

シアニ化カドミウム系による擬鉱物包接構造

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Mineralomimetic Inclusion Structures  
Built of Cadmium Cyanide Systems

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## Contents

1. Introductory Remarks -----	1
2. Cristobalite-like Cadmium Cyanide Host -----	3
2.1. Introduction: Structures of Cadmium Cyanide and Zinc Cyanide -----	
2.1.1. History -----	3
2.1.2. Preparation -----	5
2.1.3. Structural Analysis -----	6
2.1.4. Discussion -----	6
2.2. Inclusion Structures -----	
2.2.1. Preparation and properties -----	11
2.2.2. Structure Refinements -----	15
2.2.3. Refined Structure (1): $\text{CCl}_4 - \text{C}(\text{CH}_3)_4$ Series -----	28
2.2.4. Refined Structure (2): Others -----	33
2.2.5. Refined Structure (3): Mixed-metal Hosts -----	34
2.2.6. Discussion -----	36
3. Clay-like Layered Structures -----	
3.1. Fundamental Views of Clay Minerals -----	40
3.2. Preparation and Properties -----	41
3.2.1. $[\text{Cd}_3(\text{CN})_7\text{dmtnH}] \cdot \text{G}$ , group I -----	41
3.2.2. $[\text{Cd}_3(\text{CN})_8] \cdot [\text{Zonium} \cdot \text{G}]$ , group II -----	42
3.2.3. $[\text{Cd}_3(\text{CN})_6\text{L}(\text{H}_2)] \cdot [\text{S}(\text{CH}_3)_3]$ , group III -----	42
3.2.4. Properties -----	43
3.3. Structural Analyses -----	44
3.4. Refined Structures -----	54
3.4.1. Layer Structures -----	54
3.4.2. Orientation of the Guest Molecules -----	74
3.5. Discussion -----	74
4. Zeolite-like Framework Structures -----	
4.1. General Views -----	80
4.2. Preparation and Properties -----	80
4.3. Refined Structures -----	83
4.3.1. General Remarks -----	83
4.3.2. Type I Structures -----	102
4.3.3. Type II Structures -----	117
4.3.4. Type III Structures -----	118
4.3.5. Type IV Structures -----	120
4.3.6. Type V Structures -----	121
4.3.7. Type VI Structures -----	121
4.4. Classification of the structures -----	121
4.5. Discussion -----	122
Acknowledgement -----	145

## Chapetar 1.

### Introductory Remarks

## 1. INTRODUCTORY REMARKS

Prussian blue is probably the earliest recorded coordination compound in the history of chemistry [1]. Although Prussian blue is the typical cyano metal complex with a three-dimensional structure, the chemistry of inorganic polymeric coordination structures have been paid less attention in comparison with those complexes of Werner type and organometallic ones which have in general the structures of Avogadro molecule.

We have seen many of "inorganic polymeric coordination structures in minerals which are most fundamental inorganic compounds occurring in nature. This work aims to develop a new field of chemistry, "mineralomimetic chemistry," using cadmium cyanide and polycyanocadmate systems. The term "mineralomimetic chemistry" is proposed to designate a field of chemistry in which inorganic structures, never occurring in nature, are artificially designed and materialized to mimic the structures of natural minerals and to demonstrate properties similar to or different from natural minerals using the chemical components which never give stable minerals in nature. One of such chemical components is cadmium cyanide.

Among variety of the naturally occurring minerals silicate minerals including silicon dioxide itself comprise an important segment. Cadmium cyanide,  $\text{Cd}(\text{CN})_2$ , resembles  $\text{SiO}_2$  and  $\text{H}_2\text{O}$ , ice, in several features as follows: they all have the  $\text{AB}_2$  composition, A takes a tetrahedral center, the tetrahedral centers are bridged by B to form a three-dimensional framework, and, in particular, they all are capable to form an inclusion structure with other guest species. Besides the occlusion of alkali or alkaline-earth cations, polymeric  $\text{SiO}_2$  builds up three-dimensional framework structures with polygonal faces; the polyhedral cage accommodates a guest molecule to form a group of inclusion compounds called "clathrasils" like the naturally occurring mineral melanophlogite [2]. Another group of naturally-occurring inclusion compounds is the hydrate clathrates for which the structures and properties have been studied extensively [3].

Cadmium has a remarkable difference in the coordination behav-

ior from the silicon in silica and silicate minerals and the oxygen in ice. Cadmium can often take a six- and/or a five-coordination along with the tetrahedral four-coordination in a crystal structure. Hence, it is possible to build up multi-dimensional mineralomimetic structure of polycyanopolycadmiate systems containing both octahedral and tetrahedral cadmium cations. Our earlier work on the inclusion compounds of multi-dimensional cyanocadmiate hosts has also been reviewed [4].

In this work the author focuses on the mineralomimetic "inclusion" structures. The author has synthesized the mineralomimetic inclusion structures of (1) cristobalite-like three-dimensional framework of  $\text{Cd}(\text{CN})_2$  accommodating an organic guest in the cavity with the Td symmetry, (2) clay-like two-dimensionally extended layered structures of polycyanopolycadmiate accommodating the guest in the interlayer or intralayer space, and (3) zeolite-like three-dimensional anionic frameworks accommodating cationic and neutral guests in the cages surrounded by coordination polyhedra centered by octahedral and tetrahedral cadmium atoms with the catena- $\mu$ -linkage of cyanide groups. A number of single crystal structures have been solved by X-ray diffraction methods and their structural features have been summarized and discussed.

#### References

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4. T. Iwamoto, "Inclusion Compounds of Multi-dimensional Cyanometal Complex Hosts," in J. L. Atwood, J. E. D. Davies, and D. D. MacNicol edn., "Inclusion Compounds, Vol. 5," Oxford University Press, Oxford(1991), p. 177.

## Chapter 2

### Cristobalite-like Cadmium Cyanide Host

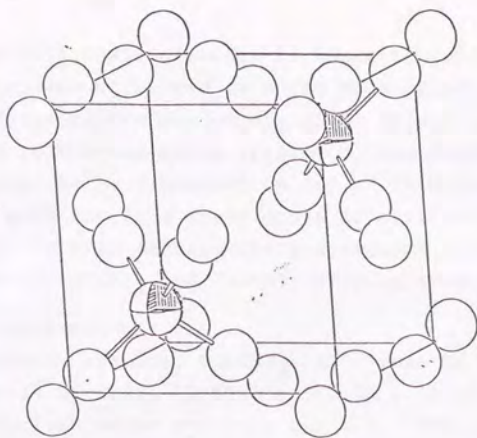
## 2. CRISTOBALITE-LIKE CADMIUM CYANIDE HOST

### 2.1. Introduction: Structures of Cadmium Cyanide and Zinc Cyanide

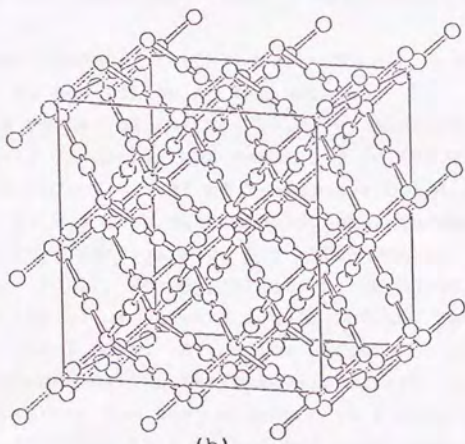
#### 2.1.1. History

Earlier works on the structures of cadmium cyanide [1] and the isomorphous zinc cyanide [2] were reported by Russian scientists, and cited in a well-known textbook [3]. The structures of the two cyanides were determined on the basis of the powder diffraction data. Cadmium cyanide has a double framework structure of the anticyprite-type as shown in Fig. 1: the Cd atom in place of the O in cuprite,  $\text{Cu}_2\text{O}$ , is on the tetrahedral center, the CN group in place of the Cu(I) bridging a pair of Cd atoms to form a three-dimensional framework. Each framework is built of the tetrahedral Cd atoms linked with the catena- $\mu$ -cyano ligands, the extension being topologically similar to that of diamond, or more closely related with those of H-cristobalite (a high-temperature phase of  $\text{SiO}_2$ ) and a cubic phase of ice Ic. The pair of the frameworks, however, have no interconnection. The Russian group applied the  $P\bar{4}3m$  (No. 215) space group to describe this structure; the  $P\bar{4}3m$  space group is consistent with the cyanide group taking a definite orientation between a pair of the crystallographically-independent Cd atoms. Namely, there should be two kinds of Cd atoms, one in a  $\text{CdC}_4$  coordination, the other in a  $\text{CdN}_4$  coordination. Recently an Australian group reinvestigated the anticyprite structure of  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$  by applying the  $P\bar{4}3m$  space group again to their single crystals [4].

In this work the crystal structures of  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$  have been reinvestigated by single crystal X-ray diffractometry in order to clarify both the similarity and difference between the neat metal cyanide and the H-cristobalite-like three-dimensional host framework of the inclusion compounds to be discussed in 2.2. The results, however, are different from the conclusions by the previous workers: the space group  $Pn\bar{3}m$  (No. 224) was selected based on the systematic absences of the observed reflections. According to this space group the cyanide groups do not take the ordered orientation both in  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$ ; only one kind of the tetrahedral metal cation is crystallographically independent in



(a)



(b)

Fig. 1 Structure of  $\text{Cd}(\text{CN})_2$ :

(a) ORTEP view of the unit cell of  $\text{Cd}(\text{CN})_2$ ;

(b) the double framework structure: each cell dimension has been doubled along each axis.

the unit cell. The disorder in the orientation of the cyanide group has been supported from the data of solid state  $^{113}\text{Cd}$  NMR for  $\text{Cd}(\text{CN})_2$  and  $\text{Cd}(\text{CN})_2 \cdot \text{C}_6\text{H}_{12}$  [5]. From viewpoint of the disorder, the  $\text{Fd}\bar{3}\text{m}$  space group applied to the  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  clathrate and others, to be discussed in 2.2 of this thesis, is also consistent with the  $\text{Pn}\bar{3}\text{m}$  space group of anticyprite  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$ . In this section the preparation and the structure analyses of  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$  of single crystals are described.

#### 2.1.2. Preparation

Cadmium cyanide,  $\text{Cd}(\text{CN})_2$  (1) - Into 60 ml of water 1.77 g (7.75 mmol) of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and 2.26 g (7.75 mmol) of  $\text{K}_2[\text{Cd}(\text{CN})_4]$  were dissolved under stirring for 1 h. The solution was filtered through a plastic membrane of  $0.45\ \mu\text{m}$  pore size, and kept standing in a refrigerator for a few weeks. Colorless truncated octahedral crystals were obtained. Anal. Found%/calcd%: C, 14.87/14.61; N, 17.08/17.04.

Zinc Cyanide,  $\text{Zn}(\text{CN})_2$  (2) - Single crystals of  $\text{Zn}(\text{CN})_2$  were prepared by the following two methods.

(a) White powder of  $\text{Zn}(\text{CN})_2$  (0.77 g; Aldrich Chemical Company), practically insoluble but suspended in 100 ml of water, was dissolved by adding 7.5 ml of 2-hydroxyethylamine. After the pH was adjusted to 9.5 with citric acid, the aqueous solution was kept standing in a refrigerator for a few months. Colorless cubes were obtained. Anal. Found%/calcd%: C, 20.30/20.46; N, 23.82/23.86.

(b) Into 100 ml of water 2.6 g of  $\text{Zn}(\text{CN})_2$  powder was suspended with stirring for 2 days. After the suspension was filtered through the plastic membrane, the filtrate was covered with a layer of 1,1,1-trichloroethane and kept standing in a refrigerator for a few months. Although this method had been examined to prepare an inclusion compound of 1,1,1-trichloroethane in a zinc cyanide host, colorless cubes obtained at the interface between the aqueous and the organic phases and the bottom of the former phase were the single crystals of zinc cyanide. Anal. Found%/calcd%: C, 20.32/20.46; N, 23.84/23.86.

### 2.1.3. Structure Analysis

Single crystals of (1) and (2) were subjected to the X-ray diffraction experiments on automatic four-circle diffractometers; the crystal data and details of the experimental conditions are summarized in Table I for (1) and Table II for (2). The refined atomic parameters are listed in Table III.

$\text{Cd}(\text{CN})_2$  (1)- The primitive cubic unit cell and the  $m\bar{3}m$  Laue class of (1) were confirmed from the diffraction data. The systematic absences of  $hk0$  for  $h+k=2n+1$  and  $h00$  for  $h=2n+1$  supported the space group  $\text{Pn}\bar{3}m$  uniquely. The intensity data observed for these reflections are listed in Table IV for (1) and (2); each of the intensities was smaller than three times its e.s.d. According to the second choice of the origin setting in the International Tables [6], the Cd atom was placed on  $1/4, 1/4, 1/4$  with the  $\bar{4}3m$  site symmetry. Since the  $\text{Pn}\bar{3}m$  space group predicts that a discrimination is impossible between the N and C atoms of the cyanide group, the atom on  $x, x, x$ , with the  $3m$  site symmetry was assumed to have 50% each probability of C and N atoms in the structure refinement.

$\text{Zn}(\text{CN})_2$  (2) - All the diffraction data observed for  $\text{Zn}(\text{CN})_2$  (2) supported that (2) is isomorphous to  $\text{Cd}(\text{CN})_2$  (1). The structure has been refined similarly to the case of (1).

### 2.1.4. Discussion

The present disordered structures of (1) and (2) should be compared with the previous works by Shugam and Zhdanov [1], Zhdanov [2], and Hoskins and Robson [4]. At first, the powder data by the Russian group never gave any reflections with intensities significant enough to break the rule of systematic absences of  $hk0$  and  $h00$  both for (1) and (2); they did not pay any attention to the possibility of disorder in the orientation of the cyanide group.

Secondly, Hoskins and Robson [4] reported the extremely great values of the final  $k$  parameters in the weighting scheme, 26.1 and 15.1 for (1) and (2) respectively, being far larger than unity, in their final structure refinements using the full-matrix least-squares calculations using SHELX-76 [7]. It is doubtful to put great confidence in the bond lengths shorter for M-C than those for

Table I

Crystallographic and selected experimental data for  $\text{Cd}(\text{CN})_2$ 

Compound	$\text{Cd}(\text{CN})_2$
Formula	$\text{C}_2\text{N}_2\text{Cd}$
F.W.	164.45
Color and habit	colorless cubic
Crystal system	cubic
Space group	$\text{Pn}\bar{3}\text{m}(\text{No. 224})$
$a/\text{\AA}$	6.300(1)
$V/\text{\AA}^3$	250.1(1)
Z	2
$D_m/\text{g cm}^{-3}$	2.19(1)
$D_x/\text{g cm}^{-3}$	2.18
Crystal size/mm	0.15x0.15x0.10
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	41.71
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.302 + 0.3 \tan \theta$
Reflections measured	699
Reflections used	49 ( $> 4 \sigma(F_o)$ )
Parameters	5
Solution program	SHELX76
Weight scheme	$w = 1/(\sigma^2 + 0.000077F^2)$
R	0.0661
Rw	0.0515
G.O.F.	3.467
Crystal decay	Not observed
max shift/esd(Host)	0.005
max & min resid $e \text{\AA}^{-3}$	+1.00(in the cavity)*, -0.86

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$R_w = [ \sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2 ]^{1/2}$$

\*near Cd atom

Table II

Crystallographic and selected experimental data for  $\text{Zn}(\text{CN})_2$ 

	experiment 1	experiment 2
Compound	$\text{Zn}(\text{CN})_2$	
Formula	$\text{C}_2\text{N}_2\text{Zn}$	
F.W.	117.43	
Color and habit	colorless octahedra	colorless octahedra
Crystal system	cubic	
Space group	$\text{Pn}\bar{3}\text{m}(\text{No.}224)$	
$a/\text{\AA}$	5.9086(7)	5.899(1)
$V/\text{\AA}^3$	206.27(7)	205.3(2)
Z	2	
$D_m/\text{g cm}^{-3}$	1.91(1)	1.90(2)
$D_x/\text{g cm}^{-3}$	1.89	1.90
Crystal size/mm	0.10x0.07x0.07	0.30x0.30x0.25
Temperature/K	294	294
Diffractometer	Rigaku AFC 5	Rigaku AFC 6A
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069	
$\mu/\text{cm}^{-1}$	58.7	
Scan type	$2\theta - \omega$	
$2\theta$ range/ $^\circ$	4-60	3-60
Peak scan width	$1.30+0.35\tan\theta$	$1.02+0.50\tan\theta$
Reflections measured	365	398
Reflections used	53 ( $>3\sigma(\text{Fo})$ )	60 ( $>3\sigma(\text{Fo})$ )
Parameters	5	5
Solution program	SHELX76	
Weight scheme	$w=1/(\sigma^2+0.000381\text{F}^2)$	$w=1/(\sigma^2+0.005743\text{F}^2)$
R	0.045	0.054
R <sub>w</sub>	0.044	0.085
G.O.F.	1.464	1.035
Crystal decay	Not observed	
max shift/esd	0.007	0.007
max & min resid $e\text{\AA}^{-3}$	0.40 -0.45	0.39 -0.37

$$R = \sum ||\text{Fo}| - |\text{Fc}|| / \sum |\text{Fo}|$$

$$R_w = [ \sum w(|\text{Fo}| - |\text{Fc}|)^2 / \sum w|\text{Fo}|^2 ]^{1/2}$$

Table III. Refined atomic parameters for  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$ 

atom	x	y	z	Biso/ $\text{\AA}^2$
$\text{Cd}(\text{CN})_2^a$				
Cd	1/4	=x	=x	11.23(7)
C,N <sup>b</sup>	0.0524(9)	=x	=x	10.5(1)
-----				
$\text{Zn}(\text{CN})_2$ : experiment 1 <sup>c</sup>				
Zn	1/4	=x	=x	3.92(4)
C,N	0.0557(7)	=x	=x	4.5(1)
-----				
$\text{Zn}(\text{CN})_2$ : experiment 2 <sup>d</sup>				
Zn	1/4	=x	=x	3.79(4)
C,N	0.0578(9)	=x	=x	4.25(9)

a. Cd-C,N = 2.159(9) Å, C,N-C,N = 1.143(19) Å

b. 50% each probability of C and N atoms

c. Zn-C,N = 1.989(7) Å, C,N-C,N = 1.139(14) Å

d. Zn-C,N = 1.964(9) Å.

Table IV

Intensities of  $hkl(h+k=2n+1)$  and  $h00(h=2n+1)$  reflections observed for  $\text{Cd}(\text{CN})_2$ 

H	K	L	Fo	sig Fo	H	K	L	Fo	sig Fo
1	0	0	3.12	2.13	1	0	0	1.06	0.55
3	0	0	0.0		3	0	0	0.48	1.86
5	0	0	3.95	7.92	5	0	0	1.26	0.98
7	0	0	7.62	3.85	7	0	0	0.0	
9	0	0	0.0		1	2	0	0.0	
1	2	0	2.93	6.65	1	4	0	0.0	
1	4	0	0.0		1	6	0	1.04	1.27
1	6	0	6.53	5.73	1	8	0	1.65	0.81
1	8	0	0.0		2	3	0	0.46	2.07
1	10	0	0.0		2	5	0	0.54	2.38
2	3	0	0.0		2	7	0	0.42	3.92
2	5	0	0.0		3	4	0	0.0	
2	7	0	0.0		3	6	0	0.56	1.92
2	9	0	6.77	8.77	4	5	0	0.0	
3	4	0	4.75	6.24	4	7	0	1.14	1.19
3	6	0	2.97	13.52	5	6	0	1.76	1.02
3	8	0	0.0						
4	5	0	0.0						
4	7	0	0.0						
4	9	0	3.46	17.41					
5	6	0	0.0						
5	8	0	0.0						
6	7	0	7.46	4.22					

M-N (M= Zn or Cd), because serious systematic errors may be included in the final results with a great k value, as the instruction for SHELX-76 [7] stated.

