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Bis(2-aminoethanol)cadmium(II) Tetracyanonickelate(II)-Pyrrole (1/1) and 2-Aminoethanolcadmium(II) Tetracyanonickelate(II)-Benzene (1/2). Variation of Metal Complex Host Structure with the Size of Aromatic Guest Molecule

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Two modifications of the host structures analogous to that of Hofmann-type $Cd(NH_3)_2Ni(CN)_4$ have been found in the crystal structures of $Cd(mea)_2Ni(CN)_4 \cdot C_4H_5N$ and $Cd(mea)Ni(CN)_4 \cdot 2C_6H_6$ which were prepared using mea (2-aminoethanol=monoethanolamine) in place of the NH_3 as the ligands in the host metal complexes. In the former pyrrole clathrate, Hofmann-mea-type(1), the mea behaves as a unidentate ligand like the NH_3 in Hofmann-type, but in the latter benzene one, Hofmann-mea-type(2), it behaves ambidently like the en in Hofmann-en-type host $Cd(en)Ni(CN)_4$. In Hofmann-mea-type(1) host, the layered metal cyanide network is puckered, whereas that in Hofmann-ema-type(2) host is coplanar. The size of the guest molecule appears to control the behavior of mea and the structure of the metal cyanide network.

In the course of our studies involving the design and synthesis of clathrate compounds analogous to Hofmann-type $M(NH_3)_2M'(CN)_4 \cdot 2G$, novel three-dimensional host structures have been developed using such ambident ligands as ethylenediamine (en), trimethylenediamine, propylenediamine (pn), in place of the NH_3 ligands in Hofmann-type host. Another strategy we have applied is to use tetrahedral tetracyanometallate(II) moieties such as $Cd(CN)_4$, $Hg(CN)_4$, in place of the square-planar $M'(CN)_4$ (M'=Ni, Pd, or Pt) in order to develop three-dimensional host structures.[1–5)] The ambident ligands used are symmetric with respect to their coordination sites, although the skeletal structure of pn is asymmetric.[6)]

In the present investigation, mea (monoethanolamine=2-aminoethanol: $NH_2CH_2CH_2OH$) was chosen as the ligand replacing the NH_3 in Hofmann-type to develop novel host structures; mea was expected to behave either as a unidentate ligand like the NH_3 in Hofmann-type or as an ambident one like the en in Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2G$.[7–11)] In the former case, mea with a bulky $-CH_2CH_2OH$ group does not have any proper rotational axes like the threefold one of NH_3; in the latter case, it is also asymmetric with respect to the coordination sites $-NH_2$ and $-OH$. Both cases have been demonstrated in the host structures of novel clathrates, $Cd(mea)_2Ni(CN)_4 \cdot C_4H_5N$ (**1**), and $Cd(mea)Ni(CN)_4 \cdot 2C_6H_6$ (**2**), as has been reported briefly in the previous communication.[12)] This paper describes their crystal structures in detail and discusses their structural features from the viewpoint of molecular inclusion phenomena occurring in the series of Hofmann-type and the analogous metal complex hosts.

Experimental

Preparation. Into 100 ml of 0.1 M $CdCl_2$ (M=mol dm^{-3}), 11.6 ml of 2-aminoethanol and 100 ml of 0.1 M $K_2[Ni(CN)_4]$ were added successively. The pH of the mixed solution was adjusted to *ca.* 9.5 by adding a few drops of 6 M HCl. The aqueous phase in a conical flask was covered with the organic phase of pyrrole-toluene (1:15) mixture, thiophene-*o*-xylene (1:1) mixture, or neat benzene to prepare the pyrrole, thiophene, or benzene clathrate, respectively. By leaving the flasks in a refrigerator at 5 °C for a few days, yellow crystals of the clathrates grew up at the interface between the aqueous and the organic phases. The freshly prepared crystals were subjected to the analyses of metal contents by chelatometry in this laboratory. The C, H, and N microanalyses were carried out for the specimens sealed in glass vials at the laboratory of elemental analysis in Department of Chemistry, Facultry of Science of this University a few days after the prepration. The pyrrole clathrate was stable enough to give the satisfiable analytical results, but the thiophene and the benzene ones were unstable even when reserved in sealed

