The Analogs of Hofmann Type Clathrate Formed between Diammine- or Diaminemetal(II) Tetracyanometallate(II) Host and Aromatic Guest Molecule

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A novel series of clathrates Cd(tn)M′(CN)$_4$·2G (M′=Cd or Hg; G=C_4H_4S, C_4H_5N, C_6H_6, or $C_6H_5NH_2$) were prepared as an analogous series of Hofmann type clathrate. Including the novel series, Hofmann type and the analogous clathrates with a general formulation M(diam)M′(CN)$_4$·2G were classified into five groups according to the combination of the host constituents and the resulting host framework structures as follows: Hofmann type M(NH$_3$)$_2$M′(CN)$_4$·2G with square-planar M′(CN)$_4$, Hofmann-en type Cd(en)NM′(CN)$_4$·2G with ambident en and square-planar M′(CN)$_4$, Hofmann-Td type Cd(NH$_3$)$_2$M′(CN)$_4$·2G with tetrahedral M′(CN)$_4$, en-Td type Cd(en)M′(CN)$_4$·2G with ambident en and tetrahedral M′(CN)$_4$, and tn-Td type Cd(tn)M′(CN)$_4$·2G with ambident tn and tetrahedral M′(CN)$_4$. Their structural features were discussed based on the flexibility of the framework whether it can enclathrate aniline as the largest guest or not.

Among the clathrates formed between metal complex host and aromatic guest molecules, a family can be grouped with a general formulation M(diam)M′(CN)$_4$·2G where M refers to a bivalent metal ion, diam to diammine or diamine ligand, M′(CN)$_4$ to a square-planar or tetrahedral tetracyanometallate(II), and G to an aromatic guest species. This family of the clathrates originates from Hofmann's benzene clathrate Ni(NH$_3$)$_2$Ni(CN)$_4$·2C_6H_6 first prepared in 1897.[1)] The naming "Hofmann type clathrate" was proposed to the clathrates with a general formulation M(NH$_3$)$_2$M′(CN)$_4$·2G (M=Mn, Fe, Co, Ni, Cu, Zn, or Cd; M′=Ni, Pd, or Pt; G=C_4H_4S, C_4H_5N, C_6H_6, $C_6H_5NH_2$, or $C_{12}H_{10}$),[2–6)] in which the host is isostructural to that of the original Hofmann's clathrate.[7–10)] Several analogous clathrates have been prepared by replacing (NH$_3$)$_2$ in Hofmann type by an ambident en ligand,[11–13)] or by replacing the square-planar M′(CN)$_4$ by tetrahedral M′(CN)$_4$ (M′=Cd or Hg).[14–16)] In this paper, a novel series of Cd(tn)M′(CN)$_4$·2G clathrates will be reported for M′=Cd or Hg and G=C_4H_4S, C_4H_5N, C_6H_6, or $C_6H_5NH_2$. Some novel members of the known series will also be described. Their structural features will be discussed on the basis of the flexibility of host framework whether the host can enclathrate aniline as the largest guest or not. According to these features the family of Hofmann type and the analogous clathrates including the present novel one can be classified into five groups.

Experimental

Preparation. *Cd(tn) M′(CN)$_4$·2G (M′=Cd or Hg; G=C_4H_4S, C_4H_5N, C_6H_6, or $C_6H_5NH_2$)*: Fifteen millimoles of tn (trimethylenediamine) was added to an aqueous solution of CdCl$_2$ (5 mmol in 50 cm^3). A white precipitate once formed did not completely dissolve away by adding the excessive amounts of tn. After the small amounts of undissolved precipitate were filtered off, K$_2$[M′(CN)$_4$] (5 mmol in 50 cm^3 aq solution) was added to the filtrate in a conical flask. The aqueous phase was kept in contact with the organic phase of the relevant guest species mixed with xylene (1: 1) in the flask covered by a stopper for a few weeks in a refrigerator. Colorless crystals grown up on the interface between the aqueous and the organic phases were picked out, washed successively with small amounts of water and ethanol, and dried on a sintered clay plate in a desiccator charged with silica gel desiccator and saturated vapor of neat liquid of the guest species.