The solid state  $^{113}\text{Cd}$  NMR observed for (1) and its cyclohexane clathrate  $\text{Cd}(\text{CN})_2 \cdot \text{C}_6\text{H}_{12}$  prepared by this work support the random distribution of the C and N atoms about the Cd atoms in the three-dimensional framework [5]: The five peaks assigned to  $\text{CdC}_4$ ,  $\text{CdC}_3\text{N}$ ,  $\text{Cd}_2\text{N}_2$ ,  $\text{CdCN}_3$ , and  $\text{CdN}_4$  did not show a 1:4:6:4:1 intensity ratio corresponding to entirely random distribution, but the  $\text{CdC}_2\text{N}_2$  band was relatively enhanced and  $\text{CdC}_4$  and  $\text{CdN}_4$  were much weakened in the observed 1:11.5:25:11.5:1 ratio. At any rate, the ordered structure predicts two bands should be observed only for  $\text{CdC}_4$  and  $\text{CdN}_4$ . As is mentioned later, the series of the cubic  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  clathrates belong to the  $\text{Fd}\bar{3}\text{m}$  space group in which the cyanide takes a random orientation of the C and N atoms. Hence, it is concluded in this work that the cyanide group in both the antiperite type three-dimensional double framework of  $\text{Cd}(\text{CN})_2$  and the host framework of the  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  takes a random distribution of the orientation with respect to the coordination to the tetrahedral Cd atom.

## 2.2. Inclusion Structure of cristobalite-like Host

### 2.2.1. Preparation and Properties

In the anticyprite structure of  $\text{Cd}(\text{CN})_2$  two identical frameworks interpenetrate to each other without any cross-connections. The cavity formed in one framework is filled by the other: the center of the assumed cavity is occupied by the Cd atom of the other framework. If one of the frameworks is replaced by appropriate guest molecules, a novel clathrate structure should be given. The idea has been materialized by the formation of a series of the  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  (G: guest molecule) inclusion compounds prepared for a number of G guest molecules in this work. The crystal structures analyzed for the single crystals of the respective  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  compounds support that these are the clathrate compounds formed between the H-cristobalite-like single host framework of  $\text{Cd}(\text{CN})_2$  and the respective guest molecule accommodated in the adamantane-like cavity built of host framework.

In the course of the present study, Hoskins and Robson [4] reported the diamond-like framework structure of  $[\text{N}(\text{CH}_3)_4][\text{CuZn}(\text{CN})_4]$  ( $= [\text{CuZn}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$ ; chemical formula in the order that the host precedes the guest has been applied throughout in this work) along with the revisit to the structures of  $\text{Cd}(\text{CN})_2$  and  $\text{Zn}(\text{CN})_2$ . The anionic framework of the copper(I)-zinc(II) mixed cyanide has the structure similar to the present host of the clathrates. A half number of the total cavities in the anionic host are occupied by the tetramethylammonium cation as the cationic guest to neutralize the negative charge of the host but the remaining half number of cavities are left vacant. The present work shows that the clathrates of carbon tetrachloride  $[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$  and  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot x\text{CCl}_4]$  ( $x=0.9$ ) are formed in which the vacant cavities are occupied by the neutral guest carbon tetrachloride. Carbon tetrachloride and cyclohexane clathrates of a novel mixed-metal neutral host  $[\text{CdM}(\text{CN})_4] \cdot 2\text{G}$  ( $\text{M}=\text{Zn}$ ,  $\text{G}=\text{CCl}_4$ ;  $\text{M}=\text{Hg}$ ,  $\text{G}=\text{CCl}_4$  or  $\text{C}_6\text{H}_{12}$ ) were also prepared as the substantially isomorphous analogs of  $\text{Cd}(\text{CN})_2 \cdot \text{G}$ . The guest species accommodated in the H-cristobalite-like hosts are listed in Table V along with the unit cell parameters, the a dimen-

Table V. Geust species accommodated in the H-cristobalite hosts and the a dimensions of the cubic unit cells

Host	Geust	a/ Å	space group
Cd(CN) <sub>2</sub>	CHCl <sub>3</sub>	12.647(6)	Fd3m
	CH(CH <sub>3</sub> ) <sub>2</sub> Cl	12.668(3)	
	CH(CH <sub>3</sub> )(Cl)CH <sub>2</sub> Cl	12.691(2)	
	CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> Cl	12.692(2)	
	CCl <sub>4</sub>	12.714(1)	
	CCH <sub>3</sub> Cl <sub>3</sub>	12.717(1)	
	cyclo-C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub>	12.729(2)	
	C(CH <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	12.731(1)	
	CH(CH <sub>3</sub> )Cl <sub>2</sub>	12.732(2)	
	cyclo-C <sub>6</sub> H <sub>12</sub>	12.735(1)	
	CF <sub>2</sub> ClCFC1 <sub>2</sub>	12.742(1)	
	C(CH <sub>3</sub> ) <sub>3</sub> Cl	12.743(2)	
	C(CH <sub>3</sub> ) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	12.744(1)	
	C(CH <sub>3</sub> ) <sub>4</sub>	12.757(2)	
	C(CF <sub>3</sub> )Cl <sub>3</sub>	12.767(2)	
-----			
CdCu(CN) <sub>4</sub>	N(CH <sub>3</sub> ) <sub>4</sub> · CCl <sub>4</sub>	12.189(2)	F43m
-----			
ZnCu(CN) <sub>4</sub>	N(CH <sub>3</sub> ) <sub>4</sub> · CCl <sub>4</sub>	11.771(2)	F43m
	N(CH <sub>3</sub> ) <sub>4</sub>	11.671(2)	
-----			
CdHg(CN) <sub>4</sub>	2CCl <sub>4</sub>	12.7138(5)	Fd3m
-----			
CdZn(CN) <sub>4</sub>	2CCl <sub>4</sub>	12.734(1)	Fd3m

ions, of the respective cubic unit cells.

(a) Preparation of  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  Series Single Crystals.

These clathrates have been prepared as single crystals in general. In 100 ml of water 7.75 mmol each of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (1.77 g) and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  (2.26 g) were dissolved. After the solution was filtered through a plastic membrane of 0.45  $\mu\text{m}$  pore size, it was covered with, or placed on, the layer of the guest organic species and kept standing in a refrigerator or at room temperature for a few days. Colorless crystals of the clathrates were formed at the interface between the organic and the aqueous phases or the bottom of the aqueous phase. Single crystals of the neopentane guest clathrate  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4$  were obtained by the procedure as follows: 100 ml of aqueous solution containing an equimolar amount each of  $\text{CdCl}_2$  and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  with the final Cd concentration of 0.1 mol/l was placed in a Schlenk tube, which was connected with a vacuum line; neopentane gas (bp/°C=9.5) was introduced into the tube at 20°C; the tube was removed from the vacuum line and kept in a refrigerator at 6°C for few days; colorless octahedral single crystals were grown on the surface of the aqueous solution.

(b) Preparation of Mixed-metal Host Series

$[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$  - Into 100 ml of water 1.95 g (3.0 mmol) of KCN and 0.090 g (1.0 mmol) of CuCN were dissolved under stirring. Fine white precipitate, once formed by addition of 2.28 g (1.0 mmol) of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and 0.57 g (2.8 mmol) of  $\text{N}(\text{CH}_3)_4\text{I}$  into the aqueous solution, was dissolved by raising the pH up to 12.0 with 2-hydroxyethylamine. After the pH was adjusted to 10 with citric acid, the solution was kept standing on a layer of carbon tetrachloride in a refrigerator for a few days; colorless crystals were obtained. Anal. Found%/calcd%: C, 20.86/21.28; H, 2.41/2.38; N, 13.62/13.77; Cl, 27.51/27.92.

$[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{xCCl}_4]$  - Colorless crystals were obtained by the procedure similar to that as above using zinc chloride in place of cadmium chloride. Anal. Found%/calcd%: C, 23.99/24.43; H, 2.90/2.72; N, 16.09/15.72; Cl, 28.64/28.93; the calculated values are those for  $\text{x}=0.9$ . Crystals of  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$  reported in literature [4] were also ob-

tained from the aqueous solution without contact with the layer of carbon tetrachloride; the procedure is different from that in literature but the product was the same.

$[\text{CdZn}(\text{CN})_4] \cdot 2\text{CCl}_4$  - In 100 ml of water 7.75 mmol each of  $\text{K}_2[\text{Cd}(\text{CN})_4]$  (1.77 g) and  $\text{ZnCl}_2$  (1.56 g) were added. White precipitate instantaneously formed was dissolved by adding 2-hydroxyethylamine and citric acid monohydrate. After the solution was filtered through a plastic membrane, it was placed on a layer of  $\text{CCl}_4$  and kept standing in a refrigerator for a few days to obtain colorless crystals.

$[\text{CdHg}(\text{CN})_4] \cdot 2\text{CCl}_4$  and  $[\text{CdHg}(\text{CN})_4] \cdot 2\text{C}_6\text{H}_{12}$  - Two routes, one using  $\text{CdCl}_2$  and  $\text{K}_2[\text{Hg}(\text{CN})_4]$  and the other  $\text{HgCl}_2$  and  $\text{K}_2[\text{Cd}(\text{CN})_4]$ , gave the same products: 7.75 mmol each of the respective salts were used in the procedures similar to that as above.

### (c) Properties

These  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  and  $[\text{CdM}(\text{CN})_4] \cdot 2\text{G}$  inclusion compounds are unstable under ambient conditions: it was difficult to determine the chemical composition precisely by usual chemical analysis. The formation and decomposition of the  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  inclusion compounds we tried were ascertained by infrared spectroscopy (IR), gas-chromatography (GC), thermal gravimetry (TG), and powder X-ray diffractometry (PXD). On the TG analyses each inclusion compound liberates the guest molecules with the ratio to support the composition  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  or  $[\text{CdM}(\text{CN})_4] \cdot 2\text{G}$  leaving white powder of  $\text{Cd}(\text{CN})_2$  or  $\text{CdM}(\text{CN})_4$ ; as for the former, it gave the PXD pattern identical with that observed for the neat  $\text{Cd}(\text{CN})_2$  of the anticyuprite structure.

In comparison with the neutral host ones, the clathrates of the anionic hosts are stable enough to give the analytical results within an acceptable range. However, it appears that the neutral guest is less than unity in  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot x\text{CCl}_4]$ : the results supported  $x=0.9$ . Additionally, the analytical results obtained for the residual complex left after the liberation of the guest molecules from  $[\text{ZnCd}(\text{CN})_4] \cdot 2\text{CCl}_4$  suggested the ratio Zn/Cd greater than 1; in the structure refinement, as will be mentioned later, the occupancy rate was refined to be

$[\text{Zn}_{1.08}\text{Cd}_{0.92}(\text{CN})_4] \cdot 2\text{CCl}_4$  at the stage of  $R=0.071$ .

The occupancy rate of the guest atoms has been refined for some of the clathrates, too: no significant deviations from the stoichiometric value were obtained.

## 2.2.2. Structure Refinements

All the crystals subjected to the single crystal experiments were coated with epoxy resin in order to prevent the spontaneous decomposition under ambient conditions. The crystal and experimental data are summarized in Table VI.

The face-centered cubic unit cell and the  $m\bar{3}m$  Laue class were limited for all the  $\text{Cd}(\text{CN})_2 \cdot G$  and  $[\text{CdM}(\text{CN})_4] \cdot 2G$  series from the diffraction data; the systematic absences of  $hkl$  for  $(h+k, h+1, k+1) = 2n+1$ , and  $hk0$  for  $h+k=4n+1, 2, 3$  supported the space group  $Fd\bar{3}m$  uniquely. According to the second choice of the origin setting in the International Tables [6], the Cd atom was placed on  $1/8, 1/8, 1/8$  with the  $\bar{4}3m$  site symmetry. Since the  $Fd\bar{3}m$  space group predicts that the discrimination is impossible between the N and C atoms of the cyanide group, the atom on  $x, x, x$  with the  $3m$  site symmetry was assumed to have 50% each probability of C and N atoms in the structure refinement. Additionally, it is also impossible to discriminate Cd and M in the  $[\text{CdM}(\text{CN})_4]$  hosts, for which the heavy atom at  $1/8, 1/8, 1/8$  was seen to have 50% each probability of Cd and M (Hg or Zn). The guest molecule was found in the cavity centered at  $3/8, 3/8, 3/8$  with the  $\bar{4}3m (=Td)$  site symmetry. When the guest has a real or pseudo-tetrahedral symmetry, the central atom CG1 was located on the center of the cavity. Other guest atoms except hydrogen were located by means of the Fourier and difference Fourier syntheses. The anisotropically refined atomic parameters are listed in Table VII; as for the disorders enforced from the symmetry elements defined by the space group, the occupancies are noted for the respective cases.

As for the series of the anionic hosts,  $[\text{MCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot G]$  ( $M=\text{Zn}$  or  $\text{Cd}$ ), the systematic absences observed were consistent with the space group  $F\bar{4}3m$  which was

Table VI-1 Crystall and experimental data for Cd(CH<sub>3</sub>)<sub>2</sub> · Guest

	0	1	2	3	4	5	6
Guest formula	C(CH <sub>3</sub> ) <sub>4</sub> C <sub>2</sub> H <sub>12</sub> N <sub>2</sub> Cd 236.60	CCl(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>10</sub> N <sub>2</sub> ClCd 257.02	CCl <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> Cl <sub>2</sub> Cd 277.43	CCl <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> Cl <sub>3</sub> Cd 297.85	CCl <sub>4</sub> C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> Cl <sub>4</sub> Cd 318.27	CF <sub>3</sub> CCl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub> Cd 351.83	CHCl <sub>2</sub> CHCl <sub>2</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> Cl <sub>2</sub> Cd 332.30
color and habit	colorless octahedra						
crst syst	cubic						
space group	Fd3m(No.227)						
a/A	12.757(2)	12.743(2)	12.731(1)	12.717(1)	12.714(1)	12.767(2)	12.743(1)
V/A <sup>3</sup>	2076(1)	2069(1)	2063(1)	2057(1)	2055(1)	2081(2)	2069(1)
Z	8	8	8	8	8	8	8
Dm/gcm <sup>-3</sup>	1.53(2)	1.64(1)	1.78(2)	1.92(1)	2.09(2)	2.27(3)	2.15(2)
Dx/gcm <sup>-3</sup>	1.51	1.65	1.79	1.92	2.06	2.25	2.13
crst size/mm	0.21x0.21x0.23	0.12x0.12x0.07	0.15x0.12x0.09	0.20x0.20x0.15	0.20x0.20x0.17	0.25x0.25x0.20	0.35x0.35x0.35
diffractionmeter	Rigaku APC 5						
radiation	Mo K $\alpha$ (0.71069)						
$\mu$ (Mo K $\alpha$ )/cm <sup>-1</sup>	20.2	22.9	25.5	28.2	30.74	28.48	30.58
scan mode	2 $\theta$ - $\omega$						
2 $\theta$ scan range/deg	4 < 2 $\theta$ < 60						
temperature	294K						
using program	SHELX76						
R	0.028	SHELX76	SHELX76	SHELX76	SHELX76	SHELX76	SHELX76
Rw	0.027	0.068	0.065	0.047	0.035	0.041	0.052
G.O.F	1.184	0.003	0.093	0.032	0.048	0.043	0.054
refs. observed	196	1.024	0.9763	1.821	0.878	1.621	2.885
ref. used	134	206	206	206	206	209	206
parameters	9	81	89	92	114	108	103
wt		9	12	14	12	21	14
w=1/( $\sigma^2$ + $ F ^2$ )	g=0.000131						
max shift/eed	0.074	g=0.007	g=0.007	g=0.00004	g=0.002	g=0.0002	g=0.0001
max residual		0.275	0.195	0.208	0.107	1.08	0.345
electron density(e/A <sup>3</sup> )	0.35	0.89	0.66	0.74	0.455	0.49	0.36

Table VI-2

Crystal and selected experimental data for  
 $[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$

Compound	$[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$
Formula	$\text{C}_9\text{H}_{12}\text{CdCuCl}_4\text{N}_5$
F.W.	508.00
Color and habit	colorless cube
Crystal system	cubic
Space group	$F\bar{4}3m$ (No. 216)
$a/\text{\AA}$	12.189(2)
$V/\text{\AA}^3$	1815(1)
Z	4
$D_m/\text{gcm}^{-3}$	1.87(2)
$D_x/\text{gcm}^{-3}$	1.86
Crystal size/mm	0.30x0.30x0.30
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	25.25
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.20 + 0.35 \tan \theta$
Reflections measured	187
Reflections used	167 ( $>3\sigma F_o$ )
Parameters	39
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.0209F^2)$
R	0.0437
Rw	0.0654
G.O.F.	0.4896
Crystal decay	Not observed
max shift/esd(Host)	0.130
max shift/esd(Guest)	0.677
max & min resid $e \text{\AA}^{-3}$	0.44, -1.35

Table VI-3

Crystal and selected experimental data for  
 $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$

Compound	$[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$
Formula	$\text{C}_9\text{H}_{12}\text{ZnCuCl}_4\text{N}_5$
F.W.	460.96
Color and habit	colorless cube
Crystal system	cubic
Space group	$F\bar{4}3m$ (No. 216)
$a/\text{\AA}$	11.771(2)
$V/\text{\AA}^3$	1628(1)
Z	4
$D_m/\text{gcm}^{-3}$	1.75-1.87
$D_x/\text{gcm}^{-3}$	1.88
Crystal size/mm	0.20x0.10x0.08
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	34.11
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.30 + 0.35 \tan \theta$
Reflections measured	675
Reflections used	133 ( $>3\sigma F_o$ )
Parameters	17
Solution program	SHELX76
Weight scheme	$w = 1/(\sigma^2 + 0.0029F^2)$
R	0.0639
R <sub>w</sub>	0.0717
G.O.F.	5.4896
Crystal decay	Not observed
max shift/esd(Host)	0.030
max shift/esd(Guest)	0.577
max & min resid $e \text{\AA}^{-3}$	0.97, -1.24

Table VI-4

Crystal and selected experimental data for  
 $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$

Compound	$[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$
Formula	$\text{C}_8\text{H}_{12}\text{ZnCuN}_5$
F.W.	307.14
Color and habit	colorless cube
Crystal system	cubic
Space group	$F\bar{4}3m$ (No. 216)
$a/\text{\AA}$	11.671(2)
$V/\text{\AA}^3$	1583(1)
Z	4
$D_m/\text{gcm}^{-3}$	1.27(2)
$D_x/\text{gcm}^{-3}$	1.29
Crystal size/mm	0.40x0.35x0.35
Temperature/K	293
Diffractionmeter	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	29.01
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	6-60
Peak scan width	$1.20 + 0.30 \tan \theta$
Reflections measured	155
Reflections used	105 ( $>3\sigma F_o$ )
Parameters	13
Solution program	SHELX76
Weight scheme	$w = 1/(\sigma^2 + 0.00777F^2)$
R	0.0479
R <sub>w</sub>	0.0568
G.O.F.	0.7450
Crystal decay	Not observed
max shift/esd(Host)	0.017
max shift/esd(Guest)	0.299
max & min resid $e \text{\AA}^{-3}$	0.49, -0.47

Table VI-5

Crystal and selected experimental data for  
 $[\text{CdHg}(\text{CN})_4] \cdot 2[\text{CCl}_4]$

Compound	$[\text{CdHg}(\text{CN})_4] \cdot 2[\text{CCl}_4]$
Formula	$\text{C}_6\text{CdHgCl}_8\text{N}_4$
F.W.	724.72
Color and habit	colorless cube
Crystal system	cubic
Space group	$\text{Fd}\bar{3}\text{m}(\text{No. } 227)$
$a/\text{\AA}$	12.7138(5)
$V/\text{\AA}^3$	2055(1)
Z	4
$D_m/\text{gcm}^{-3}$	2.37(2)
$D_x/\text{gcm}^{-3}$	2.34
Crystal size/mm	0.10x0.10x0.10
Temperature/K	293
Diffractionmeter	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	94.59
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.30 + 0.3 \tan \theta$
Reflections measured	191
Reflections used	75 ( $>3\sigma F_o$ )
Parameters	12
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.0010F^2)$
R	0.0549
$R_w$	0.0779
G.O.F.	2.012
Crystal decay	Not observed
max shift/esd(Host)	0.065
max shift/esd(Guest)	0.078
max & min resid	
$e/\text{\AA}^{-3}$	0.82, -0.82