Table 1. The analytical results and the compositions determined

Composition	Found/Calcd(%)				
	C	H	N	Cd	Ni
$Cd(NH_2CH_2CH_2OH)_2Ni(CN)_4 \cdot C_4H_5N$	31.2 31.03	4.17 4.12	21.2 21.11	23.8 24.20	12.7 12.63
$Cd(NH_2CH_2CH_2OH)_2Ni(CN)_4 \cdot C_4H_4S$	29.1 29.93	3.28 3.77	17.6 17.45	23.2 23.34	12.4 12.19
$Cd(NH_2CH_2CH_2OH)Ni(CN)_4 \cdot 2C_6H_6$	38.4 43.89	3.24 3.89	15.7 14.22	23.1 23.82	12.7 11.91

vials. The benzene clathrate was extremely unstable: it decomposed immediately at room temperature, even in contact with neat benzene. The analytical results listed in Table 1 appear to reflect the instability of the thiophene and the benzene clathrates, especially with respect to the values of C, H, and N.

Structure Determination

Data Collection. In order to avoid the spontaneous decomposition of the specimens under ambient conditions, each crystal was coated with epoxy resin before the X-ray experiments. Preliminary Weissenberg photographs were taken to check the crystal symmetries and lattice parameters for the pyrrole, the thiophene, and the benzene clathrates, respectively. The refinement of lattice parameters and the collection of Lp-corrected intensity data were carried out for the pyrrole clathrate (**1**), on a Rigaku automated four-circle diffractometer,[13] and for the benzene clathrate (**2**), on a Phillips one[14] using Mo $K\alpha$ radiation at ambient temperature. The lattice parameters were refined for **1** using 30 reflections with $45° < 2\theta < 50°$, and for **2** using 24 reflections with $20° < 2\theta < 64°$. The intensities of three standard reflections, recorded every fifty measurements, showed no significant variations. The experimental conditions and the crystallographic data are listed in Table 2.

Solution and Refinement of the Structures. The structures of **1** and **2** were solved by the heavy-atom method. The refinements were carried out by the successive Fourier and difference Fourier syntheses and by the block-diagonal least-squares method; for **2**, the full-matrix least-squares method was applied at the later stages. All the calculations were carried out on a HITAC M-200H computer at the Computer Center of this University using the programs in UNICS[15] and their local versions. The atomic scattering factors used were those in the *International Tables*.[16]

The Pyrrole Clathrate (1): The absorption correction for a cube was applied for the intensities of all the reflections used. From the observed systematic absences of reflections in the orthorhombic system, the space group was limited to either non-centrosymmetric $Pna2_1$ or centrosymmetric Pnam. On the Patterson map, the positions of Cd and Ni atoms were first found. Then those of C, N, and O atoms were revealed on the successive Fourier and difference Fourier maps.

Table 2. Crystallographic parameters and experimental data[a]

Compound Host	$Cd(mea)_2Ni(CN)_4$		$Cd(mea)Ni(CN)_4$
Guest	C_4H_5N	C_4H_4S	$2C_6H_6$
Chemical formula	$C_{12}H_{19}N_7O_2CdNi$	$C_{12}H_{18}N_6O_2SCdNi$	$C_{18}H_{19}N_5OCdNi$
Formula weight	470.44	481.48	492.49
Crystal system	orthorhombic	orthorhombic	tetragonal
Space group	$Pna2_1$	$P2_12_12_1$	P4/mmm
a/Å	14.691(1)	14.58	7.529(1)
b/Å	15.881(1)	16.34	7.529(1)
c/Å	7.575(1)	7.59	8.094(1)
Z	4	4	1
D_x/g cm^{-3}	1.76	1.74	1.75
D_o/g cm^{-3} [b]	1.74(1)	1.74(1)	1.75(1)
Crystal size/mm	0.35×0.35×0.35		0.25×0.25×0.30
Radiation	Mo $K\bar{\alpha}$[c]	Cu $K\bar{\alpha}$	Mo $K\bar{\alpha}$[c]
Monochromator	graphite		graphite
Scan mode	2θ-ω		ω
Scan range	$3.0° < 2\theta < 65°$		$7.5° < 2\theta < 70°$
No. of reflections			
in the range	3403		659
observed	3135		606
used[d]	3070		575
Systematic absences	$(0kl)$ $k+l=2n+1$ $(h0l)$ $h=2n+1$	$(h00)$ $h=2n+1$ $(0k0)$ $k=2n+1$ $(00l)$ $l=2n+1$	no
μ(Mo $K\bar{\alpha}$)/cm^{-1}	22.4		21.7
Correction	Lp and cubic absorption		Lp
No. of parameters determined	243		63
No. of variables refined	163		29
R[e]	0.041		0.047
R_w	0.047[f]		0.062[g]