Cd(en) M′(CN)$_4$·2G (M′=Cd or Hg; G=C_4H_4S or C_4H_5N): These clathrates were prepared by the methods analogous to those for Cd(en)Ni(CN)$_4$·2G[13)] and Cd(en)M′(CN)$_4$·2C_6H_6[14)] using the relevant combination of the potassium tetracyanometallate(II) and the guest species diluted with xylene.

Cd(NH$_3$)$_2$M′(CN)$_4$·2$C_6H_5NH_2$ (M′=Cd or Hg): After aniline–xylene mixture (1:1) was shaken with an aqueous solution (*ca.* 100 cm^3) containing 5 mmol each of CdCl$_2$ and K$_2$[M′(CN)$_4$], and 15 cm^3 of concd ammoniacal water at 0 °C, the whole mixture was kept standing in a refrigerator for a few weeks. Colorless crystals were grown up on the interface between the organic and the aqueous phases separated spontaneously. The crystals were treated with the procedure similar to that for Cd(tn)M′(CN)$_4$.2$C_6H_5NH_2$.

Cd(NH$_3$)$_2$Hg(CN)$_4$·2C_6H_6:[17)] A benzene–xylene (1:1) mixture was placed over an aqueous solution (*ca.* 100 cm^3)containing 5 mmol each of CdCl$_2$ and K$_2$[Hg(CN)$_4$] and 15 cm^3 of concd ammoniacal water in a conical flask. The flask covered with a stopper was kept standing in a refrigerator for a few weeks. Colorless crystals grown up on the interface between the aqueous and the organic phases were treated similarly to the above-mentioned method.

Measurements. The powder X-ray diffraction patterns were recorded on a JEOL diffractometer with Ni-filtered Cu*K*α radiation and a GM counter. Preliminary single crystal diffraction data were collected with Weissenberg photographs. The infrared spectra were recorded on a JASCO DS403G spectrometer in the 4000—400 cm^{-1} region for the Nujol and the hexachlorobutadiene mulls.

Results and Discussion

Formation and Classification of the Clathrates. The analytical results of the clathrates prepared in the present study are listed in Table 1. It was rather difficult to obtain stoichiometric results for the thiophene clathrates because of the high dissociation pressure and the small dimensions of thiophene molecule. All the clathrates presently prepared as well as those previously reported are generally not stable enough to retain guest species stoichiometrically in an open atmosphere at

TABLE 1. THE ANALYTICAL RESULTS: FOUND (CALCD) IN %

	C	H	N	Cd	Hg
$Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$	35.4(35.0)	3.6(3.6)	19.9(20.4)	40.8(41.0)	
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5NH_2$	30.5(30.2)	2.9(3.1)	17.3(17.6)	18.1(17.7)	32.0(31.5)
$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$	30.2(31.6)	3.1(3.0)	14.2(13.8)	18.4(18.5)	33.4(33.0)
$Cd(C_2H_8N_2)Cd(CN)_4 \cdot 2C_4H_4S$	28.3(30.2)	2.5(2.9)	15.7(15.1)	41.5(40.3)	
$Cd(C_2H_8N_2)Cd(CN)_4 \cdot 2C_4H_5N$	34.7(34.1)	4.0(3.5)	21.0(21.4)	43.5(43.0)	
$Cd(C_2H_8N_2)Hg(CN)_4 \cdot 2C_4H_4S$	25.1(25.7)	2.2(2.5)	13.4(12.8)	17.5(17.2)	30.6(30.7)
$Cd(C_2H_8N_2)Hg(CN)_4 \cdot 2C_4H_5N$	27.2(27.5)	2.7(3.0)	18.6(18.3)	18.5(18.4)	33.4(32.8)
$Cd(C_3H_{10}N_2)Cd(CN)_4 \cdot 2C_6H_5NH_2$	38.8(38.7)	3.9(4.1)	18.9(19.1)	38.2(38.1)	
$Cd(C_3H_{10}N_2)Cd(CN)_4 \cdot 2C_6H_6$	40.4(40.8)	4.0(4.0)	14.9(15.0)	41.2(40.9)	
$Cd(C_3H_{10}N_2)Cd(CN)_4 \cdot 2C_4H_4S$	29.6(31.5)	3.2(3.2)	16.0(14.7)	41.2(39.4)	
$Cd(C_3H_{10}N_2)Hg(CN)_4 \cdot 2C_6H_5NH_2$	33.9(33.9)	3.6(3.6)	16.7(16.6)	16.6(16.6)	29.6(29.6)
$Cd(C_3H_{10}N_2)Hg(CN)_4 \cdot 2C_6H_6$	34.8(35.3)	3.4(3.4)	13.3(13.0)	17.7(17.4)	30.7(31.0)
$Cd(C_3H_{10}N_2)Hg(CN)_4 \cdot 2C_4H_4S$	28.2(27.3)	3.0(2.8)	13.4(12.7)	17.5(17.0)	30.0(30.4)
$Cd(C_3H_{10}N_2)Hg(CN)_4 \cdot 2C_4H_5N$	28.6(28.8)	2.9(3.2)	17.6(17.9)	18.5(18.0)	34.2(32.1)