Table VI-6

Crystal and selected experimental data for  
 $[\text{CdHg}(\text{CN})_4] \cdot 2[\text{C}_6\text{H}_{12}]$

Compound	$[\text{CdHg}(\text{CN})_4] \cdot 2[\text{C}_6\text{H}_{12}]$
Formula	$\text{C}_{16}\text{H}_{24}\text{HgCdN}_4$
F.W.	585.39
Color and habit	colorless cube
Crystal system	cubic
Space group	$\text{Fd}\bar{3}\text{m}(\text{No. } 227)$
$a/\text{\AA}$	12.734(1)
$V/\text{\AA}^3$	2065(1)
Z	4
$D_m/\text{gcm}^{-3}$	1.87(1)
$D_x/\text{gcm}^{-3}$	1.88
Crystal size/mm	0.40x0.35x0.35
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	84.19
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.30 + 0.35 \tan \theta$
Reflections measured	191
Reflections used	115 ( $>3\sigma F_o$ )
Parameters	14
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.0029F^2)$
R	0.0523
$R_w$	0.0686
G.O.F.	0.9757
Crystal decay	Not observed
max shift/esd(Host)	0.030
max shift/esd(Guest)	0.177
max & min resid $e\text{\AA}^{-3}$	0.80, -0.70

Table VI-7

Crystal and selected experimental data for  
 $[\text{CdZn}(\text{CN})_4] \cdot 2[\text{CCl}_4]$

Compound	$[\text{CdZn}(\text{CN})_4] \cdot 2[\text{CCl}_4]$
Formula	$\text{C}_6\text{Cl}_8\text{ZnCdN}_4$
F.W.	589.50
Color and habit	colorless cube
Crystal system	cubic
Space group	$\text{Fd}\bar{3}\text{m}(\text{No. } 227)$
$a/\text{\AA}$	12.243(1)
$V/\text{\AA}^3$	1834.9(6)
Z	4
$D_m/\text{gcm}^{-3}$	2.07(2)
$D_x/\text{gcm}^{-3}$	2.13
Crystal size/mm	0.12x0.12x0.10
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	35.69
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.15 + 0.35 \tan \theta$
Reflections measured	862
Reflections used	96 ( $>3\sigma F_o$ )
Parameters	12
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.004F^2)$
R	0.073
R <sub>w</sub>	0.091
G.O.F.	1.064
Crystal decay	Not observed
max shift/esd(Host)	0.030
max shift/esd(Guest)	0.207
max & min resid $e\text{\AA}^{-3}$	1.36(near Cd, Zn), -0.70

Table VII-1 atomic parameters for  $\text{Cd}(\text{CN})_2 \cdot \text{G}$

for 0  $\text{G}=\text{C}(\text{CH}_3)_4$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	4.03(2)
C,N	0.0257(2)	=x	=x	0.16666	4.3(1)
CG1	0.375	=x	=x	0.04166	5.6(3)
CG2	0.3068(5)	=x	=x	0.16666	14.6(4)

Cd-C,N 2.195(5)    C,N-C,N 1.134(11)    CG1-CG2 1.508(11)

for 1  $\text{G}=\text{CCl}(\text{CH}_3)_3$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	4.2(1)
C,N	0.0257(10)	=x	=x	0.16666	4.7(5)
CG1	0.375	=x	=x	0.04166	11(2)
C,Cl	0.3058(13)	=x	=x	0.16666	26(2)

Cd-C,N 2.19(2)    C,N-C,N 1.13(5)    CG1-C,Cl 1.53(3)

for 2  $\text{G}=\text{CCl}_2(\text{CH}_3)_2$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	4.9(1)
C,N	0.0249(11)	=x	=x	0.16666	5.1(4)
CG1	0.375	=x	=x	0.04166	12(1)
C,Cl	0.2892(16)	=x	0.3356(25)	0.16666	25(1)

Cd-C,N 2.21(2)    C,N-C,N 1.10(5)    CG1-C,Cl 1.62(3)

for 3  $\text{G}=\text{CCl}_3(\text{CH}_3)$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	5.37(7)
C,N	0.0257(4)	=x	=x	0.16666	5.4(3)
CG1	0.375	=x	=x	0.04166	8.3(6)
CG2	0.3039(42)	=x	=x	0.04166	6.4(9)
Cl	0.3335(6)	=x	0.2519(10)	0.12500	13.9(6)

Cd-C,N 2.195(10)    C,N-C,N 1.13(2)    CG1-CG2 1.57(9)    CG-C1 1.74(1)

for 4  $G=CCl_4$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	6.06(3)
C,N	0.0260(3)	=x	=x	0.16666	5.7(1)
CG1	0.375	=x	=x	0.04166	8.7(4)
Cl	0.3341(4)	=x	0.2495(7)	0.16666	15.6(4)

Cd-C,N 2.187(7)    C,N-C,N 1.15(2)    CG1-Cl 1.756(9)

for 5  $G=CF_3CCl_3$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	4.84(6)
C,N	0.0259(5)	=x	=x	0.16666	4.6(2)
CG1	0.375	=x	=x	0.04166	14.9(9)
CG2	0.3052(11)	=x	=x	0.04166	13(1)
Cl	0.3409(7)	=x	0.2375(10)	0.12498	12.6(6)
F	0.254(2)	=x	0.380(2)	0.12498	26.5(9)

Cd-C,N 2.190(1)    C,N-C,N 1.15(2)    CG1-CG2 1.54(2)  
CG1-Cl 1.86(1)    CG2-F 1.34(2)

for 6  $G=CCl_2HCCl_2H$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	6.084(8)
C,N	0.0251(6)	=x	=x	0.16666	6.2(3)
CG	0.416(2)	=x	=x	0.08333	18(1)
Cl	0.3307(6)	=x	0.2313(13)	0.16666	25.4(9)

Cd-C,N 2.20(1)    C,N-C,N 1.11(3)    CG-CG 1.46(8)  
CG-Cl 1.70(5)

for 7  $G=C_6H_{12}$

	a	b	c	G	Beq/ $\text{\AA}^2$
Cd	0.125	=x	=x	0.04166	6.084(8)
C,N	0.0251(6)	=x	=x	0.16666	6.2(3)
CG	0.268(6)	0.311(2)	0.387(3)	0.25	19(1)

Table VII-2. atomic parameters for mixed-metal hosts

for  $[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$ 

	a	b	c	G	Beq/ $\text{\AA}^2$
Host					
Cu	0.0	=x	=x	0.04166	2.67(6)
Cd	0.25	=x	=x	0.04166	2.31(3)
C(1)	0.0940(8)	=x	=x	0.16666	3.2(2)
N(1)	0.1463(8)	=x	=x	0.16666	3.9(2)
Guest					
C(2)	0.5	=x	=x	0.0224	4.4(6)
N(2)	0.5	=x	=x	0.0193	4.6(6)
C(3)	0.75	=x	=x	0.0193	4.3(6)
N(3)	0.75	=x	=x	0.0224	4.2(6)
Cl(1)	0.806(2)	=x	0.870(2)	0.0771	9.6(6)
Cl(2)	0.4519(9)	=x	0.368(1)	0.0895	4.8(6)
C(4)	0.770(3)	=x	0.868(2)	0.0895	4.9(6)
C(5)	0.437(3)	=x	0.2495(7)	0.16666	15.6(4)

for  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$ 

	a	b	c	G	Beq/ $\text{\AA}^2$
Host					
Cu	0.0	=x	=x	0.04166	1.6(3)
Zn	0.25	=x	=x	0.04166	2.6(3)
C(1)	0.094(3)	=x	=x	0.16666	2.4(3)
N(1)	0.150(2)	=x	=x	0.16666	3.0(3)
Guest					
N(2)	0.5	=x	=x	0.04166	3.4(8)
C(2)	0.429(1)	=x	=x	0.144(3)	4.9(9)
C(3)	0.572(2)	=x	=x	0.022(3)	6.6(9)
C(4)	0.75	=x	=x	0.0360(7)	10(1)
Cl	0.792(1)	=x	0.884(2)	0.144(3)	22(1)

for  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$

	a	b	c	G	Beq/ Å <sup>2</sup>
Host					
Cu	0.0	=x	=x	0.04166	5.5(2)
Zn	0.25	=x	=x	0.04166	3.05(6)
C(1)	0.096(1)	=x	=x	0.16666	4.3(3)
N(1)	0.150(2)	=x	=x	0.16666	5.8(4)
Guest					
N(2)	0.5	=x	=x	0.04166	3.4(8)
C(2)	0.572(1)	=x	=x	0.16666	24.1(6)

for  $\text{CdHg}(\text{CN})_4 \cdot 2\text{CCl}_4$  ( exp.1  $\text{HgCl}_2 + \text{K}_2[\text{Cd}(\text{CN})_4]$  )

	a	b	c	G	Beq/ Å <sup>2</sup>
Cd,Hg	0.125	=x	=x	0.04166	5.7(1)
C,N	0.0236(9)	=x	=x	0.16666	3.2(4)
CG1	0.375	=x	=x	0.04166	6.0(9)
Cl	0.3339(9)	=x	0.253(2)	0.16666	13.2(9)

Hg,Cd-C,N 2.23(2) C,N-C,N 1.04(4) CG1-Cl 1.72(2)

for  $\text{CdHg}(\text{CN})_4 \cdot 2\text{CCl}_4$  ( exp.2  $\text{CdCl}_2 + \text{K}_2[\text{Hg}(\text{CN})_4]$  )

	a	b	c	G	Beq/ Å <sup>2</sup>
Cd,Hg	0.125	=x	=x	0.04166	5.6(1)
C,N	0.024(1)	=x	=x	0.16666	3.2(4)
CG1	0.375	=x	=x	0.04166	5.4(9)
Cl	0.3341(11)	=x	0.252(2)	0.16666	12.6(9)

Hg,Cd-C,N 2.22(2) C,N-C,N 1.06(4) CG1-Cl 1.73(2)

for  $\text{CdHg}(\text{CN})_4 \cdot 2\text{CCl}_4$  ( exp.3  $\text{CdCl}_2 + \text{K}_2[\text{Hg}(\text{CN})_4]$  )

	a	b	c	G	Beq/ Å <sup>2</sup>
Cd,Hg	0.125	=x	=x	0.04166	5.5(1)
C,N	0.0245(9)	=x	=x	0.16666	3.1(3)
CG1	0.375	=x	=x	0.04166	4.9(9)
Cl	0.3340(9)	=x	0.253(2)	0.16666	13.7(9)

Hg,Cd-C,N 2.22(2) C,N-C,N 1.08(4) CG1-Cl 1.71(2)

for  $\text{CdHg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_{12}$

	a	b	c	G	Beq/ Å <sup>2</sup>
Cd,Hg	0.125	=x	=x	0.04166	6.25(5)
C,N	0.0251(6)	=x	=x	0.16666	4.6(2)
CG1	0.267(5)	0.309(4)	0.386(39)	0.25000	14.5(9)

Hg,Cd-C,N 2.20(1) C,N-C,N 1.11(3)

applied for  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$  [4]. According to this space group the Cu atom was located at 0,0,0 and the M (Cd or Zn) at  $1/4, 1/4, 1/4$ ; x,x,x positions of C and N of the cyanide group were refined independently. The anisotropically refined atomic parameters are included in Table VII.

### 2.2.3. Refined Structures (1): $\text{C}(\text{CH}_3)_4\text{-CCl}_4$ Series

The host structure is compared with the anticuprite-type double framework of  $\text{Cd}(\text{CN})_2$  in Fig. 2. The cage-like cavity formed in the host is surrounded by the Cd-CN-Cd linkage like the skeleton of an adamantane molecule as shown Fig. 3. Although the ten Cd atoms involving the cage are crystallographically equivalent one another, there are apparently two kinds of Cd atoms in the cavity skeleton: four are located on the tripod corners, remaining six on the expanded edges, respectively. Hence, to the first approximation, the cavity can be seen as a tetrahedron cornered by the four tripod Cd atoms with the edge length of  $a/\sqrt{2}$  ( $\approx 9 \text{ \AA}$ ) and the height of  $a/\sqrt{3}$  ( $\approx 7.3 \text{ \AA}$ ). In fact, the center of the cavity has the  $\bar{4}3m$  site symmetry as well as each of the Cd atoms. The approximated tetrahedron is separated at every face from that of the neighboring tetrahedron by  $a/4\sqrt{3}$  ( $\approx 1.8 \text{ \AA}$ ).

First of all, the clathrate structures are described for the series of the guest  $\text{C}(\text{CH}_3)_4\text{-nCl}_n$  ( $n=0,1,2,3,4$ ), which are the series of the methyl-chloro derivatives of methane from neopentane to carbon tetrachloride as the end members. The numbering from 0 to 4 is applied to denote the respective clathrates according to the value of n. The guests in the cage are shown in Fig. 4.

The characteristic feature is the orientation of the tetrahedral guest molecules in the tetrahedral cavity. The neopentane molecule in 0 extends each of its C- $\text{CH}_3$  bonds on the threefold axis of crystal toward each of the tripod corners of the cavity as if the tetrapod of the guest skeleton supports the adamantane-like skeleton on the inside without any direct chemical bonds. In other words, methyl group is encapped by the  $\text{Cd}\{-(\text{CN})\text{-Cd}\}_3$  tripod. The distance of  $5.524(3) \text{ \AA}$  ( $=\sqrt{3}a/4$ ) between the cavity center and the Cd atom at the tripod corner is appropriate to accommodate the C- $\text{CH}_3$  moiety with a van der Waals contact. Since the direction toward the face of the tetrahedron is left vacant, considerable

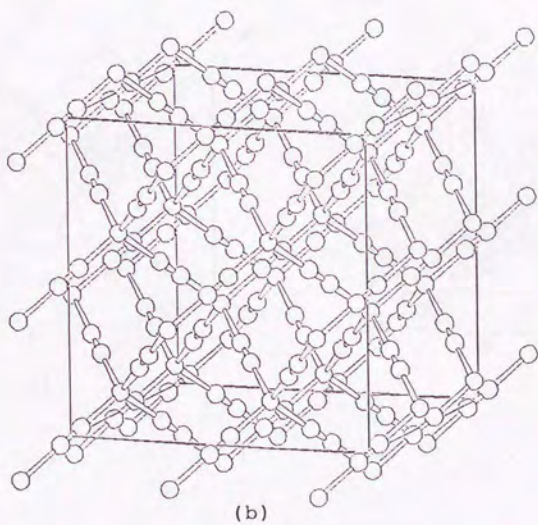
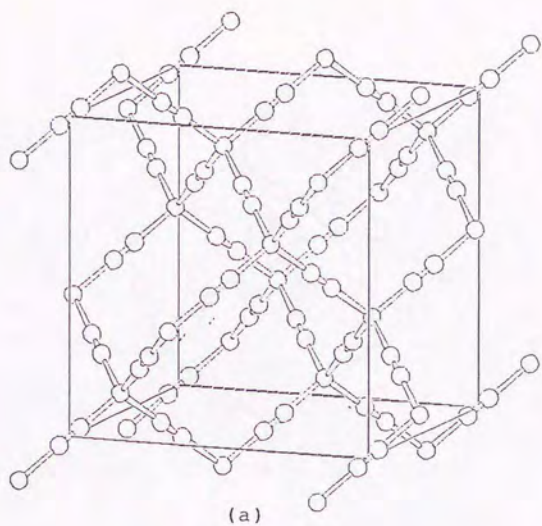
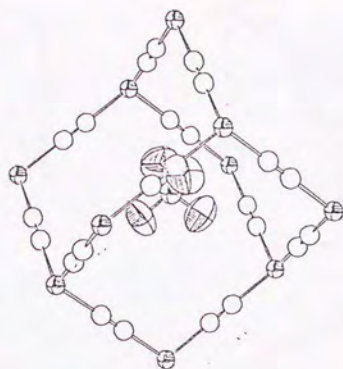
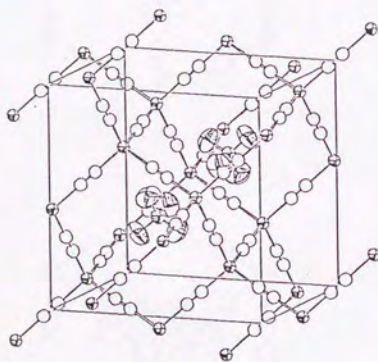


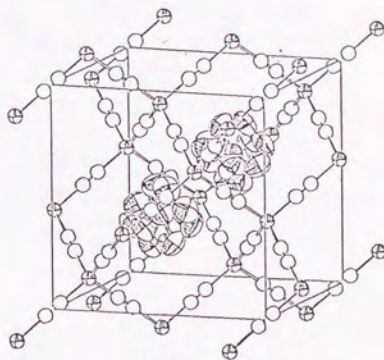
Fig. 2. (a) Host structure of  $\text{Cd}(\text{CN})_2 \cdot \text{G}$   
 (b) anticyprite-type double framework of  $\text{Cd}(\text{CN})_2$



(a)



(b)



(c)

Fig. 3.(a) an adamantane-like cavity of  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4$

(b) structure of  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4^*$

(c) structure of  $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4^*$

\* selected guest molecules at  $3/8, 3/8, 3/8$  and  $5/8, 5/8, 5/8$



n=0



n=3



n=1



n=4



n=2

Fig. 4. Views of the guests in the cage along the crystal threefold axis. The numbering from 0 to 4 is applied to denote the respective clathrates according to the  $n$  in  $C(CH_3)_{4-n}Cl_n$  ( $n=0,1,2,3,4$ ).

void space still remains in the crystal structure of  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4$ .

On the other hand, the carbon tetrachloride molecule in 4 distributes its C-Cl bonds about the threefold axis of crystal giving an occupancy factor of 1/3 at the refined atomic position,  $x, x, z$ , ( $x=0.3341(5)$ ,  $z=0.252(1)$ ) of Cl. The disorder of the  $\text{CCl}_4$  molecule, heavier than  $\text{C}(\text{CH}_3)_4$ , appears to be due to the too long C-Cl bond to be encapped by the  $\text{Cd}\{-(\text{CN})-\text{Cd}\}_3$  tripod: the C-Cl bond protrudes toward the face of the tetrahedral cavity. Since the  $a$  dimension decreases from 12.757(2) Å for  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4$ , 0, monotonously to 12.714(1) Å for  $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ , 4, in the  $\text{C}(\text{CH}_3)_{4-n}\text{Cl}_n$  guest series, the void space in the unit cell decreases successively by replacing  $\text{CH}_3$  by Cl in the guest molecule.

As for the structures of the intermediates, 1, 2, and 3, disorder is inevitable for the distribution of the substituents. The imbalance in the molecular structures of the chloro-methyl-mixed derivatives of methane makes the thermal parameters of the central Cgl atom, fixed at 3/8, 3/8, 3/8, greater than that observed for 0, 5.6(3) in  $\text{Beq}/\text{\AA}^2$ : 11(2) for 1, 12(1) for 2, and 8.3(6) for 3. Although the thermal parameter is extremely great, 25(1) for the guest atom C, Cl in 1 with the occupancy rate of 3/1 for C/Cl at  $x, x, x$  ( $x=0.3058(13)$ ), the orientation of the guest molecule has been observed similar to that in 0. In 2, the guest atom C, Cl (C/Cl=2/2) moves to position  $x, x, z$  ( $x=0.289(2)$ ,  $z=0.336(3)$ ), distributing about the threefold axis similarly to the case of the  $\text{CCl}_4$  in 4. However, the relation between the value of  $x$  and  $z$  is reversed in 2 ( $z > x$ ) from that in 4 ( $x > z$ ). It means the guest atom C, Cl in 2 comes more up to the tripod corner than the Cl in 4. As for 3 two kinds of the atomic positions were observed: one on  $x, x, x$  for the methyl C, the other on  $x, x, z$  for the Cl of  $\text{CCH}_3\text{Cl}_3$ .