a) Only the photographic data are listed for the thiophene clathrate. b) The values measured by the flotation method in bromoform-xylene mixture. c) $\lambda=0.710730$ Å. d) The reflections with $|F_o| > 3\sigma(|F_o|)$. e) $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. f) $R_w=(\Sigma w(|F_o|-|F_c|)^2/\Sigma|F_o|^2)^{1/2}$ with $w=(400/|F_o|)^2$ for $|F_o| \geq 400$, $w=1.0$ for $400 > |F_o| > 40$, and $w=0.5$ for $|F_o| \leq 40$. g) $R_w=(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ with $w=\{(\sigma(|F_o|)^2+(0.01|F_o|)^2\}^{-1/2}$.

At the stage of refinement with the anisotropic thermal parameters for the atoms of the host moieties except H's, and the isotropic ones fixed at 5.0 Å^2 for the skeletal atoms of pyrrole molecule, the possible space groups Pna2$_1$ and Pnam were compared. The Pna2$_1$ was chosen for the following reasons: (i) the *R* value of 0.043 was lower than 0.048, (ii) the preference in the Hamilton test with the significance level of 0.005, (iii) the acceptable bond lengths and angles, and (iv) the Patterson syntheses was fully supported by this space group.

In the final stage of refinement applying the Pna2$_1$ space group, the H atoms belonging to the host moieties, *i.e.*, those of the mea ligands, were located on the positions found on the difference Fourier map, except for those H's bonded to the O atoms. All the skeletal atoms of the pyrrole molecule were regarded as C because no significant discrimination of N was possible in the revealed structure. In the final block-diagonal least-squares calculations, the atomic coordinates of the host H atoms were fixed at the positions found on the difference Fourier map, and the thermal parameters of the host H atoms and the guest skeletal C atoms were fixed at 4.0 Å^2 and 5.0 Å^2, respectively, but these parameters were included in the evaluation of *R* values. After a few cycles of the calculations, the parameters to be determined converged into the range less than 0.5 times their

TABLE 3. THE FINAL POSITIONAL AND THERMAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN THE PARENTHESES FOR $Cd(mea)_2Ni(CN)_4 \cdot C_4H_5N$[a)]

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	4319(0)	7242(0)	0(2)	17(0)	32(0)	18(0)	1(0)	(0)	0(0)
Ni	3191(0)	2117(0)	47(0)	16(0)	33(0)	14(0)	−3(0)	−1(1)	−1(1)
C(1)	2262(4)	1964(4)	1678(8)	29(3)	28(3)	16(2)	−1(2)	0(2)	1(2)
C(2)	4005(4)	2321(5)	1855(9)	21(2)	38(4)	27(3)	−1(3)	5(2)	−1(3)
C(3)	881(4)	7267(4)	3360(8)	17(2)	34(3)	19(2)	2(2)	−2(2)	1(2)
C(4)	2659(4)	6995(5)	3225(9)	15(2)	53(4)	24(3)	1(3)	3(2)	7(3)
C(5)	4134(5)	5230(5)	9001(23)	36(3)	33(3)	50(8)	−3(2)	−1(4)	−1(4)
C(6)	4338(7)	4340(5)	422(12)	75(6)	35(4)	48(6)	−3(4)	4(5)	2(3)
C(7)	7807(5)	6226(5)	9727(28)	34(3)	40(4)	96(14)	−11(3)	1(6)	4(6)
C(8)	7569(6)	5310(6)	9505(14)	39(4)	53(5)	72(8)	−14(4)	6(4)	−7(5)
N(1)	1676(4)	1873(4)	2649(9)	27(3)	51(4)	31(3)	−7(3)	9(3)	−9(3)
N(2)	4542(4)	2447(4)	2967(8)	29(3)	53(4)	24(3)	−5(3)	−7(2)	−4(3)
N(3)	339(4)	7368(4)	2358(9)	31(3)	54(4)	27(3)	1(3)	−5(2)	4(3)
N(4)	3173(4)	6975(5)	2123(9)	34(3)	55(4)	25(3)	6(3)	6(3)	5(3)
N(5)	4749(4)	5879(4)	562(8)	32(3)	33(3)	34(3)	3(2)	0(2)	−1(2)
N(6)	8776(4)	6393(4)	9788(26)	29(2)	43(3)	88(10)	−4(2)	−8(5)	−20(8)
O(1)	5199(4)	4089(4)	9873(29)	60(3)	44(3)	108(9)	7(3)	−15(8)	−13(7)
O(2)	6642(5)	5242(5)	9721(38)	47(3)	56(4)	215(18)	−7(3)	−7(11)	1(11)
				B_{iso}/Å^2					
H(15)	530	580	0	4.0					
H(25)	470	590	160	4.0					
H(16)	410	880	880	4.0					
H(26)	390	890	100	4.0					
H(51)	370	540	20	4.0					
H(52)	430	520	820	4.0					
H(61)	450	440	180	4.0					
H(62)	390	390	0	4.0					
H(71)	750	660	100	4.0					
H(72)	750	660	900	4.0					
H(81)	770	540	780	4.0					
H(82)	810	500	50	4.0					
C(9)	590	80	0	5.0					
C(10)	650	960	0	5.0					
C(11)	530	40	100	5.0					
C(21)	570	960	120	5.0					
C(31)	670	40	940	5.0					
C(12)	530	40	900	5.0					
C(22)	570	960	880	5.0					
C(32)	670	40	60	5.0					

