\text{CH}_3\text{NH}(\text{CH}_2)_2\text{OH}\}_n\text{Ni}(\text{CN})_4 \cdot [x\text{G} + y\{(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{OH}\}]$							
	x/y						
32	no guest	0/0.5	14.18(1)	7.67(1)	26.93/26.32	3.93/3.51	19.58/19.86
33	C_6H_6	0.3/0.2	14.22(3)	7.78(4)	29.29/29.04	3.76/3.26	18.89/18.73
34	$\text{C}_6\text{H}_5\text{NH}_2$	0.4/0.1	14.18(4)	7.86(3)	29.25/29.49	3.31/3.23	18.97/19.50
35	$1,3,5\text{-(CH}_3)_3\text{C}_6\text{H}_3$	0.25/0.25	14.166(6)	7.705(8)	30.21/30.09	3.92/3.59	18.45/18.42

^aWhen the found contents are closer to the values than those from the assumed composition $n = 0.5$, the values of n and calculated contents are shown.

by the guest molecules but the other half unoccupied. Such a distinct deficiency of occupation has not been observed for the clathrates of other aromatic guest molecules whose bulkiness is comparable with that of ethylbenzene.

3.2.2. *dmtn-Series*

Assuming that the host structure of the *dmtn*-series is similar to that of the *mtn*-series, the volume of the cavity should decrease from that in the *mtn*-series by approximately the volume of a methyl group. In fact the *dmtn*-series of the clathrates has never been obtained for those guest molecules with a benzene ring, under the experimental conditions similar to those applied to the *mtn*-series. Stable clathrates have been obtained only for the haloalkanes which are not smaller than dichloromethane and not larger than 1,2-dibromoethane. This fact suggested that the *dmtn*-series host was able to accommodate small haloalkane molecules selectively from mixtures of haloalkanes and aromatic compounds. Preliminary experiments, however, have given contrary results: benzene, toluene, and the three isomers of xylene are accommodated into the *dmtn*-series host along with e.g. bromoform which behaves apparently as an attracting guest for the BTX aromatic molecules. The attracting behavior of the haloalkanes is different one from another: dichloromethane attracts benzene, toluene, and *o*- and *m*-xylene; chloroform attracts benzene and toluene; 1,2-dichloroethane attracts benzene and the three isomers of xylene; etc. The details will be reported elsewhere.

3.2.3. *mmea-Series*

The lattice parameters of the products listed in Table II support the formation of the clathrates isostructural to the *mtn*- and *dmtn*-series, but the analytical results do not agree with the assumed composition $\text{Cd}(\text{mmea})\text{Ni}(\text{CN})_4 \cdot 0.5 \text{G}$. The results of IR, GC and TG experiments suggest that excessive *mmea* and deficient G were contained in the products. Assuming that a mixed-guest clathrate $\text{Cd}(\text{mmea})\text{Ni}(\text{CN})_4 \cdot [x\text{G} + y(\text{mmea})]$ ($x + y = 0.5$) is formed, the compositions can be reasonably interpreted. In order to confirm this assumption, synthesis of an *mmea* clathrate of the *mmea*-series was examined; the product gave analytical results which agree with the composition $\text{Cd}(\text{mmea})\text{Ni}(\text{CN})_4 \cdot 0.5 \text{mmea}$ as listed in Table II. Such 'ligand-guest' clathrates have been known for the so-called 'Werner-type' host clathrate $[\text{Ni}(\text{NCS})_2(\gamma\text{-picoline})_4] \cdot \gamma\text{-picoline}$ [15]. Presumably the guest *mmea* molecule takes a ring structure by an intramolecular hydrogen bond between the methylamino group and the hydroxy group adaptable to the box-shaped cavity.

3.3. STRUCTURAL FEATURES

The crystal structures of the Hofmann-diam-type clathrates have been analyzed for those hosts built of the α,ω -diaminoalkanes (diams) of carbon chain length from 2 to 9 except for that of 3 [3-5, 16, 17]. The diam of an odd-numbered carbon chain gives a considerably distorted host structure in comparison with those of the diams of the adjacent even-numbered carbons. The distortion or disorder is due to the geometrical inconvenience of the odd-numbered chain in spanning almost parallel

bridges between almost parallel layers. Although no structures have been solved for the Hofmann-1,3-diaminopropane-type, the introduction of one or two methyl groups into a terminal amino group of 1,3-diaminopropane changes the ligating behavior drastically from the bridging to the chelating, as exemplified by the mtn- and the dmtn-series.

With regard to mmea, 2-aminoethanol (2-hydroxyethylamine:monoethanolamine:mea) behaves as a unidentate ligand in the Hofmann-mea-type(1) $\text{Cd}(\text{mea})_2\text{Ni}(\text{CN})_4 \cdot \text{C}_4\text{H}_5\text{N}$ similar to the NH_3 in the Hofmann-type $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$ clathrates, and as a bridging ligand in the Hofmann-mea-type(2) $\text{Cd}(\text{mea})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ similar to the en in the Hofmann-en-type $\text{Cd}(\text{en})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ [18, 19]. The introduction of a methyl group to the amino group of mea changes the ligating behavior from bridging to chelating, too.

From these observations, and the fact that the three-dimensional host structures similar to the Hofmann-diam-type have never been obtained using N-methyl derivatives of α,ω -diaminoalkanes, the methyl group at the terminal amino nitrogen atom appears to make chelate coordination preferable to bridging to the cadmium(II) atom in the present metal-complex host framework. Ring size or bulkiness of the chelate should be another factor leading to the formation of the present host structure, which involves the six-membered (mtn and dmtn) or five-membered (mmea) chelate ring. Four-membered rings may be too small and seven-membered rings may be too large to build up the three-dimensional framework along with the square-planar tetracyanonickelate(II) moieties, unless the chelating agent has substituents appropriate to make the wall of the cavity.

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