The thermal parameters of the host atoms, Cd and C, N, give us another view-point of the clathrate structure. The parameter is unusually great for Cd even in  $\text{Cd}(\text{CN})_2$  ( $\text{Beq}/\text{\AA}^2 = 11.23(7)$ ), decreasing from 6.06(3) for 4, through 5.37(7), 4.9(1), and 4.2(1) for 3, 2, 1, respectively, to 4.03(2) for 0, successively. The similar tendency is also seen in the thermal parameters of C, N.

From these observations the behavior of the guest molecules

can be interpreted in terms of the interaction between the guest methyl group and the host cyanide groups extending from the Cd at the tripod corner. When all the substituents are methyl groups as in 0, each C-CH<sub>3</sub> bond directs toward the corner to support the host framework on the inside. The supported host makes the thermal parameters of the host atom smaller, although considerable void space remains in the crystal structure as a whole like the cubic phase of ice Ic. When a methyl group is replaced by a Cl atom as in 1, the situation is still similar to that in 0. The interaction is effective in 2 and 3 with respect to the orientation of the substituents, but the host framework gets loose from the support of the guest molecule with less number of methyl groups so as to make the thermal parameters greater. In 4 no remarkable interaction other than the van der Waals contact can be expected for the CCl<sub>4</sub>. Although the crystal packing of 4 is the most compact in the Cd(CN)<sub>2</sub> · C(CH<sub>3</sub>)<sub>4-n</sub>Cl<sub>n</sub> series with the least value of a dimension, the thermal parameters of the host atoms are of the greatest degree.

The interaction between the methyl and cyanide groups may be caused from the hydrogen bond formation and/or steric hindrance between the methyl hydrogen and the  $\pi$ -electron-rich cyanide groups, although no experimental evidence has been obtained for the hydrogen bond formation.

#### 2.2.4. Refined Structures (2): Others

The single crystal structures have been refined additionally for the Cd(CN)<sub>2</sub> · G clathrates of G = CF<sub>3</sub>CCl<sub>3</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, and cyclo-C<sub>6</sub>H<sub>12</sub>. Of course these guests take disordered orientations in the tetrahedral cavity, because the respective molecular groups are all lower than the  $\bar{4}3m$  site group of the cavity center. Hence, the atomic parameters refined for the guest atoms should be seen as the data to give a tentative image of the guest molecule in the cavity. Among them, the CF<sub>3</sub>CCl<sub>3</sub> shows the similarity to the CCH<sub>3</sub>Cl<sub>3</sub>, i.e., CF<sub>3</sub> behaves like CH<sub>3</sub> in the tetrahedral cavity but the position of the F atom could be refined. The Cl atoms of the CHCl<sub>2</sub>CHCl<sub>2</sub> guest are distributed about the threefold axis of crystal like that of CCl<sub>4</sub> in Cd(CN)<sub>2</sub> · CCl<sub>4</sub>, although the two C atoms

could be distributed on three-fold axis. The coordinates given to Cg1 in the cyclohexane clathrate is not inconsistent with four sets of the chair-form skeletons of the molecule overlapped one another.

The a dimensions of the unit cell have been refined for the single crystals of the clathrate of the clathrates of  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CHCl}_2$ ,  $(\text{CH}_3)_2\text{CHCl}$ ,  $\text{CH}_3\text{CHClCH}_2\text{Cl}$ ,  $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{Cl}$ ,  $\text{CClF}_2\text{CCl}_2\text{F}$ ,  $\text{C}(\text{CH}_3)_3\text{CH}_2\text{CH}_3$ , *cyclo*- $\text{C}_6\text{H}_{11}\text{CH}_3$  respectively, on the four-circle X-ray diffractometer; the  $m\bar{3}m$  Laue class and the systematic absences supporting the  $\text{Fd}\bar{3}m$  space group have been ascertained based on the collected intensity data, too. However, the refinement was ceased at the stage of the host atoms building up the host framework isomorphous to one another; the disorder of the respective guest molecules were of too high degrees to obtain any significant information for the molecular orientations. The refined parameters have been included in Table V.

#### 2.2.5. Refined Structures (3): Mixed-metal Hosts

The framework of the anionic host,  $[\text{MCu}(\text{CN})_4]$  ( $\text{M}=\text{Zn}$ , or  $\text{Cd}$ ), has substantially the same extension as that of  $\text{Cd}(\text{CN})_2$ , but the space group  $\text{F}\bar{4}3m$  makes it possible to discriminate both heavy atoms M and Cu, and C and N of the cyanide to each other, respectively. In the previous work by the Australian group [4], only reported was the cationic guest compound,  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$ , in which a half number of the total cavities were left vacant in the structure isomorphous to the  $\text{Cd}(\text{CN})_2$  host. In the present work, besides the reconfirmation of the half-vacant structure, the additional accommodation of the neutral guest molecules into the remaining cavities has been confirmed for the previously-reported  $[\text{ZnCu}(\text{CN})_4]$  host and the novel  $[\text{CdCu}(\text{CN})_4]$ .

Unlike the  $\text{Cd}(\text{CN})_2$  host, two kinds of cavities are formed in the mixed-metal  $[\text{MCu}(\text{CN})_4]$  hosts, since the  $\text{M}^{2+}$  and  $\text{Cu}^+$  are located on the positions crystallographically independent of each other. As for the cavity approximated to the tetrahedron in the adamantane-like skeleton, one cavity is cornered by  $\text{Cu}^+$  atoms, the other by  $\text{M}^{2+}$ ; the former is designated to  $\text{Cu}_4\text{M}_6$  and the latter to  $\text{M}_4\text{Cu}_6$ . In the previous  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$  the cationic guest was reported to prefer  $\text{Zn}_4\text{Cu}_6$  to  $\text{Cu}_4\text{Zn}_6$ . The preference has been reconfirmed in this work, although residues of electron density

remained in  $\text{Cu}_4\text{M}_6$  cavity to a considerable extent in the final difference Fourier map. The preference is still sustained in the  $\text{CCl}_4$  clathrate of the Zn-Cu-mixed host

$[\text{Cu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot 0.9\text{CCl}_4]: [\text{N}(\text{CH}_3)_4]^+$  is accommodated in  $\text{Zn}_4\text{Cu}_6$ ,  $\text{CCl}_4$  in  $\text{Cu}_4\text{Zn}_6$ . In the novel  $[\text{CdCu}(\text{CN})_4]$  host, a disorder in the distribution of the cationic and neutral guests has been observed. At the final stage of the structure refinement, the occupancy ratio 0.54:0.46 was obtained for the  $[\text{N}(\text{CH}_3)_4]^+$  in  $\text{Cd}_4\text{Cu}_6$ .

The orientation of the tetrahedral guest,  $[\text{N}(\text{CH}_3)_4]^+$  and  $\text{CCl}_4$ , should be noted. The  $[\text{N}(\text{CH}_3)_4]^+$  in  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$  takes an orientation contrastive with the  $\text{C}(\text{CH}_3)_4$  in  $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$  in view of the tetrahedral guest in the tetrahedral cavity: the N-CH<sub>3</sub> bond directs toward the face-center of the tetrahedron. The a dimension of the  $\text{F}\bar{4}3\text{m}$  unit cell, 11.671(2) Å (11.609(3) Å in [4]) is contracted to ca. 91% from that of  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4$  due to the smaller radii of  $\text{Zn}^{2+}$  and  $\text{Cu}^+$  than  $\text{Cd}^{2+}$ . Hence, the distance from center to the corner of the tetrahedral cavity,  $\sqrt{3}a/4=5.5054$  Å, becomes too short to accept the N-CH<sub>3</sub> bond directing toward the corner. On additional accommodation of the neutral guest  $\text{CCl}_4$ , the a dimension is slightly elongated by 0.1 Å but both the N-CH<sub>3</sub> and C-Cl bonds are distributed about the threefold axis of crystal similar to the  $\text{CCl}_4$  in the  $\text{Cd}(\text{CN})_2$  host. The similar disorder is observed for the guests in the Cd-Cu mixed host-mixed guest clathrate,  $[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$ , with the values of  $a=12.189(2)$  Å and  $\sqrt{3}a/4=5.278$  Å, which are reduced by ca. 4% from those for  $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ . The difference in the a dimensions of  $[\text{ZnCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4]$  between the present work and previously-reported, by 0.06 Å (ca. 0.5%) greater in the former, leaves little question in this discussion.

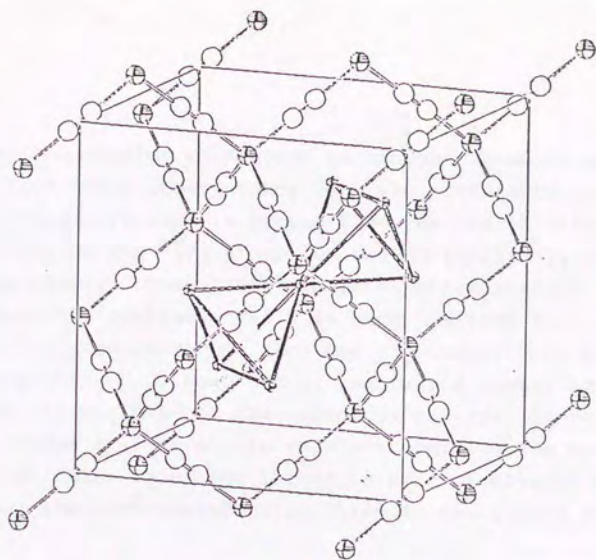
The guests in the neutral mixed-metal host,  $[\text{CdHg}(\text{CN})_4]$  and  $[\text{CdZn}(\text{CN})_4]$ , are quite similar to those in the  $\text{Cd}(\text{CN})_2$  host with respect to the orientational behavior. The a dimensions of the former host clathrates are practically the same to those of the  $\text{Cd}(\text{CN})_2$  host ones for the respective guests  $\text{CCl}_4$  and  $\text{cyclo-C}_6\text{H}_{12}$ . The a dimension of the latter host  $\text{CCl}_4$  clathrate is reduced by ca. 4% from that for  $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$  similarly to the case of  $[\text{CdCu}(\text{CN})_4] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_4]$ .

### 2.2.6 Discussion

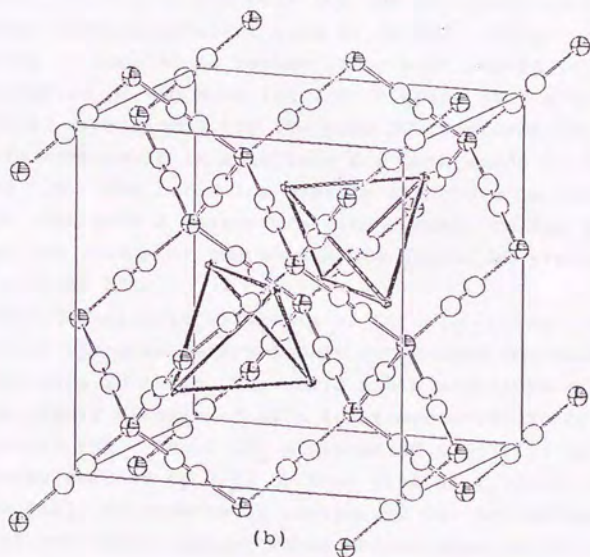
The present series of  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  clathrates have the dimensions, 12.65 - 12.77 Å, of the face-centered cubic (Fd3m) unit cells about two times that of the primitive cubic (Pn3m) unit cell of  $\text{Cd}(\text{CN})_2$  ( $a=6.300(1)$  Å). Hence the host structure is substantially similar to one of the frameworks in the double framework structure of the anticyprite  $\text{Cd}(\text{CN})_2$ . With this respect the conclusion in this work that the cyanide linkage distributes at random between the pair of Cd atoms both in the neat  $\text{Cd}(\text{CN})_2$  and the  $\text{Cd}(\text{CN})_2$  host is more reasonable than assuming an ordered orientation for the cyanide.

The anticyprite structure itself can be seen as an inclusion structure: one framework includes the other. Such an inclusion structure is sometimes called "self-clathrate" [8]. In the self-clathrate structure of the neat  $\text{Cd}(\text{CN})_2$ , the tetrahedral extension of the guest framework passes through the face of the tetrahedron to which the cavity is approximated, i.e., a pair of tetrahedra are coupled with each other by interpenetrating mutually the top of one into the face of the other. The tetrahedral guest taking this orientation, mode A (see Fig. 5a), is only the  $[\text{N}(\text{CH}_3)_4]^+$  in the half-filled structure of the  $[\text{ZnCu}(\text{CN})_4]^-$  host. Since the substituent protruding from the center of a cavity should suffer a steric repulsion from that in next cavity if it is occupied by another guest, the orientation is only possible when next cavity is vacant, so far the guest species examined in this work.

The orientation of the  $\text{C}(\text{CH}_3)_4$ , mode B (see Fig. 5b), is in contrast with that of the  $[\text{N}(\text{CH}_3)_4]^+$ : the guest tetrahedron is just fitted on the inside of the relatively large tetrahedron of the cavity. With this respect the structure can be called "cubic ice-mimetic" or "van der Waals cubic ice". The three-dimensional array of the host framework and the guest molecules inside the cavity builds up the structure similar to that of the cubic ice Ic, but every guest keeps the van der Waals contact with the host framework. The longest a dimension so far observed, 12.767(2) Å, is for the  $\text{C}(\text{CF}_3)\text{Cl}_3$  guest, that for the  $\text{C}(\text{CH}_3)_4$  one being the second longest, 12.752(2) Å. In the former clathrate the guest takes mode B orientation similar to that of  $\text{C}(\text{CH}_3)_4$ . Since the longer the a



(a)



(b)

Fig. 5 (a) Tetrahedral guest taking mode A  
(b) Tetrahedral guest taking mode B

dimension is, the greater void space is brought about in mode B structure. From these observations that the preference of the cubic ice-mimetic structure is caused from the steric fitting between the  $-\text{CH}_3$  or the  $-\text{CF}_3$  group and the  $\text{Cd}-\{(\text{CN})-\text{Cd}\}_3$  tripod corner of the cavity. The effect can be expected stronger for F than H, because the protrusion of F is more distinct than that of H. As for  $-\text{CCl}_3$ , the larger Cl atom and the longer C-Cl bond eventually expel the C-Cl bond out of the tripod corner and shift the C atom in the vicinity of the center of cavity. Since mode A orientation causes a great steric repulsion between the guests, the C-Cl bond distributes about the threefold axis of crystal to reduce the repulsion; the distributed orientation is designated to mode A'.

In mode A', the thermal parameters of the heavy Cd atom is unusually great in general not only for the self-clathrate but also for the organic-guest clathrates such as  $\text{Cd}(\text{CN})_4 \cdot \text{CCl}_4$ . Hence the crystal packing in mode A' is rather loose with regard to the thermal oscillation of the host lattice in spite of the contraction of the unit cell dimensions. In the mode B structures the thermal parameters are reasonable in magnitude for both kinds of host atoms, Cd and C,N. The cubic ice mimetic structure is thermally rather stable than mode A' structure with respect to the host atoms in spite that the volume of the void space should be greater in mode B than in mode A'.

The cubic ice-mimetic structure of  $\text{Cd}(\text{CN})_2 \cdot \text{C}(\text{CH}_3)_4$  gives us first example of the orientation-labile neopentane molecule to take a rigid orientation in solid. The solid state structure of neat neopentane is highly disordered at a low temperature to be approximated to a sphere [9]. The C- $\text{CH}_3$  distance of 1.507(11) Å in the clathrate, being shorter by 0.02 Å than that of 1.539(2) Å in the gaseous state [10], is apparently contracted due to the thermal oscillation of the methyl group, whose carbon atom  $\text{CG}''$  is given a considerably large thermal parameter of  $14.9(2) = \text{Bq}/\text{\AA}^2$ .

A part of this chapter has been published preliminarily [11,12].

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### Chapter 3

#### Clay-like Layered structures

### 3. CLAY-LIKE LAYERED STRUCTURES

#### 3.1. Fundamental View of Natural Clay Minerals

Clay minerals belong to the larger family of phyllosilicates which are characteristic of their layered structures. Among the variation of the clay minerals, the structural features are seen for some representatives.

Talc,  $\text{Mg}_3(\text{OH})_2(\text{Si}_4\text{O}_{10})$ , consists of the electrically neutral layers, in which the sheets of polysilicate, formed by the condensation of tetrahedral  $\text{SiO}_4^{4-}$ , sandwich the octahedral  $\text{Mg}^{2+}$  ions. Each sheet has eventually the structure of a triple deck surfaced by the  $\text{Si}^{4+}$  tetrahedra and centered by the  $\text{Mg}^{2+}$  octahedra. This type of triple deck, i.e., the deck stacked successively with the sub-layers of tetrahedra, octahedra and tetrahedra, is often called "T-O-T" in the field of clay science. The layer of the montmorillonite, of the ideal formula of

$\text{Na}_{1/3}(\text{H}_2\text{O})_4(\text{Al}_{5/3}\text{Mg}_{1/3})(\text{OH})_2(\text{Si}_4\text{O}_{10})_2$ , also has the T-O-T triple deck structure; the negatively charged layers intercalate the hydrated sodium cations in the interlayer space. Chlorite has a double-layer structure of the alternate stacking of talc and blucite,  $\text{Mg}(\text{OH})_2$ , where the neutral layers of the talc intercalate the neutral layer of the blucite.

Characteristic features observed for these structures are as follows: (1) the cationic species at the octahedral position, e.g.,  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$  in montmorillonite, is different from the species at the tetrahedral position,  $\text{Si}^{4+}$ , although some portions of the  $\text{Si}^{4+}$  are replaced by  $\text{Al}^{3+}$  cations in real minerals; (2) electrical charge of the layer is regulated with the number and valence of the cationic and anionic species; (3) negatively-charged layers intercalate positively-charged guests, and neutral layers do sometimes neutral guests; and (4) the surface of the layer is covered by the faces of the tetrahedra in general.

These characteristic features can be mimicked using polycyanopolycadmates, in some cases along with appropriate ligands other than cyanide. The coordination number of cadmium is versatile in a crystal structure: tetrahedral 4, trigonal-bipyramidal 5, and octahedral 6 coordinations can coexist in the polycyanopolycadmamate systems by which one can mimic the silicate structures con-

taining octahedral cations such as  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ . Negatively or positively charged or neutral ligand can join the assembly, acting as the regulator of the electrical charge on the layer. Thus, the clay-like layers made of polycyanopolycadmates have been materialized mineralomimetically in this work. Three kinds of layered structures, the neutral layers intercalating neutral guest, the negatively-charged layers intercalating both cationic and neutral guests, and the negatively-charged layer accommodating cationic guest in the intralayer cavity, have been prepared. All of them have a T-O-T or T-T-O linkage of coordination polyhedra, respectively centered by Cd atoms, as a structural unit. Unlike the clay minerals, the surface of the prepared layer is not the surface of the tetrahedral moiety but the top of the tetrahedral or the octahedral one. Their structures are discussed in this chapter.

### 3.2. Preparation and Properties

#### 3.2.1. $[\text{Cd}_3(\text{CN})_7\text{dmtnH}] \cdot \text{G}$ , group I

The clay-like inclusion compounds formed between the neutral layer of  $\text{Cd}_3(\text{CN})_7\text{dmtnH}$  ( $\text{dmtnH}^+ = \text{NH}_2(\text{CH}_2)_3\text{NH}(\text{CH}_3)_2^+$ ) and the neutral guest G (=  $\text{C}_6\text{H}_5\text{F}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ , or  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ ) were prepared by the procedures as follows. In 100 ml of water 1.77 g (7.75 mmol) of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and 3.16 g (10.72 mmol) of  $\text{K}_2[\text{Cd}(\text{CN})_4]$  were dissolved, and the pH was adjusted to 9.0 by adding citric acid monohydrate and N,N-dimethyl-1,3-diaminopropane ( $\text{NH}_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2 = \text{dmtn}$ ). After the solution was filtered through a plastic membrane of 0.45  $\mu\text{m}$  pore size, it was placed under or over an organic layer of the neat guest. In the case of the isobutyl alcohol as the guest, it was diluted into the aqueous solution. A few days' leaving in a refrigerator gave colorless crystals of the inclusion compounds at the interface between the organic and the aqueous phases, the bottom of the aqueous phase, and/or the top of the aqueous phase. Anal. Found%/calcd% for G =  $\text{C}_6\text{H}_5\text{F}$  (I-1): C, 28.78/30.03; H, 2.87/2.87; N, 18.25/17.54; Cd, 47.1/46.9; for G =  $\text{C}_6\text{H}_6$  (I-2): C, 30.45/30.85; H, 3.02/3.02; N, 18.01/17.99; for G =  $\text{CCl}_4$  (I-3): C, 19.88/20.11; H, 1.96/1.94; N, 16.08/16.23; Cd, 43.2/43.4; for G =  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$  (I-4): C, 25.83/27.59; H,

3.35/3.62; N, 16.69/18.09; Cd, 48.2/48.4.