a) The U_{ij}'s are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hla^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. The positional and thermal parameters are multiplied by 10^4 and 10^3, respectively, for the atoms from Cd to O(2); those positional parameters for the atoms from H(15) to C(32) are multiplied by 10^3. The parameters lacking the estimated standard deviations were not refined, but were included in the evaluation of the *R* values (see text).

estimated standard deviations, except those for O(1) and O(2) atoms, and the R and R_w went down to 0.041 and 0.053, respectively.[17)]

*The Benzene Clathrate (**2**)*: On the Patterson map, the atomic coordinates of Cd and Ni atoms were fixed uniquely. Since the possible space groups predicted from the photographs and the collected intensity data are P4/mmm, P4mm, P422, P$\bar{4}$2m, and P$\bar{4}$m2, there should be statistical distributions at least in the orientation of mea molecule in the crystal structure. In the successive Fourier and difference Fourier syntheses and the block-diagonal least-squares calculations, the positions of the C and N atoms of cyanide group and the C atoms of benzene molecule were found out. By applying the anisotropic thermal parameters for the Ni and Cd, and the isotropic ones for the C and N atoms, the full-matrix least-squares calculations were done for the check of the most proper space group.

TABLE 4. THE FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN THE PARENTHESES FOR $Cd(mea)Ni(CN)_4 \cdot 2C_6H_6$ [a)]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0	0	0	22(0)	$=U_{11}$	34(0)	0	0	0
Ni	5000	5000	0	22(0)	$=U_{11}$	36(1)	0	0	0
C(1)	3263(5)	$=x$	0	29(1)	29(0)	41(2)	0(2)	0	0
N(1)	2185(5)	$=x$	0	33(1)	33(0)	65(3)	−3(2)	0	0
C(2)	5000	0	3275(13)	61(5)	84(6)	47(4)	*0*	0	0
C(3)	5000	1526(9)	4143(9)	123(7)	57(4)	77(4)	*0*	0	8(3)
				$B_{iso}/Å^2$					
N(2)	668(15)	0	2779(14)	3.1(2)					
C(4)	503(18)	0	4177(14)	3.1(3)					

a) The positional and thermal parameters U's are multiplied by 10^4 and 10^3, respectivealy. The U_{ij}'s are defined by: $\exp[-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$.

