Three-dimensional Metal Complex Structures with Ambident Propylenediamine Ligands Serving as the Hosts of the Aromatic Guest Molecules. Hofmann-pn and pn-Td Type Clathrates

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Novel clathrate compounds, Hofmann-pn type $Cd(pn)Ni(CN)_4 \cdot 3/2G$ ($G=C_4H_5N$, C_4H_4S, or C_6H_6) and pn-Td type $Cd(pn)Cd(or\ Hg)(CN)_4 \cdot 3/2C_6H_6$, have been prepared. Their host structures are analogous to those of the known Hofmann-en type $Cd(en)Ni(CN)_4 \cdot 2G$ and en-Td type $Cd(en)Cd(or\ Hg)(CN)_4 \cdot 2C_6H_6$. The propylenediamine (pn: 1,2-diaminopropane) molecule ambidently bridges six-coordinate Cd atoms, as the en (ethylenediamine) does in the latter types of clathrates. The guest molecules occupy at random three quarters of the cavities in the host structures: every remaining cavity contains two methyl groups of the pn molecules. The crystal structure of $Cd(l\text{-}pn)Ni(CN)_4 \cdot 3/2C_4H_5N$ has been analyzed in order to demonstrate the structural features. The crystal is tetragonal with the space group P422, $a=7.575(2)$ and $c=7.742(2)$ Å, and $Z=1$. The degree of disorder is extremely high with regard to the arrangement and orientation of the *l*-pn molecule.

We have developed the synthetic and structural chemistry of the Hofmann type and the analogous clathrates with the general formula of $Cd(diam)M(CN)_4 \cdot 2G$ (diam=$(NH_3)_2$, en, or tn; M=square-planar Ni, Pd, or Pt, or tetrahedral Cd or Hg; G=C_4H_5N, C_4H_4S, C_6H_6, or $C_6H_5NH_2$), as has been summerized in a previous paper.[1] Among these clathrates, the Hofmann-en type (diam=en, M=Ni, Pd, or Pt), the en-Td type (diam=en, M=Cd or Hg), and the tn-Td type (diam=tn, M=Cd or Hg) have ambident α,ω-diamines bridging two six-coordinate Cd atoms in their host structures. In this paper we wish to add to them two novel series, the Hofmann-pn type $Cd(pn)Ni(CN)_4 \cdot 3/2G$ and the pn-Td type $Cd(pn)M(CN)_4 \cdot 3/2G$ (M=Cd or Hg), the hosts of which contain an ambident pn (propylenediamine) ligand as diam in the general formula of $Cd(diam)M(CN)_4 \cdot nG$ for the clathrates ($n=2$) reported previously.[1] However, the participation of the pn as a constituent of the host gives rise to a decrease in n from 2 to 3/2. Based on the present results of structural analysis, this decrement is interpreted in terms of the random distribution of a pair of pn-methyl groups with a 1/4 probability, and a guest molecule with a 3/4 probability, in the cavity formed in the metal-complex host structure. Our idea at the beginning of this investigation was to develop a stereospecific host structure using optically-active *l*-pn as one of the host constituents. Although this idea has not been realized, it has been suggested that the space volume of a cavity available for a guest molecule can be regulated by introducing bulky substituents into the ambident diamine ligand building up the three-dimensional host structure.