### 3.2.2. $[\text{Cd}_3(\text{CN})_8] \cdot [\text{2onium} \cdot \text{G}]$ , group II

Group II has the structure that the anionic layers intercalate the cationic onium ( $= \text{N}(\text{CH}_3)_4^+$  or  $\text{N}(\text{CH}_3)_3\text{H}^+$ ) and the neutral guest  $\text{CCl}_2=\text{CCl}_2$  or  $\text{C}_6\text{H}_6$ . At the earlier stage of the investigation tetramethylammonium iodide was used as the source or the cationic guest. The obtained product contained the iodide nonstoichiometrically as the unidentate ligand in place of the cyanide so that it gave the composition  $[\text{Cd}_3(\text{CN})_{6+x}\text{I}_{2-x}] \cdot [\text{2N}(\text{CH}_3)_4 \cdot \text{CCl}_2=\text{CCl}_2]$  for II-1. Using tetramethylammonium chloride the product of the title host composition, II-2, was obtained. The procedures for the three compounds prepared are noted successively.

$[\text{Cd}_3(\text{CN})_{6+x}\text{I}_{2-x}] \cdot [\text{2N}(\text{CH}_3)_4 \cdot \text{CCl}_2=\text{CCl}_2]$  (II-1) - In the aqueous solution containing  $\text{CdCl}_2$  and  $\text{K}_2[\text{Cd}(\text{CN})_4]$  similar to that used in 3.2.1. (solution 1), 1.35 g (6.75 mmol) of  $\text{N}(\text{CH}_3)_4\text{I}$  was dissolved. After the solution was filtered through the plastic membrane, it was placed on a layer of tetrachloroethylene, and kept standing at room temperature for a few days. Colorless plate-like crystals were obtained. Anal. Found%/calcd% for  $x=0.26$ : C, 18.61/18.87; H, 2.33/2.34; N, 11.26/11.18; Cl, 13.58/13.76; I, 21.54/21.33; Cd, 32.8/32.6

$[\text{Cd}_3(\text{CN})_8] \cdot [\text{2N}(\text{CH}_3)_4 \cdot \text{CCl}_2=\text{CCl}_2]$  (II-2) - Instead of  $\text{N}(\text{CH}_3)_4\text{I}$  1.00 g (9.24 mmol) of  $\text{N}(\text{CH}_3)_4\text{Cl}$  was used. Colorless hexagonal plate-like crystals were obtained. Anal. Found%/calcd%: C, 24.23/25.15; H, 2.88/2.82; N, 15.48/16.29; Cl, 15.71/16.49; Cd, 39.9/39.2

$[\text{Cd}_3(\text{CN})_8] \cdot [\text{2N}(\text{CH}_3)_3\text{H} \cdot \text{C}_6\text{H}_6]$  (II-3) - To solution 1 1.55 g of citric acid monohydrate was dissolved. The pH was adjusted to 8.5 by adding 5.5 ml of a 30% aqueous solution of trimethylamine. After the filtration through the plastic membrane, the solution was covered with the neat liquid of benzene. Colorless plate-like crystals were obtained by standing at room temperature for a few days. Anal. Found%/calcd%: C, 31.93/32.30; H, 3.62/3.52; N, 18.72/18.83.

### 3.2.3. $[\text{Cd}_3(\text{CN})_6\text{L}(\text{H}_2\text{O})] \cdot [\text{S}(\text{CH}_3)_3]$ , group III

When trimethylsulfonium salt was used as the source of the

cationic guest, the sulfonium cation was accommodated in the cavity formed in the anionic layer itself. The use of trimethylsulfonium iodide brought about the non-stoichiometric coordination of univalent iodide similar to the case for II-1.

$[\text{Cd}_3(\text{CN})_{6+y}\text{I}_{1-y}(\text{H}_2\text{O})] \cdot [\text{S}(\text{CH}_3)_3]$  (III-1) - Into an aqueous solution of 50 ml containing 4.60 mmol of  $\text{CdCl}_2$  and 4.11 mmol of  $\text{K}_2[\text{Cd}(\text{CN})_4]$  0.55 g (2.27 mmol) of  $\text{S}(\text{CH}_3)_3\text{I}$  was added. After the solution was filtered through the plastic membrane, it was kept standing in a refrigerator for a few days. Colorless needle-like crystals were obtained. Anal. Found%/calcd% for  $y=0.3$ : C, 16.23/16.30; H, 1.65/1.62; N, 12.98/12.87; S, 5.95/4.68; I, 12.58/12.96; Cd, 50.1/49.2.

$[\text{Cd}_3(\text{CN})_7(\text{H}_2\text{O})] \cdot [\text{S}(\text{CH}_3)_3]$  (III-2) - In order to avoid the nonstoichiometric coordination of the iodide, the trimethylsulfonium iodide was converted to the nitrate by the metathesis reaction with silver nitrate. After the precipitate of  $\text{AgI}$  was filtered out, the filtrate containing 6.00 mmol of  $\text{S}(\text{CH}_3)_3^+$  was added to 100 ml of solution 1. The solution was filtered through the plastic membrane, and kept standing in a refrigerator for a few days. Colorless needle-like crystals were obtained. Anal. Found%/calcd%: C, 19.33/19.54; H, 1.82/1.80; N, 15.75/15.95; Cd, 53.7/54.0

#### 3.2.4. Properties

The chemical compositions were identified also by infrared spectroscopy and thermal gravimetry. These compounds are much more stable than those of the cristobalite-like host clathrates discussed in the previous chapter: the crystals are stable at room temperature at least for a few days without any decomposition in appearance. However, they gradually liberate their guests and become powdery by leaving longer under ambient conditions.

As a general tendency of the layered inclusion compounds, the analytical results show the non-stoichiometric character with respect to the host-to-guest ratio. Furthermore, the nonstoichiometric coordination of the iodide was observed in the host composition, when the onium iodide were used as the source of the onium guest to neutralize the negative charge of the host. The coordination of the iodide anion as the iodide ligand was interpreted in

terms of the more stable ligation of  $I^-$  than  $Cl^-$  and  $NO_3^-$  to  $Cd^{2+}$  in aqueous solution. The densities of crystal measured by the flotation method were distributed between 2.04-2.09 g/cm<sup>3</sup> for II-1, and 2.21-2.31 g/cm<sup>3</sup> for III-1. Since the analytical results were obtained for the bulk products, the crystals subjected to the X-ray experiment mentioned later should have their own particular compositions. The refined multiplicities obtained in the structure refinements have supported that  $\bar{x}=0.26$  (II-1) and  $\bar{y}=0.46$  (III-1) for the respective crystals used in the X-ray experiments.

### 3.3. Structure Analyses.

The single crystals subjected to the X-ray experiments were coated with epoxy resin in order to prevent decomposition under ambient conditions. During the collection of intensity data, three representative reflections were measured after every 100 reflections to monitor the stability of each crystal; no significant decay was observed. The crystallographic and selected experimental conditions are listed in Table I.

In the previous communication reporting a part of this work preliminarily[1], the space group  $PI$  had been applied for I-1; however, the latest refinement supported the  $C2/m$  (No.12).

Problems in solving the structures of II-1 and III-1 were the non-stoichiometry of and the disorder between  $I^-$  and  $CN^-$  as the unidentate ligands in their layer structures. Each of the unidentate ligands was assumed to be  $I^-$ , and its occupancy was refined, i.e., the contribution from the cyanide group in place of the iodide ligand was neglected. Therefore, the occupancy has been estimated a little bit greater than the real occupancy. Because of this approximation the distances 2.701(1) Å of  $Cd(t)-I$  in II-1 and 2.674(3) Å of  $Cd(t')-I$  in III-1 became shorter than the usual 3.0 Å due to the less electron densities of  $CN$  in comparison with  $I$ . The non-centrosymmetric  $Cm$  (No.8) space group applied for II-1 in the previous paper [2] has been revised to the centrosymmetric  $C2/m$ , because the refinement for the centrosymmetric structure gave the convergence better than for the non-centrosymmetric one with respect to the host framework.

Table I-1

Crystallographic selected experimental data for Group I-1

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [\text{C}_6\text{H}_5\text{F}]$
Formula	$\text{C}_{18}\text{H}_{20}\text{Cd}_3\text{FN}_9$
F.W.	718.65
Color and habit	colorless plate
Crystal system	monoclinic
Space group	$\text{C2/m}(\text{No. } 12)$
a/Å	20.589(5)
b/Å	9.172(2)
c/Å	14.891(6)
$\beta / ^\circ$	115.60(3)
$V/\text{\AA}^3$	2614(2)
Z	4
$D_m/\text{gcm}^{-3}$	1.82(1)
$D_x/\text{gcm}^{-3}$	1.83
Crystal size/mm	0.25x0.25x0.25
Temperature/K	293
Diffractionmeter	Rigaku AFC5
Radiation, $\lambda / \text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	24.36
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-55
Peak scan width	$1.01 + 0.5 \tan \theta$
Reflections measured	5085
Reflections used	2110( $> 3 \sigma(\text{Fo})$ )
Parameters	168
Solution program	SHELX76
Weight scheme	$w = 1/(\sigma^2 + 0.001012F^2)$
R	0.0407
Rw	0.0631
G.O.F.	1.531
Crystal decay	Not observed
max shift/esd(Host)	0.199
max shift/esd(Guest)	0.797
max & min resid $e \text{\AA}^{-3}$	+1.00(in the cavity)*, -0.68

Table I-2

Crystallographic and selected experimental data for Group I-2

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [\text{C}_6\text{H}_6]$
Formula	$\text{C}_{19}\text{H}_{20}\text{Cd}_3\text{N}_9$
F.W.	700.65
Color and habit	colorless plate
Crystal system	monoclinic
Space group	$\text{C2/m}(\text{No.12})$
a/Å	20.662(7)
b/Å	9.219(4)
c/Å	14.819(5)
$\beta / ^\circ$	115.43(3)
V/Å <sup>3</sup>	2628(2)
Z	4
Dm/gcm <sup>-3</sup>	1.76(1)
Dx/gcm <sup>-3</sup>	1.77
Crystal size/mm	0.30x0.25x0.20
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda$ / Å	Mo K $\alpha$ 0.71069
$\mu$ / cm <sup>-1</sup>	23.99
Scan type	2 $\theta$ - $\omega$
2 $\theta$ range/ $^\circ$	4-60
Peak scan width	1.365+0.3tan $\theta$
Reflections measured	4240
Reflections used	3317( >3 $\sigma$ (Fo) )
Parameters	164
Solution program	SHELX76
Weight scheme	w=1/( $\sigma^2$ +0.006673F <sup>2</sup> )
R	0.0407
Rw	0.0754
G.O.F.	0.8069
Crystal decay	Not observed
max shift/esd(Host)	0.312
max shift/esd(Guest)	0.897
max & min resid e Å <sup>-3</sup>	+1.48*, -2.28

\* near Cd atom

Table I-3

Crystallographic and selected experimental data for Group I-3

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [\text{CCl}_4]$
Formula	$\text{C}_{14}\text{H}_{14}\text{Cd}_3\text{N}_9\text{Cl}_4$
F.W.	776.37
Color and habit	colorless plate
Crystal system	monoclinic
Space group	$\text{C2/m}(\text{No. } 12)$
a/Å	20.405(5)
b/Å	9.067(3)
c/Å	15.181(6)
$\beta / ^\circ$	111.48(3)
V/Å <sup>3</sup>	2614(2)
Z	4
Dm/gcm <sup>-3</sup>	1.97(2)
Dx/gcm <sup>-3</sup>	1.99
Crystal size/mm	0.40x0.25x0.15
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, $\lambda / \text{\AA}$	Mo K $\alpha$ 0.71069
$\mu / \text{cm}^{-1}$	28.40
Scan type	2 $\theta$ - $\omega$
2 $\theta$ range/ $^\circ$	3-60
Peak scan width	$0.903 + 0.35 \tan \theta$
Reflections measured	5586
Reflections used	3317( $>3 \sigma(\text{Fo})$ )
Parameters	164
Solution program	SHELX76
Weight scheme	$w = 1 / ( \sigma^2 + 0.006673F^2 )$
R	0.0703
Rw	0.1129
G.O.F.	1.035
Crystal decay	Not observed
max shift/esd(Host)	0.217
max shift/esd(Guest)	0.897
max & min resid	
e Å <sup>-3</sup>	+0.48 , -0.56k

Table I-4

Crystallographic and selected experimental data for Group I-4

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [(\text{CH}_3)_2\text{CHCH}_2\text{OH}]$
Formula	$\text{C}_{16}\text{H}_{19}\text{Cd}_3\text{N}_9\text{O}$
F.W.	696.67
Color and habit	colorless plate
Crystal system	monoclinic
Space group	$\text{C2/m}(\text{No. } 12)$
a/Å	20.481(3)
b/Å	9.091(2)
c/Å	15.030(3)
$\beta / ^\circ$	111.29(1)
V/Å <sup>3</sup>	2607(1)
Z	4
Dm/gcm <sup>-3</sup>	1.76(2)
Dx/gcm <sup>-3</sup>	1.78
Crystal size/mm	0.50x0.35x0.30
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda / \text{Å}$	Mo K $\alpha$ 0.71069
$\mu / \text{cm}^{-1}$	24.39
Scan type	2 $\theta$ - $\omega$
2 $\theta$ range/ $^\circ$	4-60
Peak scan width	1.20+0.35tan $\theta$
Reflections measured	4172
Reflections used	3311( >3 $\sigma$ (Fo) )
Parameters	178
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2+0.01F^2)$
R	0.0480
Rw	0.0881
G.O.F.	0.799
Crystal decay	Not observed
max shift/esd(Host)	0.188
max shift/esd(Guest)	0.797
max & min resid	
e Å <sup>-3</sup>	+1.33*, -2.61

\*near amine

Table I-5

Crystallographic and selected experimental data for Group II-1

Compound	$[\text{Cd}_3(\text{CN})_{6.29}\text{I}_{1.71}] \cdot [2\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_2=\text{CCl}_2]$
Formula	$\text{C}_{16.29}\text{H}_{12}\text{Cd}_3\text{N}_9\text{I}_{1.71}\text{Cl}_4$
F.W.	1035.04
Color and habit	colorless plate
Crystal system	monoclinic
Space group	$\text{C2/m}(\text{No.}12)$
a/Å	15.467(3)
b/Å	8.541(7)
c/Å	12.84(2)
$\beta / ^\circ$	92.01(7)
V/Å <sup>3</sup>	1696(2)
Z	2
Dm/gcm <sup>-3</sup>	2.04-2.09
Dx/gcm <sup>-3</sup>	2.03
Crystal size/mm	0.25x0.25x0.09
Temperature/K	293
Diffractometer	Rigaku AFC5R
Radiation, $\lambda / \text{\AA}$	Mo K $\alpha$ 0.71069
$\mu / \text{cm}^{-1}$	38.68
Scan type	2 $\theta$ - $\omega$
2 $\theta$ range/ $^\circ$	4-60
Peak scan width	0.97+0.35tan $\theta$
Reflections measured	5015
Reflections used	1925( >3 $\sigma$ (Fo) )
Parameters	192
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2+0.028244F^2)$
R	0.0778
Rw	0.1188
G.O.F.	0.666
Crystal decay	Not observed
max shift/esd(Host)	0.028
max shift/esd(Guest)	0.303
max & min resid	
e Å <sup>-3</sup>	+1.33, -2.61

Table I-6

Crystallographic and selected experimental data for Group II-2

Compound	$[\text{Cd}_3(\text{CN})_8] \cdot [\text{2N}(\text{CH}_3)_4 \cdot \text{Cl}_2\text{C}=\text{CCl}_2]$
Formula	$\text{C}_{18}\text{H}_{24}\text{Cd}_3\text{N}_{10}\text{Cl}_4$
F.W.	859.50
Color and habit	colorless hexagonal plate
Crystal system	trigonal
Space group	$\text{P}\bar{3}\text{m1}(\text{No. } 162)$
$a/\text{\AA}$	8.7675(7)
$c/\text{\AA}$	12.695(2)
$V/\text{\AA}^3$	845.1(2)
Z	1
$D_m/\text{gcm}^{-3}$	1.70(2)
$D_x/\text{gcm}^{-3}$	1.69
Crystal size/mm	0.20x0.10x0.07
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	Mo K $\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	21.68
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.52 + 0.30 \tan \theta$
Reflections measured	1918
Reflections used	786 ( $>4 \sigma(F_o)$ )
Parameters	54
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.001302F^2)$
R	0.0531
Rw	0.0863
G.O.F.	1.945
Crystal decay	Not observed
max shift/esd(Host)	0.128
max shift/esd(Guest)	0.503
max & min resid $e \text{\AA}^{-3}$	+1.02*, -1.19

\*near Cd

Table I-7

Crystallographic and selected experimental data for Group II-3

Compound	$[\text{Cd}_3(\text{CN})_8] \cdot [2\text{N}(\text{CH}_3)_3\text{H} \cdot \text{C}_6\text{H}_6]$
Formula	$\text{C}_{20}\text{H}_{26}\text{Cd}_3\text{N}_{10}$
F.W.	743.72
Color and habit	colorless plate
Crystal system	monoclinic
Space group	$\text{C2/m}(\text{No.12})$
a/Å	17.979(5)
b/Å	9.027(3)
c/Å	11.187(4)
$\beta/^\circ$	99.70(3)
$V/\text{\AA}^3$	1491(1)
Z	2
$D_m/\text{gcm}^{-3}$	1.65(2)
$D_x/\text{gcm}^{-3}$	1.66
Crystal size/mm	0.20x0.15x0.15
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	21.18
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$0.70+0.30\tan\theta$
Reflections measured	2530
Reflections used	1544( $>3\sigma(\text{Fo})$ )
Parameters	107
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2+0.0018\text{F}^2)$
R	0.0602
Rw	0.0851
G.O.F.	1.370
Crystal decay	Not observed
max shift/esd(Host)	0.024
max shift/esd(Guest)	0.373
max & min resid	
$e\text{\AA}^{-3}$	+0.99*, -2.92

\* In the cavity

Table I-8

Crystallographic and selected experimental data for Group III-1

Compound	$[\text{Cd}_3(\text{CN})_{6.49}\text{I}_{0.51}\text{H}_2\text{O}] \cdot [\text{S}(\text{CH}_3)_3]$
Formula	$\text{C}_{20}\text{H}_{26}\text{Cd}_3\text{N}_{10}$
F.W.	665.99
Color and habit	colorless needle-like
Crystal system	orthorhombic
Space group	$\text{Pnam}(\text{No. } 62)$
$a/\text{\AA}$	20.745(5)
$b/\text{\AA}$	11.362(2)
$c/\text{\AA}$	8.299(2)
$V/\text{\AA}^3$	1956(1)
$Z$	4
$D_m/\text{gcm}^{-3}$	2.21-2.31
$D_x/\text{gcm}^{-3}$	2.26
Crystal size/mm	0.30x0.30x0.20
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	40.35
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	4-60
Peak scan width	$1.03 + 0.30 \tan \theta$
Reflections measured	3324
Reflections used	2220 ( $>3 \sigma(F_o)$ )
Parameters	119
Solution program	SHELX76
Weight scheme	$w = 1/(\sigma^2 + 0.0018F^2)$
$R$	0.0535
$R_w$	0.1016
G.O.F.	0.6975
Crystal decay	Not observed
max shift/esd(Host)	0.016
max shift/esd(Guest)	0.044
max & min resid $e \text{\AA}^{-3}$	+1.12*, -1.85

\* near Cd atom

Table I-9

Crystallographic and selected experimental data for Group III-2

Compound	$[\text{Cd}_3(\text{CN})_7\text{H}_2\text{O}] \cdot [\text{S}(\text{CH}_3)_3]$
Formula	$\text{C}_{20}\text{H}_{26}\text{Cd}_3\text{N}_{10}$
F.W.	602.52
Color and habit	colorless needle-like
Crystal system	orthorhombic
Space group	Pnam(No. 62)
a/Å	20.761(3)
b/Å	11.331(1)
c/Å	8.277(2)
V/Å <sup>3</sup>	1947(1)
Z	4
Dm/gcm <sup>-3</sup>	2.11(2)
Dx/gcm <sup>-3</sup>	2.10
Crystal size/mm	0.25x0.20x0.15
Temperature/K	293
Diffractionmeter	Rigaku AFC5
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	33.28
Scan type	2θ-ω
2θ range/°	4-60
Peak scan width	0.87+0.30tan θ
Reflections measured	3307
Reflections used	2426( >3 σ(Fo) )
Parameters	124
Solution program	SHELX76
Weight scheme	w=1/( σ <sup>2</sup> +0.0372F <sup>2</sup> )
R	0.0716
Rw	0.1121
G.O.F.	0.5731
Crystal decay	Not observed
max shift/esd(Host)	0.124
max shift/esd(Guest)	0.244
max & min resid e Å <sup>-3</sup>	+1.63*, -3.17

\* near Cd atom

All the non-hydrogen atoms were refined anisotropically; the atomic parameters are listed in Table II. The guest species including the onium cations in general take disorder in their orientations.