room temperature. There is a tendency that the guest species with lower boiling point of its neat liquid is more easily released from the clathrate. Even in the case of Hofmann type biphenyl clathrate, the decomposition occurs gradually.[6] Therefore, analytical results were often poor for finely crystallized samples owing to the partial decomposition of the products. However, it is again difficult to evacuate the guest completely from the host for those clathrates with ambident diamine ligands and tetrahedral $M'(CN)_4$ in the host framework. For example, it took longer than 24 h to evacuate benzene completely from $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$ under a reduced pressure at 80 °C.

The formation of clathrate is feasibly diagnosed on the infrared spectrum of the product. The characteristic bands are those of the out-of-plane CH bending modes for the aromatic guest, and additionally those of the NH or NH_2 vibration modes for pyrrole or aniline guest. Some of the typical results are given in Table 2.

Those clathrates which so far have been prepared with the general formulation $M(diam)M'(CN)_4 \cdot 2G$ are seen in Table 3 with the classification and the tentative namings. The M metal was limited to cadmium(II) for those clathrates other than Hofmann type. Zinc(II) did not give any stable clathrates, and mercury(II) precipitates its cyanide or diaminedicyanomercury(II) complexes under the preparation procedures described in Experimental section. The bivalent metal cations of Mn, Fe, Co, Ni, and Cu which give the host complex of Hofmann type[5] never gave the clathrates with the diamine ligands presumably because of the high stabilities of their en or tn chelated species in solution.

The classification is defined on the combination of host constituents diam and $M'(CN)_4$, the geometrical features of which rule the size and shape of the cavities for guest molecule. The host framework with square-planar $M'(CN)_4$ gives a tetragonal[10,12] or rhombic[18] rectangular box to a guest molecule. There are two

TABLE 2. THE CHARACTERISTIC IR BANDS OF THE GUESTS IN SEVERAL HOST FRAMEWORKS (in cm^{-1})

Benzene in		Aniline in		Thiophene in		Pyrrole in	
I[a]	III[c]	I	III	II[b]	III	II	III
3076 w	3077 mw	3450 w	3461 m	3138 vw		3470 s	3460 s
3056 w	3057 w	1620 s	1617 s	3091 w	3092 vw	3160 m	3153 mw
3024 w	3024 mw	1603 s	1602 s	1495 mw	1495 m	1532 m	1532 mw
1980 vw		1501 s	1498 s	1253 ms	1254 m	1455 w	1442 w
1966 w	1970 wbr						
1955 vw		1278 m	1280 ms	1081 s	1084 ms	1139 w	1122 m
1842 w 1823 vw	1828 wbr	1176 m	1177 ms	1032 w	1031 w	1087 s	
		1027 w	1028 m	831 ms	833 m		1077 s
1480 s	1478 s						
		997 w	997 mw	725 vs	738 vs	1047 s	1047 ms
1035 m	1036 ms			713 s	728 s		
		883 m	882 mw			1014 s	1014 s
701 vs	697 s				697 m		
688 vs	687 vs	761 s	766 vs			867 w	867 vw
676 s	677 msh			454 w	467 w		
						741 vs	744 vs
						725 msh	726 msh
						694 wsh	698 wsh

a) $I=Cd(NH_3)_2Hg(CN)_4$. b) $II=Cd(en)Hg(CN)_4$. c) $III=Cd(tn)Hg(CN)_4$.