Experimental

Preparation. *Cd(*dl*-pn)Ni(CN)$_4 \cdot 3/2C_4H_5N$*: From a concentrated aqueous solution containing $CdCl_2$, $K_2[Ni(CN)_4]$, and racemic pn (*dl*-pn) in a 1:1:3 mole ratio, tris(*dl*-propylenediamine)cadmium tetracyanonickelate(II) $[Cd(dl\text{-}pn)_3][Ni(CN)_4]$ was precipitated as pale yellow crystals. They were then recrystallized from hot water. Found: C, 30.9; H, 6.44; N, 28.2; Cd, 22.3; Ni, 11.7%. Calcd for $C_{13}H_{30}N_{10}CdNi$: C, 31.4; H, 6.08; N, 28.2; Cd, 22.6; Ni, 11.8%. The recrystallized complex was dissolved into water (0.2 g/50 cm^3) in a 300-cm^3 stoppered conical flask, and the solution was covered with an organic mixture of pyrrole and xylene (1:15 v/v). By leaving the flask in a refrigerator for a week, pale yellow plate-like crystals of the clathrate were obtained on the interface between the aqueous and the organic phases. Although the needle-like crystals of $[Cd(dl\text{-}pn)_3][Ni(CN)_4]$ were occasionally mixed with those of the clathrate, it was easy to discriminate between the complex and the clathrate visually. The clathrate was filtered off on a sintered glass, washed with small amounts of water and ethanol successively, and preserved in a silica gel desiccator under the saturated vapor pressure of pyrrole.

*Cd(*dl*-pn)Ni(CN)$_4 \cdot 3/2C_4H_4S$* and *Cd(*dl*-pn)Ni(CN)$_4 \cdot 3/2C_6H_6$*: These clathrates were prepared by procedures similar to the above one using a 1:1 thiophene–xylene mixture for the thiophene clathrate and a 1:2 benzene–xylene mixture for the benzene clathrate. They were obtained as coagulated polycrystals.

*Cd(*l*-pn)Ni(CN)$_4 \cdot 3/2C_4H_5N$*: *l*-Propylenediamine (*l*-pn) was obtained from racemic propylenediamine.[2] $[Cd(l\text{-}pn)_3][Ni(CN)_4]$ and $Cd(l\text{-}pn)Ni(CN)_4 \cdot 3/2C_4H_5N$ were prepared by a method similar to that used for the *dl*-pn compounds. Since $[Cd(l\text{-}pn)_3][Ni(CN)_4]$ is less soluble in water than the *dl*-pn complex, an aqueous solution containing 0.1 g of the *l*-pn complex in 50 cm^3 of water was used for the preparation of the clathrate.

*Cd(*dl*-pn)Cd(CN)$_4 \cdot 3/2C_6H_6$* and *Cd(*dl*-pn)Hg(CN)$_4 \cdot 3/2C_6H_6$*: To 25 cm^3 of a 0.2 M (1 M=1 mol dm^{-3}) $CdCl_2$ aqueous solution in a 300-cm^3 stoppered conical flask, 150 mmol of *dl*-pn and 25 cm^3 of 0.2 M $K_2[Cd(CN)_4]$ or $K_2[Hg(CN)_4]$ were added successively. After the pH had been adjusted to 8.0 by adding 6 M HCl drop by drop, the solution was covered with a benzene–xylene (1:1) mixture. After the flask had been left in a refrigerator for a week, colorless crystals of the clathrate were formed on the interface and at the bottom of the aqueous solution.

Powder X-Ray Diffraction. X-Ray diffraction patterns of powdered specimens were recorded on a JEOL DX diffractometer using Ni-filtered Cu $K\alpha$ radiation.

Structure Determination

Single crystals of $Cd(l\text{-}pn)Ni(CN)_4 \cdot 3/2C_4H_5N$ (**1**) and $Cd(dl\text{-}pn)Ni(CN)_4 \cdot 3/2C_4H_5N$ (**2**) were used for X-ray diffraction experiments to determine the crystal struc-

tures.

Data Collection. Each of the crystals of **1** and **2** cut into the cube with dimensions of *ca.* 0.3×0.3×0.3 mm was coated with epoxy resin in order to prevent the decomposition of the crystal under ambient conditions. Preliminary Weissenberg photographs showed 4/mmm symmetries for both **1** and **2** crystals; the lack of any systematic absences of reflections indicated that the possible space groups are P4/mmm, P422, P4mm, P$\bar{4}$2m, and P$\bar{4}$m2. As will be mentioned later, the P422 and P4/mmm space groups were adopted for **1** and **2** respectively. The precise determination of lattice parameters and the collection of the intensity data were carried out on a Philips automated four-circle diffractometer[3] for **1** and on a Rigaku automated four-circle diffractometer[4] for **2**. In both cases, the reflections with $2\theta \leq 60°$ were collected using Mo $K\alpha$ radiation. The intensities of three standard reflections recorded every fifty measurements showed no significant variations. The densities were measured by the flotation method using bromoform–xylene mixture. The crystal data are:

$C_{13}H_{17.5}N_{7.5}CdNi$,	F.W.=449.94, Tetragonal	
	1 (*l*-pn host)	**2** (*dl*-pn host)
Space group	P422	P4/mmm
$a(=b)$/Å	7.575±0.002	7.570±0.002
c/Å	7.742±0.002	7.741±0.004
Unit cell volume/Å^3	444.2±0.3	443.6±0.4
Z	1	1
D_m/g cm^{-3}	1.67	1.68
D_x/g cm^{-3}	1.68	1.68
Number of reflections used for refinement ($\|F_o\|>3\sigma(\|F_o\|)$)	414	425

Solution and Refinement of the Structures. The structures were solved by the heavy-atom method. The refinements were carried out by successive Fourier and difference Fourier syntheses and by the block-diagonal least-squares method on a HITAC 8800/8700 computer at the Computer Center of this University, using the programs in UNICS[5] and their local versions. The atomic scattering factors used were those in the International Tables.[6]

There is no significant difference in the unit cell dimensions between **1** and **2**. The Patterson maps of **1** and **2** showed that, in both structures, Cd and Ni atoms lie at 0,0,0 and 1/2,1/2,0, and that the cyanide group bridges these atoms. The two-dimensional extension of the metal cyanide sheet on the {001} plane is similar to those observed for Hofmann type and Hofmann-en type clathrates.[1] Therefore, the pn ligands were assumed to bridge two Cd atoms in adjacent metal cyanide sheets along the fourfold axis of crystal, as the en ligand does in Hofmann-en type clathrate.[7,8]

Because the *l*-pn molecule has no symmetry, the non-centrosymmetric space group P422 was assumed for **1**. As the *l*-pn molecule is located about a special position, 0,0,1/2 with the point symmetry 42, it should have an orientational disorder. The centrosymmetric space group P4/mmm was assumed for **2**. The other three space groups, P4mm, P$\bar{4}$2m, and P$\bar{4}$m2, giving the arrangement of pn-methyl groups with an unacceptable overlapping or the arrangements of pn and pyrrole molecules about the unacceptable $\bar{4}$ axis, were discarded.

For both **1** and **2**, the Fourier syntheses phased by the Cd and Ni atoms gave the positions of the C and N atoms of the cyanide group and the pyrrole molecule. The pyrrole molecule was found in the cavity between the metal cyanide sheets; like the pyrrole molecule in Hofmann-en type Cd(en)Ni(CN)$_4$·2C$_4$H$_5$N,[8] the molecular dipole axis is arranged with an equal probability parallel and antiparallel to the c axis of crystal.

At this stage, the atomic parameters for the Cd, Ni, and C and N atoms of the cyanide and pyrrole were refined by the block-diagonal least-squares procedure to minimize $\sum w(||F_o|-|F_c||)^2$; $w=1$ for $|F_o|<F_{max}$ and $w=(F_{max}/|F_o|)^2$ for $|F_o|\geq F_{max}$, $F_{max}=35.0$ for **1**, and 50.0 for **2**. After several cycles of the calculations by applying the anisotropic temperature factors to Cd and Ni atoms, and the isotropic ones to C and N atoms, the conventional reliability index, $R_1=\sum w(||F_o|-|F_c||)/\sum|F_o|$, became 0.088 for **1** and 0.128 for **2**. At this point a trial was made to find the positional parameters for the pn molecule, though the electron density due to the pn molecule was predicted to be very low because of the great extent of orientational disorder. The electron densities appearing on the difference Fourier map of **2** were so vague that we could hardly locate any atoms. In the case of **1** we could barely find two sets of the atomic coordinates forcibly assigned to the C and N atoms of the *l*-pn molecule. However, the positional and thermal parameters of a few atoms of *l*-pn obtained after several cycles of the least-squares calculations gave too large estimated standard deviations. Therefore, we ceased to refine the structures of **1** and **2** at this stage.[9] The atomic parameters determined for **1** are listed in Table 1, while an illustrative sketch of the structure is shown in Fig. 1.