### 3.4. Refined Structures

#### 3.4.1. Layer Structures

The structures analyzed are illustrated in Fig. 1 for group I, in Fig. 2 for group II, and in Fig. 3 for group III. As these show, the layered inclusion compounds prepared in this work have the structure like clay minerals. The three types of the layers are compared one another in Fig. 4.

The T-O-T or T-T-O structure units are seen for all the layers of groups I, II, and III. Each unit cell of group I and group III compounds contains crystallographically independent one octahedral Cd(o), and two tetrahedral Cd(t) and Cd(t') atoms. In those of group II the two Cd(t) is correlated with each other to the Cd(o) at the inversion center. Although some options are possible to select a T-O-T or T-T-O unit moiety, one can select the unit on the mirror plane of each crystal. The Cd atoms are bridged one another by the cyanide groups behaving ambidentately; Cd(t) has always been selected as such that it is coordinated with four C ends of cyanide groups.

The layer of I consists of Cd(t) in  $\text{CdC}_4$ , Cd(t') in  $\text{CdC}_3\text{N}$ , and Cd(o) in  $\text{CdN}_6$  coordination. Cd(o) is coordinated with five N ends of the cyanide groups, two each from two each of Cd(t) and Cd(t') and one from another Cd(t); the sixth N is of the amino group of the unidentate  $\text{dmtnH}^+$  which is protonated at the dimethylamino side. Cd(t) provides the four N ends for two each Cd(o) and Cd(t'). Cd(t') provides the two N ends for two Cd(o) and receives one N end from Cd(t) to join the framework of the layer, but leaves one CN group as a unidentate ligand protruding from the layer. Thus the framework of the layer has the composition  $\text{Cd}_3(\text{CN})_6\text{LL}'$ , where both  $\text{L} = \text{CN}^-$  and  $\text{L}' = \text{dmtnH}^+$  behave unidentately. The frameworks of groups II and III also have the same composition. Since  $\text{Cd}_3(\text{CN})_6 = 3\text{Cd}(\text{CN})_2$  is electrically neutral, charge of the layer depends on

Table II-1 Atomic parameters for group I-1  
 $[\text{Cd}_3(\text{CN})_7] \cdot \text{dmtnH} \cdot \text{C}_6\text{H}_5\text{F}$  clathrate

Host $\text{Cd}_3(\text{CN})_7\text{dmtnH}$				
Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(t)	0.14455(3)	0.0	0.08551(5)	2.96(1)
Cd(t')	0.03061(4)	0.0	0.36536(5)	3.48(1)
Cd(o)	0.43352(3)	0.0	0.15054(5)	3.00(1)
N(1)	0.3156(4)	0.0	0.1253(6)	4.3(1)
C(1)	0.2589(5)	0.0	0.1137(7)	3.7(1)
N(2)	0.1258(5)	0.0	0.5991(6)	5.7(1)
C(2)	0.0930(5)	0.0	0.5191(6)	3.8(1)
N(3)	0.1046(5)	0.0	0.2820(7)	6.0(1)
C(3)	0.1233(6)	0.0	0.2191(8)	5.0(1)
N(4)	0.4606(3)	0.1867(7)	0.2619(4)	4.7(1)
C(4)	0.4814(4)	0.2916(8)	0.3016(5)	4.0(1)
N(5)	0.4111(3)	0.1858(7)	0.0298(4)	4.3(1)
C(5)	0.3957(3)	0.2947(7)	-0.0072(5)	3.6(1)
N(6)	0.5487(4)	0.0	0.1565(6)	5.1(1)
C(6)	0.6040(6)	0.0	0.2499(8)	7.2(1)
C(7)*	0.6755(7)	0.048(2)	0.2590(9)	5.2(1)
C(8)*	0.7049(6)	0.034(2)	0.1970(9)	5.8(1)
N(7)	0.7786(4)	0.0	0.2103(6)	4.2(1)
C(9)	0.7965(7)	0.132(2)	0.1679(9)	13.1(2)
C(G1)	0.264(1)	0.0	0.452(2)	13.3(2)
C(G2)	0.410(1)	0.0	0.446(2)	14.0(2)
C(G3)	0.306(1)	0.118(2)	0.458(2)	18.6(2)
C(G4)	0.3636(9)	0.106(2)	0.425(1)	16.5(2)
F*	0.251(2)	0.198(3)	0.453(3)	18.2(2)

\* Occupancy of 0.5 has been given due to disorder.

Table II-2 Atomic parameters for type I-2  
 $[\text{Cd}_3(\text{CN})_7] \cdot \text{dmtnH} \cdot \text{C}_6\text{H}_6$  clathrate

Host  $\text{Cd}_3(\text{CN})_7\text{dmtnH}$

Atom	x	y	z	Beq/Å <sup>2</sup>
Cd(t)	0.14314(2)	0.0	0.08362(3)	2.78(2)
Cd(t')	0.02779(3)	0.0	0.36516(3)	3.21(2)
Cd(o)	0.43228(2)	0.0	0.15247(3)	2.81(2)
N(1)	0.3140(3)	0.0	0.1250(5)	4.0(3)
C(1)	0.2565(4)	0.0	0.1129(6)	3.7(3)
N(2)	0.1281(4)	0.0	0.6004(5)	4.9(3)
C(2)	0.0926(4)	0.0	0.5190(5)	3.4(3)
N(3)	0.1008(3)	0.0	0.2794(5)	5.4(3)
C(3)	0.1201(5)	0.0	0.2166(6)	4.2(3)
N(4)	0.4582(3)	0.1878(5)	0.2631(4)	4.5(2)
C(4)	0.4784(3)	0.2922(6)	0.3023(4)	3.5(2)
N(5)	0.4108(3)	0.1875(5)	0.0317(4)	4.4(2)
C(5)	0.3971(3)	0.2943(5)	-0.0049(3)	3.4(2)
N(6)	0.5487(3)	0.0	0.1594(5)	5.0(4)
C(6)	0.6032(5)	0.0	0.2569(7)	7.6(8)
C(7)*	0.6764(6)	0.044(1)	0.2648(8)	5.0(5)
C(8)*	0.7040(5)	0.042(1)	0.2032(8)	4.0(4)
N(7)	0.7764(3)	0.0	0.2090(5)	3.8(2)
C(9)	0.7973(7)	0.130(2)	0.1644(8)	13.2(8)

Guest  $\text{C}_6\text{H}_6$

C(G1)	0.268(1)	0.0	0.456(2)	18(2)
C(G2)	0.399(2)	0.0	0.440(3)	15(2)
C(G3)	0.307(1)	0.118(2)	0.453(2)	16(1)
C(G4)	0.373(1)	0.104(2)	0.450(2)	16(2)

\* Occupancy of 0.5 has been given due to disorder.neutral guest

Table II-3 Atomic parameters for group I-3  
 $[\text{Cd}_3(\text{CN})_7\text{dmtnH}] \cdot \text{CCl}_4$  clathrate

Host $\text{Cd}_3(\text{CN})_7\text{dmtnH}$				
Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(t)	0.14428(2)	0.0	0.08816(3)	2.68(3)
Cd(t')	0.03528(3)	0.0	0.36874(3)	3.08(3)
Cd(o)	0.43609(2)	0.0	0.14878(3)	2.58(3)
N(1)	0.3165(3)	0.0	0.1197(5)	3.5(2)
C(1)	0.2592(4)	0.0	0.1099(6)	2.8(2)
N(2)	0.1280(4)	0.0	0.6014(5)	5.0(2)
C(2)	0.0936(4)	0.0	0.5212(5)	3.5(2)
N(3)	0.1129(2)	0.0	0.2863(5)	5.5(2)
C(3)	0.1285(5)	0.0	0.2230(6)	4.4(2)
N(4)	0.4627(3)	0.1903(5)	0.2568(4)	4.3(2)
C(4)	0.4835(3)	0.2937(6)	0.3006(4)	3.7(2)
N(5)	0.4143(3)	0.1863(5)	0.0305(4)	4.3(2)
C(5)	0.3969(3)	0.2937(5)	-0.0102(3)	3.3(2)
N(6)	0.5533(3)	0.0	0.1563(5)	4.5(2)
C(6)	0.6090(5)	0.0	0.2467(7)	7.7(2)
C(7)*	0.6821(6)	0.0462(14)	0.2522(8)	6.9(2)
C(8)*	0.7135(5)	0.0483(12)	0.1998(8)	5.4(2)
N(7)	0.7847(3)	0.0	0.2090(5)	3.3(2)
C(9)	0.8036(7)	0.1316(16)	0.1637(8)	13.0(2)
Guest $\text{CCl}_4$				
				O.C
C(10)	0.341(1)	0.0	0.451(1)	7.7(2)
Cl(1)	0.3244(17)	0.0	0.3364(6)	16.2(2) 0.6
Cl(2)	0.3057(8)	0.152(1)	0.4843(9)	14.5(2) 0.6
Cl(3)	0.4169(8)	0.078(1)	0.5250(9)	19.6(2) 0.684(2)
Cl(4)	0.260(2)	0.0	0.475(2)	19.7(2) 0.430(4)

\* Occupancy of 0.5 has been given due to disorder

Table II-4 Atomic parameters for group I-4

 $[\text{Cd}_3(\text{CN})_7 \cdot \text{dmtnH}] \cdot (\text{CH}_3)_2\text{HCH}_2\text{OH}$  clathrateHost  $\text{Cd}_3(\text{CN})_7\text{dmtnH}$ 

Atom	x	y	z	Beq/Å <sup>2</sup>
Cd(t)	0.14432(3)	0.0	0.08711(4)	2.61(2)
Cd(t')	0.03316(3)	0.0	0.36883(3)	2.97(2)
Cd(o)	0.43482(2)	0.0	0.15074(4)	2.56(2)
N(1)	0.3172(4)	0.0	0.1241(6)	3.8(1)
C(1)	0.2594(4)	0.0	0.1130(6)	3.3(1)
N(2)	0.1262(5)	0.0	0.6009(5)	5.0(2)
C(2)	0.0954(5)	0.0	0.5230(5)	3.7(2)
N(3)	0.1092(5)	0.0	0.2870(6)	5.4(2)
C(3)	0.1247(5)	0.0	0.2207(7)	4.4(2)
N(4)	0.4611(3)	0.1890(6)	0.2622(4)	4.3(1)
C(4)	0.4822(3)	0.2926(7)	0.3007(4)	3.7(1)
N(5)	0.4131(3)	0.1873(6)	0.0330(4)	4.0(1)
C(5)	0.3983(3)	0.2935(6)	-0.0052(4)	3.4(1)
N(6)	0.5511(4)	0.0	0.1538(6)	4.7(2)
C(6)	0.6056(6)	0.0	0.2470(7)	6.7(2)
C(7)*	0.6810(6)	0.046(2)	0.2577(9)	5.6(2)
C(8)*	0.7096(5)	0.044(2)	0.1965(8)	5.0(2)
N(7)	0.7821(3)	0.0	0.2069(5)	3.1(2)
C(9)	0.8047(8)	0.124(1)	0.1672(8)	11.5(2)

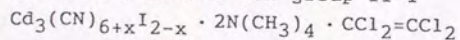
Guest  $(\text{CH}_3)_2\text{HCH}_2\text{OH}$ 

O	0.129(1)	0.5	0.554(2)	17.4(2)
C(10)	0.194(2)	0.418(2)	0.555(2)	13.8(2)
C(11)	0.207(2)	0.375(2)	0.519(2)	12.4(2)
C(12)	0.209(2)	0.378(2)	0.628(2)	13.6(2)
C(13)	0.204(2)	0.277(2)	0.638(2)	14.2(2)

\* Occupancy of 0.5 has been given due to disorder

Table II-5

Atomic parameters for group II-1



Host $\text{Cd}_3(\text{CN})_{6+x}\text{I}_{2-x}$				
Atom	x	y	z	Beq/ Å <sup>2</sup>
Cd(t)	0.32889(5)	0.0	0.19325(7)	2.72(3)
Cd(o)	0.0	0.0	0.0	2.50(4)
I	0.3619(1)	0.0	0.4012(1)	7.32(9)
N(1)	0.1196(8)	0.0	0.1162(9)	4.2(2)
C(1)	0.1898(8)	0.0	0.149(1)	3.5(2)
N(2)	-0.0707(6)	0.191(1)	0.0917(7)	4.6(2)
C(2)	-0.1073(6)	0.293(1)	0.1261(7)	3.8(2)
Guest $\text{CCl}_2=\text{CCl}_2$				
Cl(1)	0.1360(4)	0.0	0.4714(5)	7.3(2)
Cl(2)	0.0294(5)	0.0	0.6619(4)	10.2(2)
C(3)	0.028(2)	0.0	0.529(2)	7.4(2)
Guest $\text{N}(\text{CH}_3)_4$				
N(3)	0.3422(8)	0.0	0.7511(9)	4.4(2)
C(4)	0.333(2)	0.162(2)	0.703(2)	10.4(2)
C(5)	0.274(2)	0.105(2)	0.703(2)	8.8(2)
C(6)	0.334(2)	0.054(3)	0.860(2)	11.7(2)
C(7)	0.404(2)	0.133(2)	0.724(2)	10.6(2)

\* Occupancy of 0.5 has been given due to disorder.

Table II-6

Atomic parameters for group II-2,  $\text{Cd}_3(\text{CN})_8 \cdot 2\text{N}(\text{CH}_3)_4 \cdot \text{CCl}_2=\text{CCl}_2$ Host  $\text{Cd}_3(\text{CN})_8$ 

Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(t)	1/3	2/3	0.19859(7)	2.95(2)
Cd(o)	0.0	0.0	0.0	2.80(2)
N(1)	1/3	2/3	0.460(1)	9.7(1)
C(1)	1/3	2/3	0.373(1)	5.9(1)
N(2)	0.1274(5)	=-X	0.1022(6)	4.6(1)
C(2)	0.1965(5)	=-X	0.1356(6)	3.8(1)

Guest  $\text{CCl}_2=\text{CCl}_2$ 

					occupancy
Cl(1)	0.0406(7)	=-X	0.3371(6)	8.9(1)	1/3
Cl(2)	0.1349(7)	=-X	0.4628(8)	8.7(1)	1/3
C(3)	0.038(1)	=-X	0.535(1)	5.9(1)	1/3

Guest  $\text{N}(\text{CH}_3)_4$ 

N(3)	1/3	2/3	0.751(1)	5.5(1)
C(4)	1/3	2/3	0.867(1)	10.2(1)
C(5)	0.2523(4)	=-X	0.713(1)	16.9(1)

Table II-7 Atomic parameters for II-3  
 $\text{Cd}_3(\text{CN})_8 \cdot 2\text{N}(\text{CH}_3)_3\text{H} \cdot \text{C}_6\text{H}_6$

Host $\text{Cd}_3(\text{CN})_8$				
Atom	x	y	z	Beq/Å <sup>2</sup>
Cd(t)	0.37129(6)	0.0	0.22753(8)	2.45(5)
Cd(o)	0.0	0.0	0.0	2.31(5)
N(1)	0.366(1)	0.0	0.526(1)	7.0(3)
C(1)	0.371(1)	0.0	0.423(1)	3.8(3)
N(2)	0.1505(9)	0.0	0.010(1)	4.0(3)
C(2)	0.225(1)	0.0	0.139(1)	3.6(3)
N(3)	-0.0425(6)	0.191(1)	0.1210(7)	3.7(3)
C(3)	-0.0677(7)	0.298(1)	0.1601(8)	3.2(3)
Guest $\text{C}_6\text{H}_6$				
C(4)	0.043(2)	0.0	0.402(2)	9.8(3)
C(5)	0.021(1)	0.137(2)	0.451(1)	7.9(3)
Guest $\text{N}(\text{CH}_3)_3\text{H}$				Occupancy
N(4)	0.2052(8)	0.5	0.263(1)	3.6(3)
C(6)	0.197(3)	0.348(4)	0.202(4)	8.3(4) 0.375
C(7)	0.299(2)	0.5	0.307(3)	11.1(4) 0.75
C(8)	0.239(3)	0.351(4)	0.277(4)	9.8(4) 0.375
C(9)	0.151(3)	0.418(4)	0.151(3)	7.0(4) 0.375

Table II-8 Atomic coordinate for type Group III-1  
 $\text{Cd}_3(\text{CN})_{6+y}\text{I}_{1-y}(\text{H}_2\text{O}) \cdot \text{S}(\text{CH}_3)_3$

Host $\text{Cd}_3(\text{CN})_{6+y}\text{I}_{1-y}(\text{H}_2\text{O})$				
Atom	x	y	z	Beq/ Å <sup>2</sup>
Cd(t)	0.35667(5)	0.75982(8)	0.25	2.62(2)
Cd(t')	0.51499(5)	0.36100(9)	0.25	2.67(2)
Cd(o)	0.09701(5)	0.58975(9)	0.25	2.43(2)
I*	0.6395(1)	0.4219(3)	0.25	6.28(6)
O	-0.0072(6)	0.496(1)	0.25	4.5(2)
N(1)	0.2016(7)	0.663(1)	0.25	3.5(2)
C(1)	0.2540(8)	0.693(1)	0.25	3.1(2)
N(2)	0.4525(7)	0.525(1)	0.25	3.9(2)
C(2)	0.4201(7)	0.606(1)	0.25	2.7(2)
N(3)	0.0541(5)	0.7076(9)	0.448(1)	3.8(1)
C(3)	0.0288(4)	0.7628(9)	0.544(1)	3.0(1)
N(4)	0.1214(3)	0.4499(8)	0.446(1)	3.8(1)
C(4)	0.1310(5)	0.382(1)	0.542(1)	3.2(1)
$\text{S}(\text{CH}_3)_3$				
S(1)**	0.3372(4)	0.3238(8)	0.25	3.5(1)
S(2)**	0.2660(4)	0.3140(9)	0.25	5.4(2)
C(G1)	0.314(1)	0.178(2)	0.25	7.8(6)
C(G2)	0.300(1)	0.386(2)	0.419(2)	7.0(3)

\* The occupancy has been refined to 0.514(3)

\*\* Occupancy of 0.5 has been given due to disorder.