TABLE 3. HOFMANN TYPE AND THE ANALOGOUS CLATHRATES: $M(diam)M'(CN)_4 \cdot 2G$

Naming	M	diam	M′	G
Hofman	a)	$(NH_3)_2$	Ni, Pd, Pt	C_4H_5N, C_4H_4S, C_6H_6, $C_6H_5NH_2$, $C_{12}H_{10}$
Hofmann-en	Cd	en[b)]	Ni, Pd	C_4H_5N, C_4H_4S, C_6H_6
Hofmann-Td	Cd	$(NH_3)_2$	Cd, Hg	C_6H_6, $C_6H_5NH_2$
en-Td	Cd	en	Cd, Hg	C_4H_5N, C_4H_4S, C_6H_6
tn-Td	Cd	tn[c)]	Cd, Hg	C_4H_5N, C_4H_4S, C_6H_6, $C_6H_5NH_2$

a) M=Mn, Fe, Co, Ni, Cu, Zn, Cd. b) en=ethylenediamine: $C_2H_8N_2$. c) tn=trimethylenediamine: $C_3H_{10}N_2$.

kinds of cavities in the host framework with tetrahedral $M'(CN)_4$. One is similar to the rectangular box in the square-planar framework, and the other is a biprismatic box as has been demonstrated for $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$[15)] and $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$.[16)] When diam is $(NH_3)_2$ there is no bridge between two six-coordinate M metals. On the other hand, ambident en or tn bridges two Cd atoms to make the host framework less flexible.

Structural Features of the Classified Clathrates. The host of Hofmann type $M(NH_3)_2M'(CN)_4 \cdot 2G$ is built of two-dimensional sheets of square-planar $M(NC)_4$ and $M'(CN)_4$ arrays in which the ambident CN ligand bridges adjacent M and M′ atoms; the two NH_3 ligands coordinate to an M metal up and down from the sheet.[6-10)] Among the stacked sheets guest molecules are enclathrated. The larger the dimensions of guest are, the longer becomes the distance between the sheets.[5)] The observed distance ranges from 7.97 Å for a pyrrole clathrate to 9.33 Å for an aniline clathrate. An exceptionally long distance 12.65 Å has been observed for a biphenyl clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_{12}H_{10}$.[6)]

Hofmann-en type $Cd(en)M'(CN)_4 \cdot 2G$ (M′=Ni or Pd) is obtained by replacing two NH_3 ligands of Hofmann type structure between the adjacent square-planar sheets by an ambident en ligand bridging two Cd atoms in the respective sheets. The resulting three-dimensional host framework gives a limit to the dimensions of guest molecule within the distance between the sheets. Therefore, aniline molecule can no longer be enclathrated in Hofmann-en type host. The longest distance between the sheets has been observed for a benzene clathrate $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ to be 8.06 Å,[12)] and the distance decreases to 7.86 Å in the pyrrole clathrate $Cd(en)Ni(CN)_4 \cdot 2C_4H_5N$.[18)]

Hofmann-Td and en-Td types are derived from Hofmann and Hofmann-en types by replacing the square-planar $M'(CN)_4$ by tetrahedral $M'(CN)_4$. In Hofmann-Td type host $Cd(NH_3)_2M'(CN)_4$ (M′=Cd or Hg), three-dimensional host framework is built of *catena*-tetra-*μ*-cyanometallate(II) bridging M′ and $Cd(NH_3)_2$. This structure resembles PdO structure when the square-planar Pd and tetrahedral O sites are occupied by $Cd(NH_3)_2$ and $M'(CN)_4$, respectively, and the PdO linkage is replaced by the Cd–NC–M′ linkage.[16)] In en-Td type, the six-coordinate Cd atoms are additionally bridged by an ambident en ligand instead of two protrusions of ammine ligands.[15)] This additional Cd–en–Cd bridge makes the en-Td host framework less flexible than Hofmann-Td host framework. The former cannot enclathrate aniline molecule but the latter can.