Table 1. The atomic parameters of Cd(*l*-pn)Ni(CN)$_4$·3/2C$_4$H$_5$N and their estimated standard deviations (in parentheses)[a]

Atom[b]	x/a	y/b	z/c	B_{iso}
Cd	000	000	000	—[c]
Ni	500	500	000	—[c]
C(CN)	328 (1)	328	000	3.3 (2)
N(CN)	219 (2)	219	000	4.4 (2)
N(prl)[d]	500	000	335 (5)	5.4 (6)
C(prl)[d]	500	169 (5)	422 (4)	6.8 (6)
C(prl)[d]	500	087 (5)	598 (4)	6.7 (6)

a) The positional parameters have been multiplied by 10^3. b) The parameters of the C and N atoms of the *l*-pn molecule have not been determined accurately. c) The anisotropic thermal parameters have been obtained for Cd ($B_{11}=0.0063(1)=B_{22}$, $B_{33}=0.0144(2)$, and $B_{12}=B_{13}=B_{23}=0$) and Ni ($B_{11}=0.0060(2)=B_{22}$, $B_{33}=0.0179(4)$, and $B_{12}=B_{13}=B_{23}=0$) in the form of $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\}$. d) Each of the occupancy factors of the N and C atoms of the pyrrole molecule is 0.375.

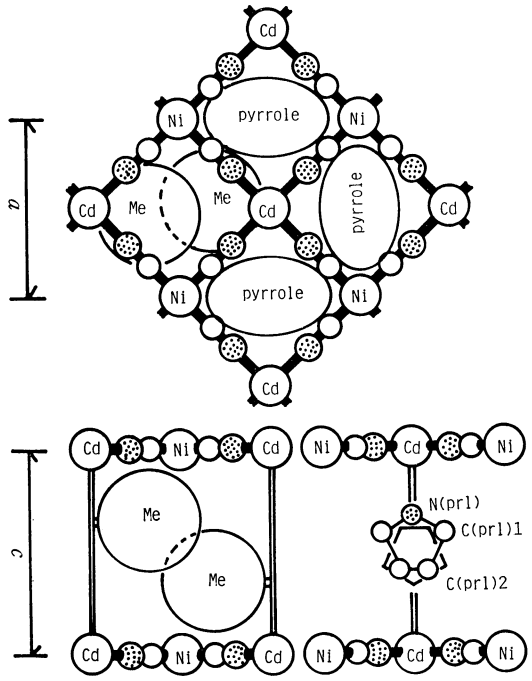

Fig. 1. Illustrative views of the structure of Cd(*l*-pn)-$Ni(CN)_4 \cdot 3/2C_4H_5N$.
Open circle: carbon atom; dotted cricle: nitrogen atom; doubled line: –N–C–C–N– skeleton of *l*-pn.

Table 2. The hormann-pn and pn-Td type clathrates and their analytical results [found/(calcd)]

Hofmann-pn type:	C	H	N	Cd	Ni
Cd(*dl*-pn)$Ni(CN)_4 \cdot 3/2C_4H_5N$	34.2 (34.7)	3.94 (3.92)	23.3 (23.4)	25.2 (25.0)	12.7 (13.1)
Cd(*l*-pn)$Ni(CN)_4 \cdot 3/2C_4H_5N$	34.2 (34.7)	4.03 (3.92)	23.2 (23.4)	25.2 (25.0)	13.2 (13.1)
Cd(*dl*-pn)$Ni(CN)_4 \cdot 3/2C_4H_4S$	32.9 (32.8)	3.77 (3.39)	18.1 (18.0)	23.7 (23.6)	12.3 (12.3)
Cd(*dl*-pn)$Ni(CN)_4 \cdot 3/2C_6H_6$	41.0 (41.2)	4.18 (4.11)	18.2 (18.0)	24.5 (24.1)	12.4 (12.6)
pn-Td type:					
Cd(*dl*-pn)$Cd(CN)_4 \cdot 3/2C_6H_6$	37.5 (36.9)	3.81 (3.68)	16.5 (16.1)	43.1 (43.2)	
Cd(*dl*-pn)$Hg(CN)_4 \cdot 3/2C_6H_6$	31.7 (31.6)	3.29 (3.15)	14.0 (13.8)	18.1 (18.5)	