Table II-9 Atomic coordinate for type  $\text{Cd}_3(\text{CN})_7(\text{H}_2\text{O}) \cdot \text{S}(\text{CH}_3)_3$

Host  $\text{Cd}_3(\text{CN})_7(\text{H}_2\text{O})$

Atom	x	y	z	Beq/ Å <sup>2</sup>
Cd(t)	0.35627(4)	0.75860(6)	0.25	2.64(2)
Cd(t')	0.51604(4)	0.36035(6)	0.25	2.76(2)
Cd(o)	0.09677(3)	0.58943(6)	0.25	2.47(2)
O	-0.0077(4)	0.4975(9)	0.25	4.9(1)
N(1)	0.2021(5)	0.6622(8)	0.25	3.5(1)
C(1)	0.2537(5)	0.6937(7)	0.25	3.0(1)
N(2)	0.4538(5)	0.5236(7)	0.25	3.6(1)
C(2)	0.4221(5)	0.6063(8)	0.25	3.1(1)
N(3)	0.0549(3)	0.7083(6)	0.4473(7)	3.5(1)
C(3)	0.0280(3)	0.7630(6)	0.5416(8)	3.0(1)
N(4)	0.1214(4)	0.4489(5)	0.4447(8)	3.9(1)
C(4)	0.1312(4)	0.3797(6)	0.5413(8)	3.3(1)
N(5)	0.663(1)	0.427(2)	0.25	15.3(1)
C(5)	0.6164(8)	0.404(1)	0.25	6.7(1)

$\text{S}(\text{CH}_3)_3$

S(1)*	0.3366(3)	0.3219(5)	0.25	3.8(1)
S(2)*	0.2647(4)	0.3131(5)	0.25	4.9(1)
C(G1)	0.3145(1)	0.176(1)	0.25	4.9(1)
C(G2)	0.3010(6)	0.391(1)	0.423(2)	7.3(1)

\* Occupancy of 0.5 has been given due to disorder.

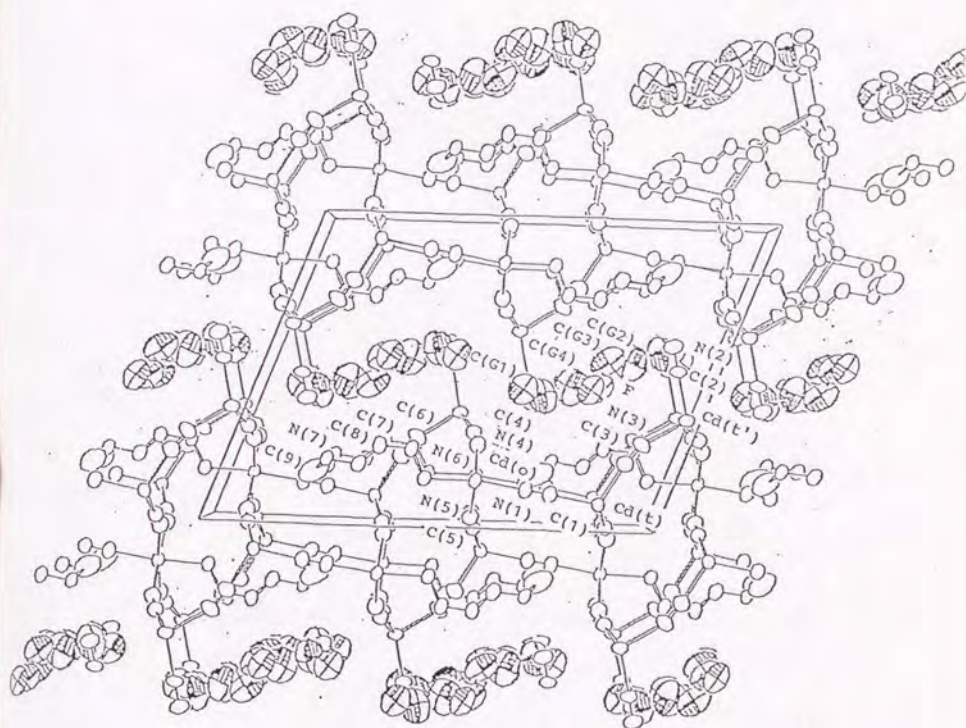


Fig. 1-1 View of the unit cell of I-1 along the b-axis.

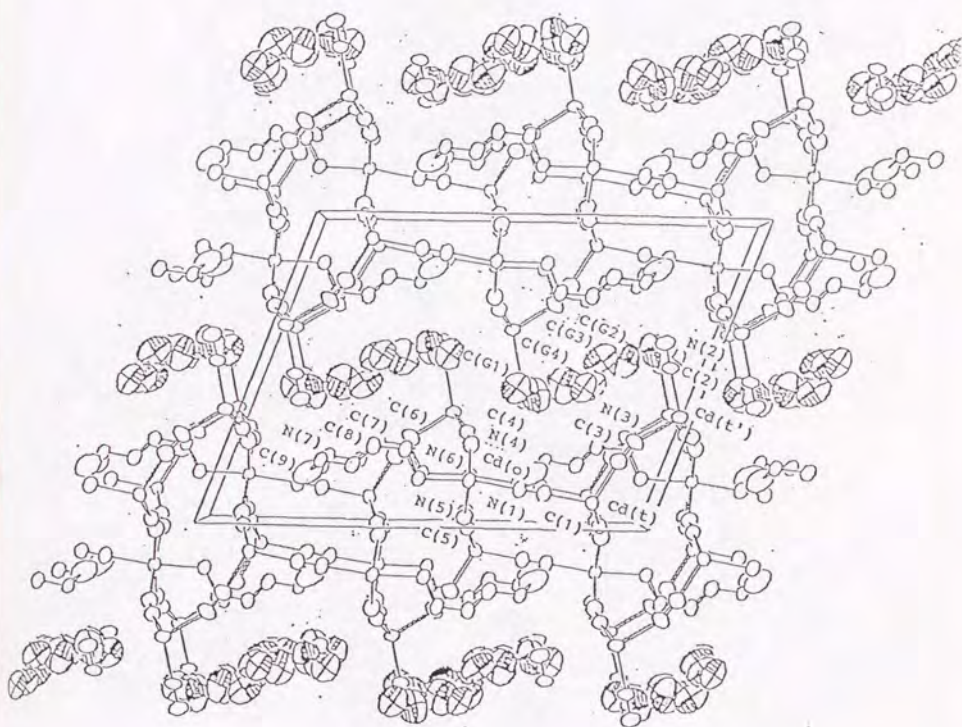


Fig. 1-2 View of the unit cell of I-2 along the b-axis.

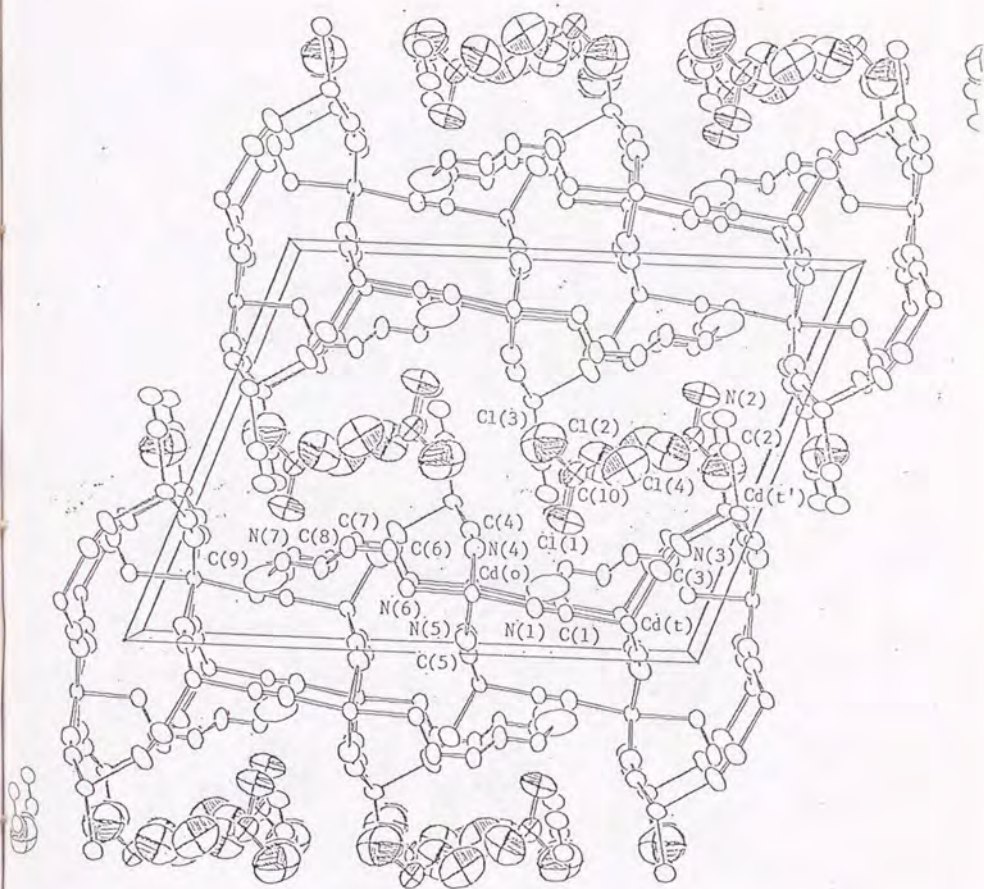


Fig. 1-3 View of the unit cell of I-3 along the b-axis.

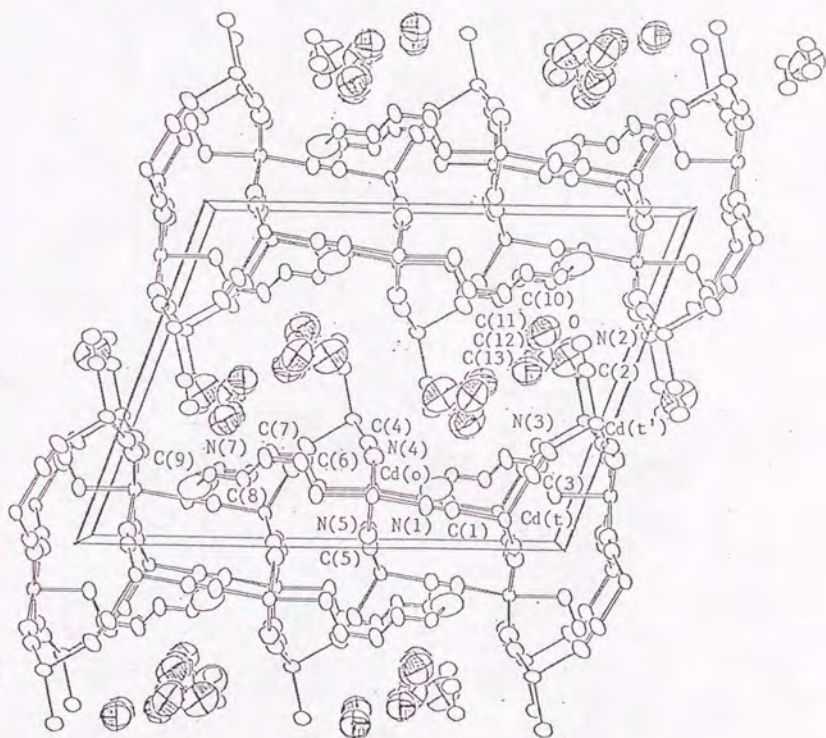


Fig. 1-4 View of the unit cell of 1-4 along the b-axis.

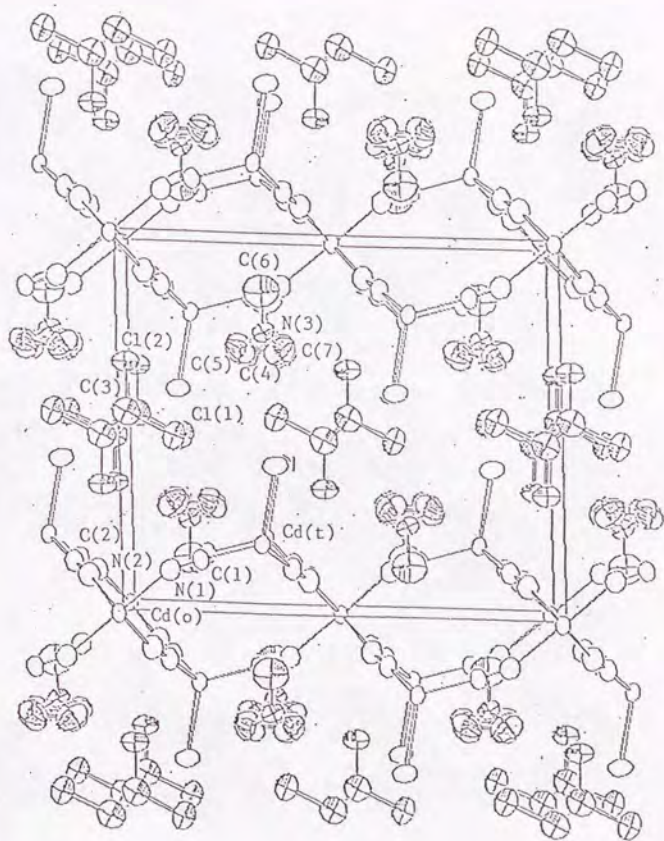


Fig. 2-1 View of the unit cell of II-1 along the b-axis.

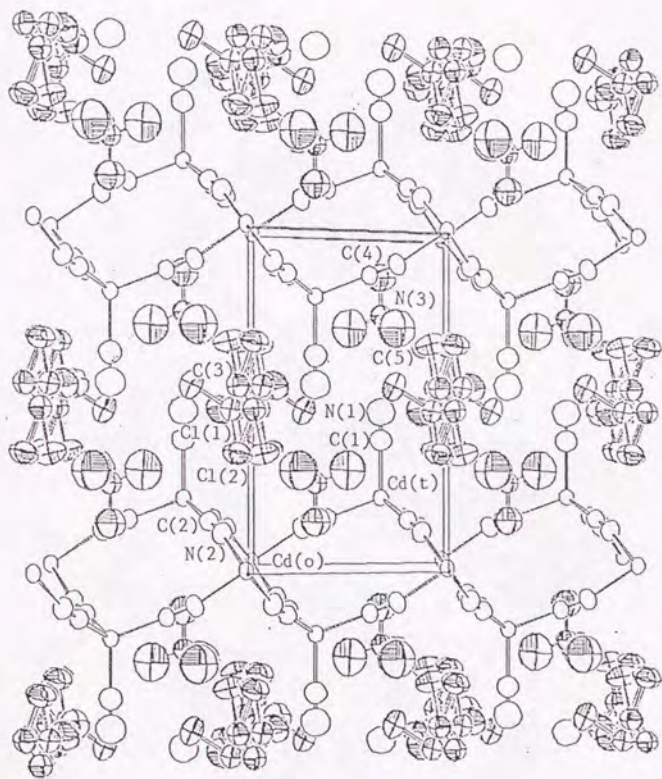


Fig. 2-2 View of the unit cell of II-2 along the *a*-axis.

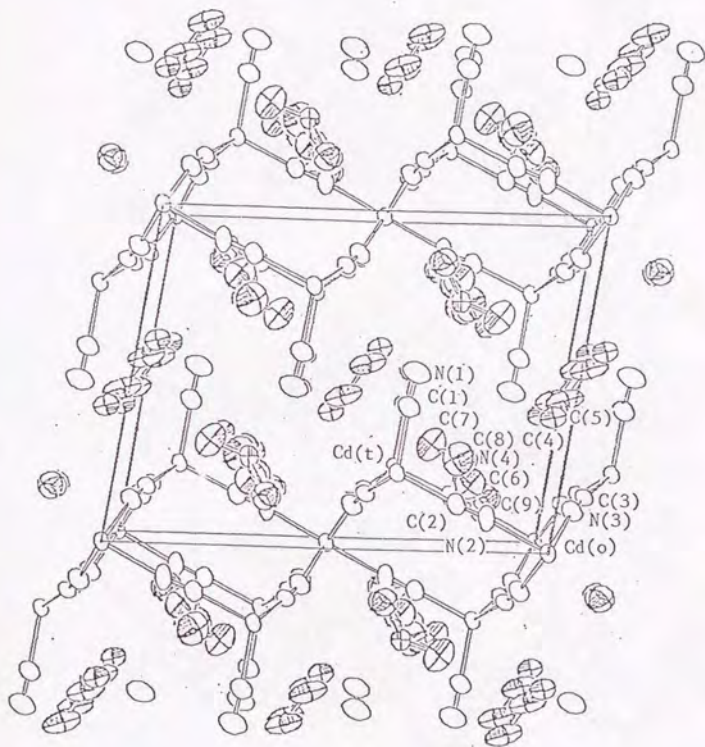


Fig. 2-3 View of the unit cell of II-3 along the b-axis.

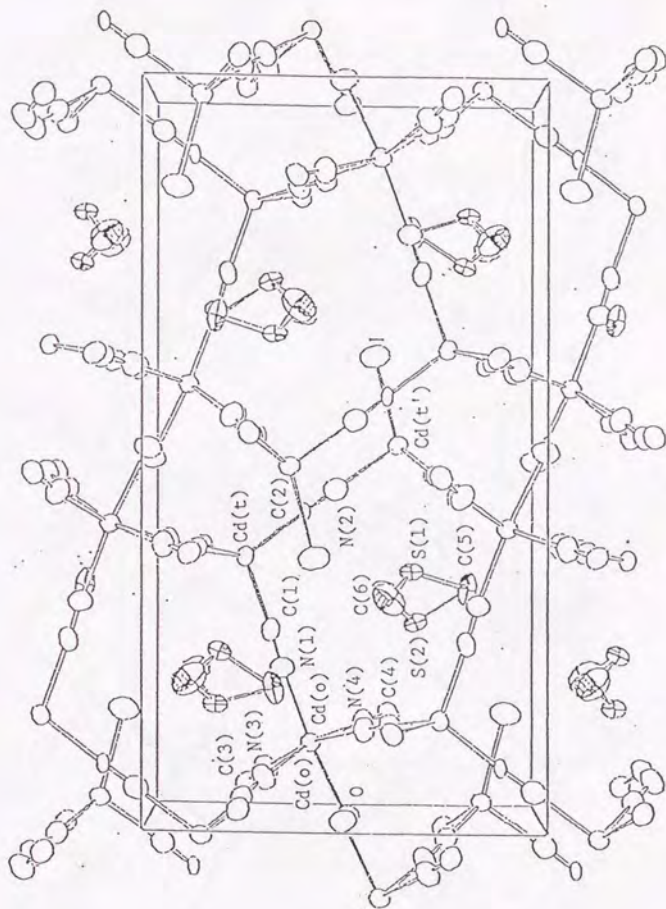


Fig. 3-1 View of the unit cell of III-1 along the c-axis.

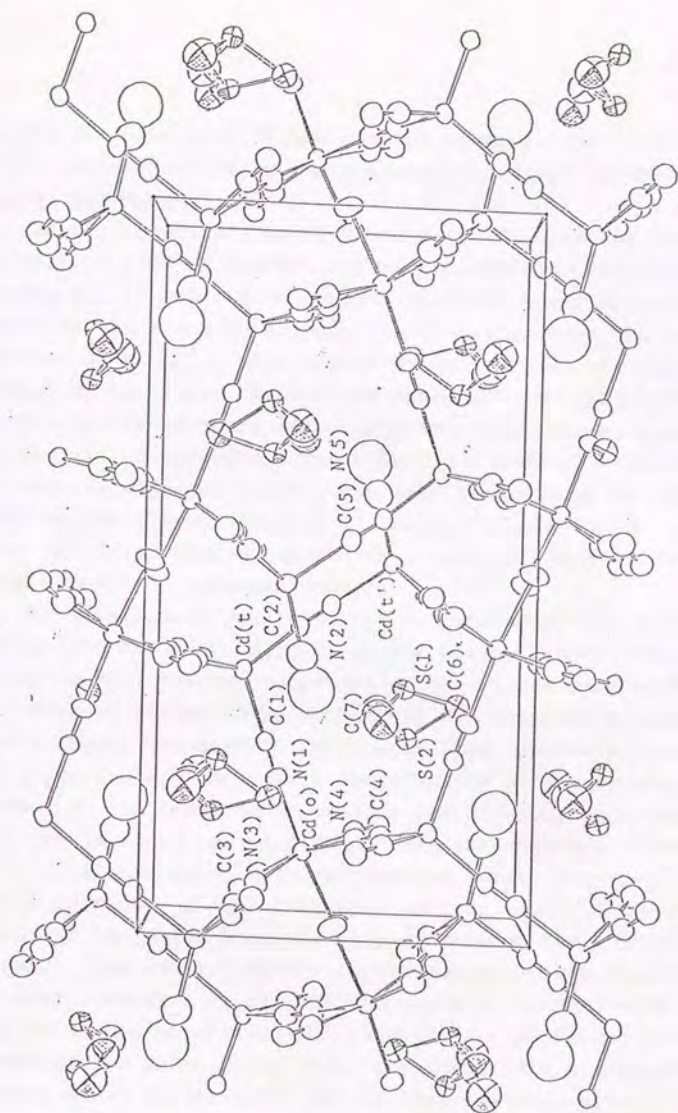


Fig. 3-2 View of the unit cell of III-2 along the c-axis.

charges of L and L'. In the case of group I, the negative charge of  $\text{CN}^-$  is neutralized by the positive charge of  $\text{dmtnH}^+$  to give the neutral framework.