TABLE 5. SELECTED BOND LENGTHS AND ANGLES FOR $Cd(mea)_2Ni(CN)_4 \cdot C_4H_5N$ AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Ni-C(1)	1.856(6)	C(1)-N(1)	1.142(9)	N(1)-Cd	2.378(7)
Ni-C(2)	1.847(7)	C(2)-N(2)	1.172(9)	N(2)-Cd	2.326(6)
Ni-C(3)	1.885(6)	C(3)-N(3)	1.111(9)	N(3)-Cd	2.412(7)
Ni-C(4)	1.871(7)	C(4)-N(4)	1.126(9)	N(4)-Cd	2.367(7)
Cd-N(5)	2.295(6)	Cd-N(6)	2.320(7)		
N(5)-C(5)	1.49(1)	C(5)-C(6)	1.52(1)	C(6)-O(1)	1.391(1)
N(6)-C(7)	1.44(1)	C(7)-C(8)	1.51(1)	C(8)-O(2)	1.381(1)
C(5)-H(51)	0.76(1)	C(5)-H(52)	1.24(2)	C(6)-H(61)	1.075(9)
C(6)-C(62)	1.003(9)	C(7)-H(71)	1.22(2)	C(7)-H(72)	0.93(1)
C(8)-H(81)	1.31(1)	C(8)-H(82)	1.19(1)	N(5)-H(15)	0.93(1)
N(5)-H(25)	0.790(6)	N(6)-H(16)	0.95(2)	N(6)-H(26)	1.05(2)
C(9)-C(11 or 12)	1.33	C(11 or 12)-C(12 or 22)	1.41		
C(12 or 22)-C(10)	1.49	C(10)-C(31 or 32)	1.38		
C(31 or 32)-C(9)	1.41				
Bond angle	ϕ/°	Bond angle	ϕ/°		
C(1)-Ni-C(2)	90.3(3)	C(2)-Ni-C(3)	90.7(3)		
C(3)-Ni-C(4)	89.7(3)	C(4)-Ni-C(1)	89.3(3)		
Ni-C(1)-N(1)	178.3(6)	Ni-C(2)-N(2)	178.0(6)		
Ni-C(3)-N(3)	178.9(6)	NI-C(4)-N(4)	175.7(6)		
C(1)-N(1)-Cd	156.2(6)	C(2)-N(2)-Cd	175.2(6)		
C(3)-N(3)-Cd	170.9(6)	C(4)-N(4)-Cd	167.4(6)		
N(4)-Cd-N(5)	84.3(2)	N(5)-Cd-N(6)	172.0(2)		
N(1)-Cd-N(2)	89.4(2)	N(2)-Cd-N(3)	89.4(2)		
N(3)-Cd-N(4)	89.1(2)	N(4)-Cd-N(1)	91.6(2)		
Cd-N(5)-C(5)	114.5(5)	N(5)-C(5)-C(6)	113.8(9)		
C(5)-C(6)-O(1)	110.8(8)	H(15)-N(5)-H(25)	123.1(7)		
H(51)-C(5)-H(52)	125(2)	H(61)-C(6)-H(62)	120.9(9)		
Cd-N(6)-C(7)	121.3(5)	N(6)-C(7)-C(8)	114.2(7)		
C(7)-C(8)-O(2)	107.0(8)	H(16)-N(6)-H(26)	120.9(9)		
H(71)-C(7)-H(72)	88.8(8)	H(81)-C(8)-H(82)	124.8(8)		

Dihedral angle between the statistically distributed pyrrole molecular planes: 71.8°