Results and Discussion

The clathrates prepared are listed in Table 2 along with their analytical results. In the earlier stage of the investigations of the Hofmann type clathrates, some clathrates were reported to have non-stoichiometric or substoichiometric compositions with regard to the number of guest molecules for a formula unit of the metal complex host, $M(NH_3)_2Ni(CN)_4$ (M=Ni, Cu, Zn, or Cd);[10–12] these observations were due to inadequate conditions in the preparation or to careless treatment of the prepared specimens.[13] It is well known that some hydrate clathrates and *p*-hydroxybenzene clathrates are non-stoichiometric.[14] However, in the novel clathrates the number of guest molecules can be counted as 3/2 for a formula unit of the metal complex host, within the limits of experimental error. As has been verified with regard to the crystal structures of **1** and **2**, the novel $Cd(pn)Ni(CN)_4$ host has linkages of the ambident CN and pn ligands substantially similar to those of the Hofmann-en type host; the structure of the $Cd(pn)Cd(or\ Hg)(CN)_4$ host is also concluded to be similar to that of the en-Td type, as will be discussed later. By analogy with the naming of the Hofmann-en type and the en-Td type, we can name the novel clathrates, $Cd(pn)Ni(CN)_4 \cdot 3/2G$ and $Cd(pn)Cd(or\ Hg)(CN)_4 \cdot 3/2G$, the "Hofmann-pn type" and the "pn-Td type" respectively.

Hofmann-pn Type Clathrates. The stoichiometry of the novel clathrates suggests that one of the four cavities is not occupied by a guest molecule. Since, in general, the crystal structure cannot be stable with vacant cavities, it is also suggested that the cavity unoccupied by a guest molecule should be occupied by another species instead of the guest. The crystal structures of **1** and **2** can be interpreted most plausibly in terms of the random distributions of the cavity occupied by a pyrrole molecule and that occupied by a pair of pn-methyl groups in a 3: 1 ratio throughout the crystal. As Fig. 1 shows, the square-planar metal cyanide sheet has a structure similar to those in the Hofmann type and the Hofmann-en type, with interatomic distances of Ni–C-(CN)=1.840(8) Å, C(CN)–N(CN)=1.17(2) Å, and Cd–N(CN)=2.35(2) Å in **1**. One of the four cavities formed between the metal cyanide sheets is occupied by a pair of methyl groups protruding from the confronting pair of pn molecules; each of the pn molecules bridges two Cd atoms in adjacent metal cyanide sheets. The other three cavities are occupied by pyrrole molecules oriented randomly upward and downward with regard to the molecular dipole axis. The apparent tetragonal symmetry of the crystal is derived from a random distribution of both kinds of cavities and from random orientations of the pn molecules.