Among the powder diffraction patterns of the novel members of en-Td type clathrates, that of $Cd(en)Cd(CN)_4 \cdot 2C_4H_4S$ can be interpreted in terms of a tetragonal system as likely to those of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ and $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$.[14,15)] The unit cell dimensions a=8.16 Å and c=15.62 Å are shorter in a by 0.1 Å and longer in c by 0.1 Å than those of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ (a=8.26 Å and c=15.50 Å).[15)] Since the a dimension of the latter corresponds to the Cd–en–Cd bridge length in its host framework, the length decreases to 8.16 Å in the thiophene clathrate by assuming that the both framework structures are isostructural to each other. The decrement in a appears to be cancelled by the increment in c to keep the host framework tetragonal. Those diffraction patterns of $Cd(en)Cd(CN)_4 \cdot 2C_4H_5N$, $Cd(en)Hg(CN)_4 \cdot 2C_4H_4S$, and $Cd(en)Hg(CN)_4 \cdot 2C_4H_5N$ could not be assigned to any tetragonal system or those systems with higher symmetries. Monoclinic or triclinic distortion may occur in these host frameworks to hold the smaller guest molecules with optimal fitness.

TABLE 4. THE POWDER X-RAY DIFFRACTION OF $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$.

CuKα (λ=1.5418 Å), Ni-filtered, GM-Counter

$Cd(C_3H_{10}N_2)Hg(CN)_4 \cdot 2C_6H_6$
tetragonal a=8.67_4 and c=14.80_5 Å

$2\theta/°$	I	d_{obsd}Å[a)]	hkl	d_{calcd}Å
10.17	36	8.70	100	8.67_4
11.83	45	7.48	101	7.48_5
15.52	19	5.71	111	5.66_7
15.84	55	5.60	102	5.63_2
18.77	100	4.73	112	4.72_8
20.42	94	4.35	200	4.33_7
26.00	30	3.43	104	3.41_1
30.90	19	2.89	300	2.89_4
32.08	20	2.79	204	2.81_8
33.76	19	2.66	214	2.68_0
34.92	26	2.57	312	2.57_5

a) The eleven strong lines are listed.

When the ambident en in Cd–en–Cd bridge in en-Td type is replaced by an ambident tn, the novel host tn-Td type is derived. In tn-Td type, the powder diffraction pattern of $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$ was assigned to a tetragonal system with a=8.67 Å and c=14.81 Å as listed in Table 4. Assuming that the tn-Td benzene clathrate has the structure similar to that of the en-Td type $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ except that the en is replaced by the tn, the a dimension 8.67 Å corresponds to the Cd–tn–Cd bridge length. The 0.4 Å increment in *a* appears to be cancelled by the 0.7 Å decrement in *c* from those for $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ so that the volumes per a benzene molecule in the both structures are 278 and 284 Å^3, respectively.

Another fact to be noted is that tn-Td host can enclathrate aniline molecule which is rejected by en-Td host. The Cd–tn–Cd bridge length appears to be 8.80 Å in $Cd(tn)Cd(CN)_4 \cdot 2C_6H_5NH_2$ structure preliminarily refined using the single crystal diffraction data. The refinement has not been advanced from the present stage with $R=0.18$ because of disorders in the conformation of tn molecules and in the orientation of aniline molecules in the monoclinic unit cell with dimensions $a=11.86$ Å, $b=13.01$ Å, $c=15.14$ Å, and $\beta=89.01°$ ($Z=4$). However, the distance between two Cd atoms linked with a tn molecule can be read on the Fourier projection at the present stage.

Since Baur and Schwarzenbach examined to develop "Hofmann type clathrate" from Hofmann's $Ni(NH_3)_2$-$Ni(CN)_4 \cdot 2C_6H_6$ by replacing the octahedral Ni by Cu, Zn, and Cd,[19] the present authors and coworkers have developed several types of M(diam)M′(CN)$_4$·2G clathrates. The purpose of these investigations was to materialize an idea to design a host framework of metal complex with an appropriate combination of host constituents in order to enclathrate desired guest molecule. A successful example may be seen in the case of tn-Td type host enclathrating aniline molecule. However, tn-Td host appears not to have a capability to enclathrate styrene molecule.

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