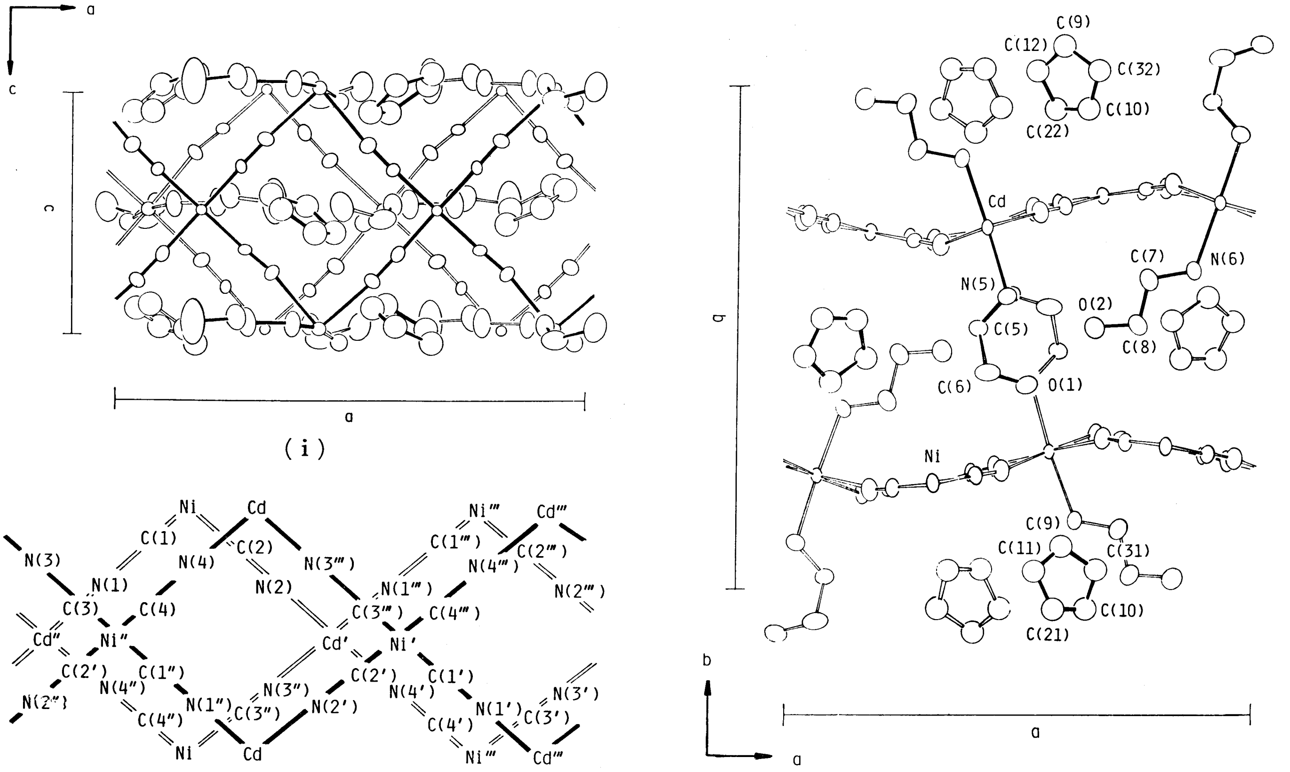
Since the space groups P$\bar{4}$2m and P$\bar{4}$m2 require the mea and the benzene molecules to take extremely unusual arrangements and orientations, these two were discarded. Although no significant differences were observed in R values among the three possible space groups, those other than P4/mmm required the mea and the benzene molecules to be arranged with higher disorder. Because there are no positive reasons to take such unusual disorder, the space group P4/mmm was adopted. In this space group, however, the mea molecule should be distributed statistically about the fourfold axis and three sets of mirror planes of crystal. Therefore, the N and O atoms of mea were not distinguishable but the O atom was regarded as N, and each of the C and N(=O) of mea was distributed with the occupancy factor of 0.25 about the fourfold axis and the mirror planes in the refinement. By applying the anisotropic thermal parameters to the Cd, Ni, C, and N atoms of cyanide, and C atoms of benzene, and the isotropic ones to the C and N(=O) atoms of mea, the final full-matrix calculations converged to the R and R_w values of 0.047 and 0.063, respectively.[17)]

Description of Structures and Discussion

As is shown in Table 1, the pyrrole and the thiophene clathrates have the composition Cd(mea)$_2$Ni(CN)$_4$·G (G=C$_4$H$_5$N or C$_4$H$_4$S) different from that of the benzene clathrate Cd(mea)Ni(CN)$_4$·2C$_6$H$_6$ in the numbers of the mea ligands and of the guest molecules in the formula unit. The thiophene clathrate can be thought of as having a structure similar to the pyrrole one, as the crystallographic data in Table 2 show.

The atomic parameters determined for **1** and **2** are listed in Tables 3 and 4, and the illustrations of the structures are shown in Figs. 1 and 2 with the atomic notations; the selected bond lengths and angles are summarized in Tables 5 and 6.

*The Structure of Pyrrole Clathrate (**1**).* The pyrrole clathrate has the structure which is considerably distorted from those of the Hofmann-type and those of the analogous clathrates with the hosts containing square-planar Ni(CN)$_4$ moiety so far known, although some similarity to Hofmann-type host Cd(NH$_3$)$_2$Ni(CN)$_4$ is seen with regard to the layered two-dimensional network of metal cyanide and the projections of mea ligands from the six-coordinate Cd atoms in the network. The Ni(CN)$_4$ moiety, being almost coplanar by itself, is distorted from the D$_{4h}$ symmetry with the bond angles slightly deviated from 90° about the central Ni atom and with the alignment of Ni–C–N linkages slightly bent from 180°. Furthermore, the joint between the Ni(CN)$_4$ moiety and the Cd atom is bent by 23.8° at the N(1) and by 12.6° at the N(4)



(i) (ii) (iii)

Fig. 1. The structure of Cd(mea)$_2$Ni(CN)$_4$·C$_4$H$_5$N. (i) Projection along the b axis: the bonds of the moieties belonging to the upper layer are shown with solid lines. (ii) Numbering of the atoms in the metal cyanide networks. Key: normal, x, y, z; with ′, $\bar{x}$, $\bar{y}$, $\frac{1}{2}+z$; with ″, $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$; and with ‴, $\frac{1}{2}+x$, $\frac{1}{2}-y$, z. (iii) Projection along the c axis with numbering of the atoms: the bonds of the moieties viewed on this side are shown with solid lines. In (i) and (ii), the hydrogen atoms of the pyrrole molecule and those of the mea, H(n5) at N(5), H(n6) at N(6) (n=1 or 2), H(mn) at C(m) (m=5—8, n=1 or 2), and those at O(1) and O(2), are not shown.