The cause of disorder in this structure can be understood from the calculation of the void space of the cavity occupied by the methyl groups. According to Immirzi and Perini,[15] the volume of an organic molecule packed in a crystal can be approximated by a simple additivity rule within an error of *ca.* 3%. On the assumption that the pyrrole molecules have close packing in the Hofmann-en type pyrrole clathrate, $Cd(en)Ni(CN)_4 \cdot 2C_4H_5N$,[8] the volume of the Hofmann-en type host, $V_{en\text{-}host}$, is calculated to be 267.4 Å^3 by subtracting that of two pyrrole molecules, 2×95.1 Å^3, from that of the unit cell, 457.6 Å^3. By adding the volume of a methyl group, 31.7 Å^3, and that of 1.5 times pyrrole molecules, 1.5×95.1 Å^3, to, and subtracting that of a hydrogen, V_H 6.8 Å^3, from, $V_{en\text{-}host}$, we obtain the calculated unit cell volume of the Hofmann-pn type *l*-pn host clathrate **1** as 434.9 Å^3, nearly equal to the observed value, V_{cell} 444.2 Å^3. Since the approximation can be seen to be valid, we may calculate the volume of the cavity, V_{cav}, in **1** thus:

$$V_{cav} = [V_{cell} - (V_{en\text{-}host} - V_H)] \times 0.5 = 91.9\ \text{Å}^3$$

a value nearly equal to that of a pyrrole molecule. However, the volume of two methyl groups, 63.4 Å^3, is smaller by *ca.* 30 Å^3 than V_{cav}, the occupation ratio

TABLE 3. POWDER X-RAY DIFFRACTION DATA OF Cd(*dl*-pn)Cd(CN)$_4$·3/2C$_6$H$_6$ AND Cd(*dl*-pn)Hg(CN)$_4$·3/2C$_6$H$_6$

Ni-filtered Cu $K\alpha$ (λ=1.5418 Å), GM counter

Cd(*dl*-pn)Cd(CN)$_4$·3/2C$_6$H$_6$ Tetragonal a= 8.26 Å, b=15.31 Å					Cd(*dl*-pn)Hg(CN)$_4$·3/2C$_6$H$_6$ Tetragonal a= 8.23 Å, b=15.23 Å				
2θ	I	d_{obsd}/Å	hkl	d_{calcd}/Å	2θ	I	d_{obsd}/Å	hkl	d_{calcd}/Å
10.7_3	21	8.25	100	8.26	10.8_0	34	8.19	100	8.23
11.5_3	5	7.68	002	7.65_5					
12.1_7	69	7.27	101	7.27	12.2_5	34	7.23	101	7.24
					15.1_9	4	5.83	110	5.82
15.7_8	56	5.62	102	5.62	15.8_5	54	5.59	102	5.59
19.1_0	100	4.65	112	4.64	19.2_0	100	4.62	112	4.62
20.4_5	11	4.34	103	4.34	20.5_4	4	4.32	103	4.32
21.5_1	94	4.13	200	4.13	21.6_0	68	4.11	200	4.11_5
23.2_2	14	3.83	113	3.84_3	23.3_0	11	3.82	113	3.82_6
			004	3.82_7				004	3.80_8
24.5_3	4	3.63	202	3.63_5					
24.7_8	6	3.59	211	3.59_1	24.8_1	13	3.59	211	3.57_8
25.5_6	4	3.49	104	3.47_3	25.7_3	5	3.46	104	3.45_6
26.7_8	47	3.33	212	3.32_7	26.8_9	45	3.32	212	3.31_4
27.7_6	17	3.21	203	3.21_0	27.8_9	11	3.20	203	3.19_7
29.8_4	32	2.99	213	2.99_2	29.9_4	11	2.98	213	2.98_0
30.5_7	11	2.92	220	2.92_0	30.6_5	5	2.92	220	2.91_0
31.8_5	32	2.88	221	2.86_9	31.9_9	24	2.86	221	2.85_8
			105	2.87_1				105	2.85_7
32.5_0	19	2.76	300	2.75_3	32.6_3	21	2.74	300	2.74_3
32.9_8	14	2.72	301	2.71_0	33.1_7	11	2.70	301	2.70_0
			115	2.71_2				115	2.69_9
33.6_9	27	2.66	214	2.65_8	33.8_4	31	2.65	214	2.64_6
					34.4_2	4	2.61	310	2.60_3
34.5_7	6	2.59_5	302	2.59_1	34.7_8	6	2.57_9	302	2.58_1
36.3_1	39	2.47_4	312	2.47_2	36.4_8	25	2.46_3	312	2.46_3
					37.0_0	5	2.43_0	106	2.42_6
38.1_0	11	2.36_2	215	2.35_7	38.3_2	9	2.34_9	215	2.34_7
38.4_3	11	2.34_2	116	2.33_8	38.6_3	9	2.33_1	116	2.32_7
38.7_2	11	2.32_5	313	2.32_5	39.9_2	17	2.31_4	313	2.31_6
			224	2.32_2				224	2.31_2
39.3_0	4	2.29_2	320	2.29_1					
39.7_5	7	2.26_8	321	2.26_6					
					40.4_9	9	2.22_8	304	2.22_6

of the cavity being 69%. The void space may give much freedom of motion to the pn molecule.

pn-Td Type Clathrates. The powder X-ray diffraction patterns of pn-Td type benzene clathrates Cd(*dl*-pn)Cd(CN)$_4$·3/2C$_6$H$_6$ and Cd(*dl*-pn)Hg(CN)$_4$·3/2C$_6$H$_6$ were assigned to the tetragonal systems, as Table 3 shows. The unit cell dimensions of these clathrates are very close to those of the corresponding en-Td type benzene clathrates.[16] Since their diffraction patterns showed a close resemblance to those of the corresponding en-Td type clathrates, the substantial structure of the pn-Td type host can be thought of as being similar to that of the en-Td type host. One of the four cavities must be occupied at random by a pair of pn-methyl groups, too. The calculated volume (117 Å^3) of a cavity in the pn-Td type host gave a *ca.* 46% void space in the cavity occupied by the methyl groups. However, the three-dimensional framework, built of the tetrahedral Cd(CN)$_4$ or Hg(CN)$_4$ moieties and the ambident pn ligands, which are linked together at the six-coordinate Cd atoms, appears to be tight enough to keep the tetragonal crystal lattice, even with the considerably large void space in the cavity occupied by the methyl groups.

Conclusion. These observations suggest that the number of cavities available for the guest molecules can be regulated by introducing bulky substituents into the ambident diamine ligand building up the host structures of these types of clathrates. 2,3-Diaminobutane (bn) has two methyl groups. In the clathrate with the Cd(bn)M(CN)$_4$·*n*G formula, *n* can be expected to be one if such a clathrate is successfully prepared using bn in place of pn. The investigations are now in progress.

References

1) T. Iwamoto, M. Kiyoki, Y. Ohtsu, and Y. Takeshige-Kato, *Bull. Chem. Soc. Jpn.*, **51**, 488 (1978).
2) F. P. Dwyer, F. L. Garvan, and A. Schulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).
3) The diffractometer was used by the courtesy of Professor Yoichi Iitaka of the Faculty of Pharmaceutical Science of this University.
4) The diffractometer was used by the courtesy of Professor Yukiyoshi Sasaki of the Department of Chemistry, Faculty of Science of this University.
5) "The Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).
6) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.
7) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, **6**, 59 (1972).
8) T. Iwamoto and M. Kiyoki, *Bull. Chem. Soc. Jpn.*, **48**, 2412 (1975).
9) The table of the structure factors for **1** is kept as Document No. 8026 at the Chemical Society of Japan.
10) K. A. Hofmann and H. Arnoldi, *Chem. Ber.*, **39**, 339 (1906).
11) R. S. Drago, J. T. Kwon, and R. D. Archer, *J. Am. Chem. Soc.*, **80**, 2667 (1958).
12) R. Baur and G. Schwarzenbach, *Helv. Chim. Acta*, **43**, 842 (1960).
13) T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki, and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **40**, 1174 (1967).
14) "Non-stoichiometric Compounds," ed by L. Mandelcorn, Academic Press, New York and London (1964).
15) A. Immirzi and B. Perini, *Acta Crystallogr., Sect. A*, **33**, 216 (1977).
16) T. Iwamoto and D. F. Shriver, *Inorg. Chem.*, **11**, 2570 (1972); T. Iwamoto, *Chem. Lett.*, **1973**, 723.