Table 6. Selected bond lengths and angles for $Cd(mea)Ni(CN)_4 \cdot 2C_6H_6$ and their estimated standard deviations (in parentheses)

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Ni-C(1)	1.865(4)	C(1)-N(1)	1.158(5)	N(1)-Cd	2.346(4)
Cd-N(2)	2.31(1)	N(2)-C(4)	1.44(2)	C(4)-C(4′)	1.54(2)
Bond angle	ϕ/°	Bond angle	ϕ/°		
Ni-C(1)-N(1)	180.0(4)	C(1)-N(1)-Cd	180.0(4)		
N(1)-Cd-N(2)	81.1(3)	Cd-N(2)-C(4)	129.2(8)		
N(2)-C(4)-N(4′)	112(1)	C(2)-C(3)-N(3′)	121.2(7)		
C(3)-C(2)-C(3′)	117.6(9)				

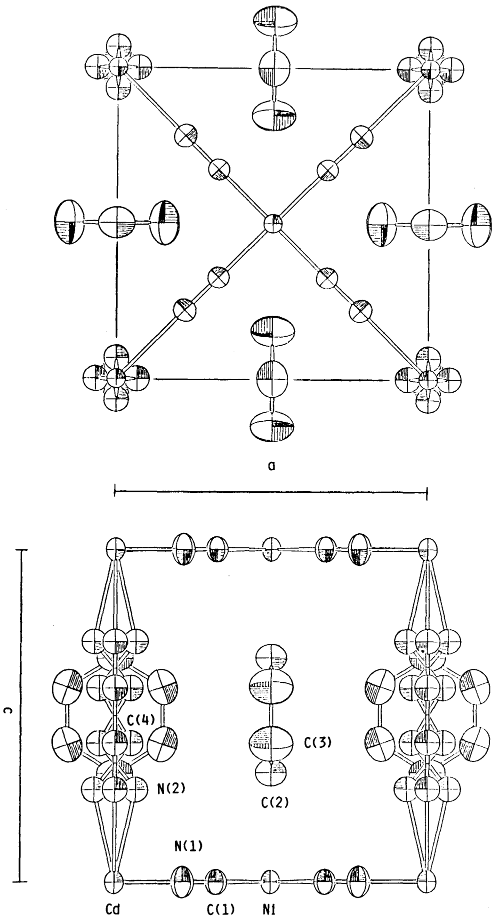


Fig. 2. The structure of $Cd(mea)Ni(CN)_4 \cdot 2C_6H_6$. Top: projection along the c axis, bottom: projection along the b axis.

atom, the distortion leading the layered network to a puckered structure along the crystal a-axis. However, the related bond distances are not unusual. The puckered metal cyanide networks are stacked along the crystal b-axis with an alternate shift approximately by $a/4$ and $c/2$, so that the six-coordinate Cd atom is approximately placed over or beneath the square-planar Ni atom along the crystal b-axis; in Hofmann-type host, the metal cyanide layers are arranged completely parallel to each other. There can be seen two kinds of cavities: one is a real cavity occupied by a guest pyrrole molecule; the other appears to be a pseudo-cavity occupied by the tail parts of two crystallographically-independent mea ligands. One mea plays a role of the column dividing the two kinds of cavities but its OH-end intrudes into the pseudo-cavity occupied mainly by another mea. The latter mea behaves as a pseudo-guest to insert its $-CH_2CH_2OH$ skeleton into the pseudo-cavity. The column mea has approximately a cis form of the N–C–C–O skeleton, and the pseudo-guest mea has a trans form. The O(2) of the latter appears to form hydrogen bonds with the O(1) and the N(5) of the former; the distances are 2.80(1) Å for O(2)–O(1), 3.30(1) Å for O(2)–N(5), and *ca.* 2.2 Å for O(2)–H(51). On the Fourier and difference Fourier maps, it was difficult to find out the positions of protons assigned to the OH groups of O(1) and O(2). As relatively large thermal parameters and their estimated standard deviations have been observed for the O(1) and O(2) atoms, the supposed hydrogen bonds are thought to be not so strong.

Although there should be only one crystallographically-independent pyrrole molecule in an asymmetric unit, three skeletal atoms (not C(9) and C(10)) are statistically distributed about a pseudo-mirror plane (001). If the space group Pnam had been applied, the symmetry operations would have required the statistical distributions not only for the pyrrole molecule but also for the mea ligands. The fact that the estimated standard deviations of the positional parameters are relatively large for the skeletal atoms of the mea ligands suggests the possibility of the Pnam space group. However, this space group was exclude from the consideration of structure because of the unacceptable molecular forms of the mea, as has been described in the Structure Determination section. Both the possible orientations of pyrrole molecule in a cavity appear to be almost equivalent to each other with respect to the host-guest contacts. Therefore, the respective atomic coordinates have been listed in Table 3, and both the orientations have been illustrated in Fig. 1.

*The Structure of the Benzene Clathrate (**2**).* The structure of $Cd(mea)Ni(CN)_4 \cdot 2C_6H_6$ is similar to that of Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ (**2′**),⁹⁾ as expected from the similarity in the formula. The metal cyanide network keeps a D_{4h} symmetry and the unit cell contains a formula unit. Trivial differences between **2** and **2′** are found in that the aromatic plane of the guest benzene molecule is vertical to the (100) or (010) plane of the crystal in **2** (space group P4/mmm), whereas the inclination angle is 85° in **2′** (space group P4/m). Additionally, the N- and Oends of the mea ligand are indistinguishable from each other in the P4/mmm space group of **2**. The axial disorder of mea which bridges adjacent metal cyanide networks in **2** is also similar to that observed for en in **2′**. Although a rotating model about the fourfold axis of crystal has been applied for en in **2′**, the N(=O) and C atoms of mea in **2** are located on the (100) and (010) planes with an equal probability of 0.25. The deviation from the fourfold axis, *i.e.*, the radius in a rotating model, is 0.507 Å for the N(=O) and 0.382 Å for the C, whereas that of the N in **2′** is 0.63 Å.

Discussion. Each series of Hofmann-type and the analogous clathrates so far known, *e.g.*, Hofmann-type $M(NH_3)_2M'(CN)_4\cdot 2G$, en-Td-type $Cd(en)M'(CN)_4\cdot 2G$ ($M'=Cd$ or Hg), Hofmann-pn-type $Cd(pn)Ni(CN)_4\cdot 1.5G$, *etc.*, has a general composition common to each member of the series for the various guests G, and the hosts are almost isostructural to each other. However, in the case of mea-containing hosts, two kinds of structures have been obtained under similar preparation conditions. In Hofmann-mea-type(1) $Cd(mea)_2Ni(CN)_4\cdot G$ ($G=C_4H_5N$ or C_4H_4S), the mea ligand behaves as a unidentate ligand, whereas in Hofmann-mea-type(2) $Cd(mea)Ni(CN)_4\cdot 2C_6H_6$, it behaves ambidently. The behavior of mea either as a unidentate in type(1) or as an ambident in type(2) probably depends on the size of the guest molecule, the diameter of which, approximated to a ring, is smaller by 0.75 Å for the pyrrole and thiophene than for the benzene in the gaseous state.

As the instability of the benzene clathrate shows, the mea-bridged structure appears to be essentially unfavorable owing to the lower affinity of the O atom of mea as the ligating site to the Cd(II) atom in the metal cyanide network. Except for the present type-(2) structure, few cases have been known where mea behaves as an ambident ligand between different metal atoms. Therefore the unidentate behavior in type(1) appears preferable to the ambident one in type(2) from the viewpoint of the coordination chemistry about the central Cd atom and the ligating atoms. However, the distortion of the metal complex network demonstrated in type(1) structure is unfavorable in terms of the conjugation of π-electrons of cyanide groups throughout the network. This unfavorable outcome may be recovered in a some extent by the interactions between the host mea ligands and the guest pyrrole molecule occupying the larger cavity, and by the interactions of the mea ligands through hydrogen bonds in the smaller pseudo-cavity. A benzene molecule may be too large as a guest to be enclathrated in type(1) host, because the distortion of the metal cyanide network should become too much to cancel the imbalance of the volumes between the benzene molecule in the larger cavity and the mea ligands in the smaller pseudo-cavity.

These observations suggested that we develop another way of design and synthesis of the clathrate compounds analogous to Hofmann-type, using the amine ligands with bulky substituents which bring about distortion of the cyanide network but provide cavities with the guest molecules in various size and shape. The first attempt has been reported briefly.$^{18,19)}$

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