A unit moiety  $\text{NC-Cd(t')-NC-Cd(t)-CN-Cd(o)-dmtnH}$  is selected on the mirror plane of crystal, where the CN from  $\text{Cd(t')}$  is the unidentate L. One moiety is coupled with the moieties related to the center of the  $2/m$  site symmetry to give the layer thicker than those of II and III. The ligand  $\text{dmtnH}^+$  extends its skeleton on the surface of the layer through the space between the  $\text{Cd(t)-CN-Cd(t')}$  bridges on the adjacent mirror planes. The dimethylammonium group at the tail of skeleton forms a hydrogen bond with the unidentate CN from the adjacent layer. Two methylene groups of the  $\text{dmtnH}$  skeleton are distributed out of the mirror plane. The guest molecules are intercalated between the layers pillared with the  $\text{Cd(o)-dmtnH} \cdots \text{NC-Cd(t')}$  hydrogen bond.

The layer of II consists of the centrosymmetric unit moiety  $\text{NC-Cd(t)-CN-Cd(o)-NC-Cd(t)-CN}$  on the mirror plane; the moieties are linked by the cyanide groups out of the mirror plane with others on the adjacent planes. The unidentate  $\text{CN}^-$  was partly replaced by  $\text{I}^-$  when  $\text{N(CH}_3)_4\text{I}$  was used in the preparation procedure; using  $\text{N(CH}_3)_4\text{Cl}$  non-stoichiometric coordination of the counter anion was prevented. In order to neutralize the bivalent negative charge of the host layer, 2 mol of  $\text{N(CH}_3)_4^+$  are intercalated between the negative layers along with the neutral guest  $\text{CCl}_2=\text{CCl}_2$ ; in II-3 the cation is  $\text{N(CH}_3)_3\text{H}^+$  and the guest is  $\text{C}_6\text{H}_6$ . One of the methyl groups of the onium guest is clipped between the  $\text{Cd(t)-CN-Cd(o)}$  bridges. The packing of the layers including the guest species is the most symmetric in II-2 of the space group  $\text{P3m1}$  with the protrusion of the unidentate  $\text{CN}^-$  vertical to the layer. In the two others of the space group  $\text{C2/m}$ , the monoclinic distortion is brought about by the shift of the layers with a slight inclination of the protrusion. Hence, the frameworks of the layers have substantially the same structure in group II one another.

The layer of Group III has a cavity inside the layer itself. The unidentate ligand  $\text{L}' = \text{H}_2\text{O}$  coordinates to  $\text{Cd(o)}$  and  $\text{L} = \text{CN}^-$  or  $\text{I}^-$  to  $\text{Cd(t')}$ , eventually giving univalent negative charge to the layer. The unit moiety  $\text{NC-Cd(t')-NC-Cd(t)-CN-Cd(o)-OH}_2$  across the

layer is selected on the mirror plane, in which moiety the  $\text{CN}^-$  protruding from  $\text{Cd}(\text{t}')$  was partly replaced by  $\text{I}^-$  in III-1. The layers run approximately on the planes parallel to the bc-plane of the crystal at ca.  $a = 1/4$  and  $3/4$ . A cage is formed inside the framework of the layer: it is surrounded by a chair-formed  $\text{Cd}(\text{o})$ - $[\text{Cd}(\text{t}')\text{-Cd}(\text{t})]_2\text{-Cd}(\text{o})$  hexagon at the top, a  $\text{Cd}(\text{t})\text{-}[\text{Cd}(\text{o})]_2\text{-Cd}(\text{t}')$  tetragon at the bottom, and four pentagons, say  $\text{Cd}(\text{o})\text{-Cd}(\text{t}')\text{-Cd}(\text{t})\text{-Cd}(\text{o})\text{-Cd}(\text{t})$ -, at sides connecting the top and the bottom. The  $\text{S}(\text{CH}_3)_3^+$  is accommodated in one side of this cavity, the other side being invaded by the unidentate cyano or iodo ligand from the adjacent layer through the gap between the  $\text{Cd}(\text{t})\text{-Cd}(\text{t}')$  bridges. Thus, the layers are successively stacked with the interlocking of L ligands.

#### 3.4.2. Orientation of the Guest Molecules

The guests in the clay-like layered host are all more or less in disorder except for  $\text{C}_6\text{H}_6$  in I-2,  $\text{CCl}_2=\text{CCl}_2$  in II-1 and  $\text{C}_6\text{H}_6$  in II-3. Since the benzene ring of  $\text{C}_6\text{H}_5\text{F}$  in I-1 is intersected by the mirror plane from which the F atom is deviate, the F is statistically distributed about the plane. The aromatic plane of the aromatic guests in I-1, I-2, and II-3 is laid in almost parallel to the layers. The molecular plane of  $\text{CCl}_2=\text{CCl}_2$  in II-1 and II-2, however, is rather vertical to the layers. The tetrahedral guest,  $\text{CCl}_4$  and  $\text{N}(\text{CH}_3)_4^+$ , distribute their substituents with respect to the mirror plane;  $\text{S}(\text{CH}_3)_3^+$  in the intralayer cavity distributes the S atom with respect to the mirror plane, too. At any rate, the disorder of the guest species may represent the nature of the interlayer space of the intercalation compounds as such that orientation-labile guests are accommodated between the layers of rather rigid structure.

#### 3.5 Discussion

Although a number of intercalation compounds have been paid much attention from the view-point of their peculiar physical and chemical properties [3], their structures have been known in general with accuracy far less than those enough to discuss in detail the chemical environments of the layer surface and guest molecules

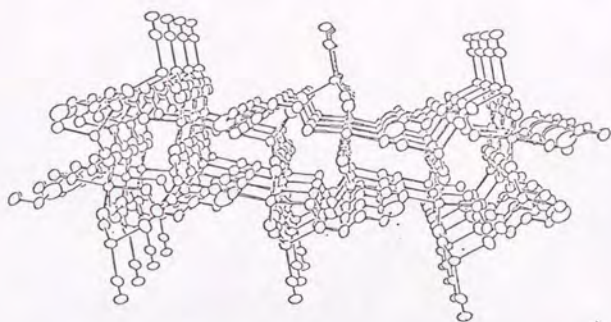
accommodated in the interlayer space. Attempts to obtain single crystals suitable for X-ray diffraction experiments are desirable but still remain as tough jobs. An alternate is to design layered structure artificially and to simulate the environment in the intercalation compound.

The present clay-mimetic structures provide such examples. Group I is an example of surface-modified layer to form a pillared intercalation structure. The charge of layer will be controlled by appropriate selection of the modifiers. The cationic ligand  $\text{dmtnH}^+$  in this case is an unusual example in coordination chemistry that a cation coordinates to a cation. The non-stoichiometry of the unidentate ligands between  $\text{I}^-$  and  $\text{CN}^-$  observed for those protruding from the layers in group II and group III mimics that in natural clay minerals between e.g.  $\text{OH}^-$  and  $\text{O}^{2-}$  at surface. A remarkable difference between the present clay-mimetic and natural structures is the orientation of coordination polyhedra at surface; the tops of tetrahedra and/or octahedra are arranged in the former. This is just the characteristic of the mineralomimetic chemistry: the mimicked one should be similar to the natural one in some points but different in other points. The difference will contribute to put functionalites on the surface of layer by introducing functional group on the top.

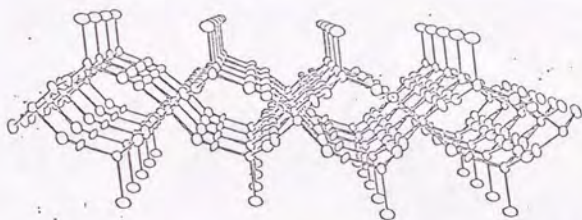
The structure of group III can be denoted as "layered zeolite" because of the cage formed inside the layer entrapping the guest cation. Similar polyhedral cages are formed in the zeolite-like structures to be discussed in next chapter.

#### References

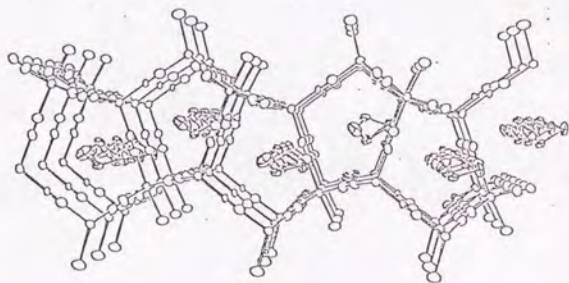
1. T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto, *Chem. Lett.*, 459 (1988).
2. T. Kitazawa, S. Nishikiori, and T. Iwamoto, *Mater. Sci. Forum.*, in press.
3. R. Schollhorn, " Intercalation compounds" in " Inclusion Compounds, Vol 1," edn. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press. London (1984), p.249.



I



II



III

Fig. 4-1 View of the layers for group I, II, and III along the sheet plane

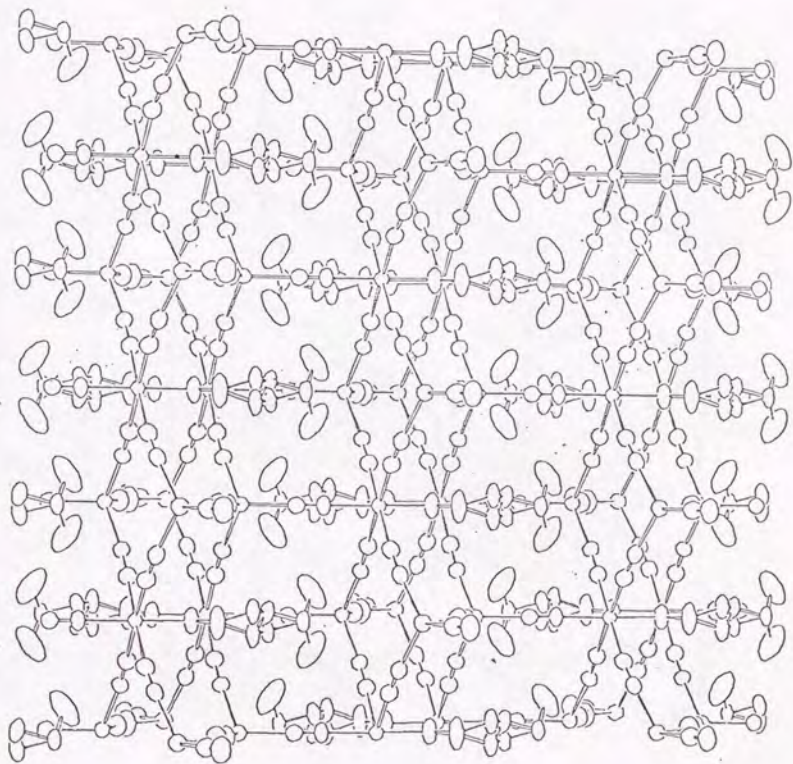


Fig. 4-2 View of the layers for group I normal to the sheet plane

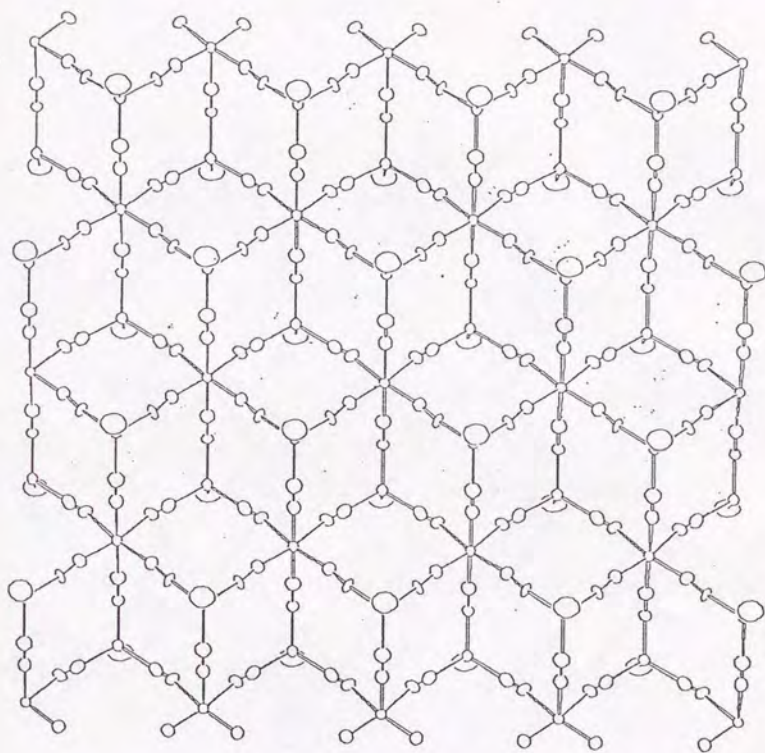


Fig. 4-3 View of the layers for group II normal to the sheet plane

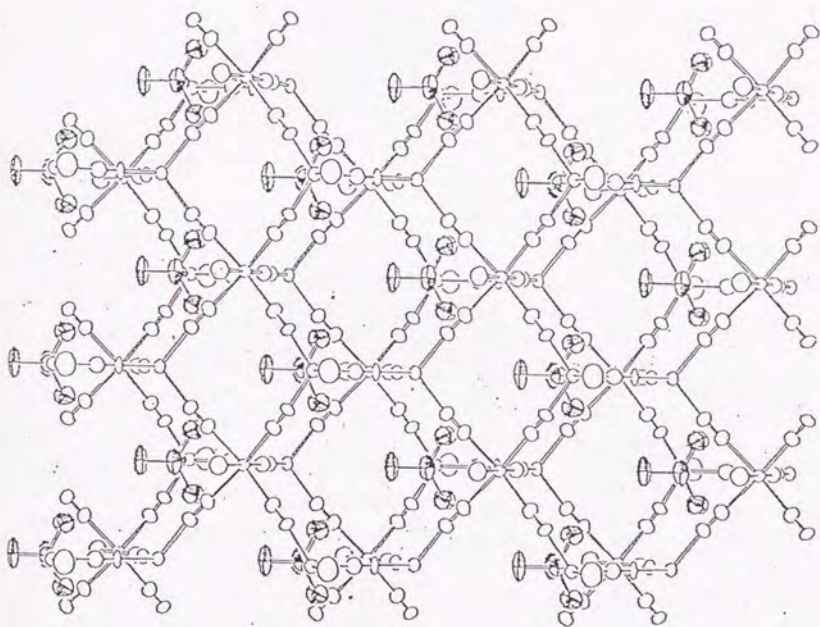


Fig. 4-4 View of the layers for group III normal to the sheet plane

## Zeolite-like framework structures

## Zeolite-like framework structures

## 4. ZEOLITE-LIKE FRAMEWORK STRUCTURES

### 4.1. General Views

The zeolites, as the large family of porous tectosilicates, are the most extensively investigated inclusion species occurring in nature as well as hydrate clathrates. Artificially synthesized zeolites are the variation of natural zeolites including those obtained by the isoelectronic substitution of  $2\text{SiO}_2$  with e.g.  $\text{AlPO}_4$ . More than sixty kinds of the three-dimensional frameworks different in topology have been discovered among those occurring in nature and synthesized artificially. Their structural features have been summarized in an excellent review [1]. Several kinds of chains, each of which is the linking of coordination tetrahedra, have been found in the structures of zeolites to denote the characteristic features of framework topology. In this work as the last example of the mineralomimetic chemistry based on polycyanopolycadmates, zeolite-like three-dimensional structures are discussed.

The zeolite-like structures prepared in this work are built of the coordination polyhedra of Cd atoms, mainly of tetrahedra and octahedra sharing the cyanide groups. The participation of octahedra should be the remarkable difference from the zeolites in nature and synthesized artificially. Among the six types of zeolite-like framework structures, Type IV contains five-coordinated Cd in addition to the four-coordinated tetrahedral and six-coordinated octahedral Cd atoms. Chain structures built of T-O-T units have been found similarly to the case of the zeolites. The difference of the structures in the respective type are due to the difference in the conformation of chain and the combination of the infinite chains to build up framework.

### 4.2 Preparation and Properties

The inclusion compounds prepared and analyzed in this work are listed in Table I. The compounds have been grouped into six types according to their structural features determined by the single crystal X-ray diffraction method; the type is denoted with a Roman numeral from I to VI, and each compound is given a serial number of an Arabic numeral within every type. The preparative procedures are described successively according to the species of the onium

Table I. The inclusion compounds with the zeolite-like framework structures.

	composition	space group
I-1	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{Sn}(\text{CH}_3)_3]$	$R\bar{3}m$ (No. 166)
I-2	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_4 \cdot \text{CH}_2\text{Cl}_2]$	or $C2/m$ (No. 12)
I-3	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_2\text{H}(\text{CH}_2)_3\text{NH}_2 \cdot \text{CHCl}_3]$	
II-1	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot (\text{E})-\text{CHCl}=\text{CHCl}]$	$\text{Pn}2_1m$ (No. 31)
II-2	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2 \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$	
II-3	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_2\text{H}(\text{CH}_2)_3\text{NH}_2 \cdot \text{C}_6\text{H}_6]$	
III-11	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{S}(\text{CH}_3)_3 \cdot 2[\text{C}_6\text{H}_6]]$	$\text{Pnam}$ (No. 62)
III-12	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot 1.5[\text{C}_6\text{H}_6]]$	
III-21	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot \text{C}_6\text{H}_5(\text{CH}_3)]$	
III-22	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot (2/3)[1,3,5-\text{C}_6\text{H}_3(\text{CH}_3)_3]]$	
IV-1	$[\text{Cd}_3(\text{CN})_7] \cdot \{\text{N}(\text{CH}_3)_3\}_{1/2} \cdot [\text{N}(\text{CH}_3)_3\text{H} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$	$\text{Pnam}$ (No. 62)
V-1	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot 2\text{CH}_2\text{ClCH}_2\text{Cl}]$	$\text{P}6_3/\text{mmc}$ (No. 194)
V-2	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot 2\text{Cl}_2\text{C}=\text{CH}_2]$	or $\text{Bbmm}$ (No. 67)
V-3	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot 2\text{C}_2\text{H}_5\text{CN}]$	
V-4	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{S}(\text{CH}_3)_3 \cdot 2\text{CH}_2\text{ClCH}_2\text{Cl}]$	
V-5	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2 \cdot 2\text{CH}_2\text{Cl}_2]$	
VI-1	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2\text{N}(\text{CH}_3)_2 \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$	$\text{Pb}2_1m$ (No. 26)

cations used as the cationic guest to neutralized the negative charge of the host framework.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot n\text{G}]$  (I-1, II-1, III-12, III-21, III-22, V-1, V-2, V-3) - The aqueous solution 1, prepared by dissolving 1.77 g (7.75 mmol) of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and 3.16 g (10.72 mmol) of  $\text{K}_2[\text{Cd}(\text{CN})_4]$  in 100 ml of water was used as the source of the host complex in all the preparation procedures. After 1.35 g (6.75 mmol) of  $\text{N}(\text{CH}_3)_4\text{I}$  was dissolved in solution 1, the aqueous solution was filtered through a plastic membrane of  $0.45 \mu\text{m}$  pore size and kept contact with each organic layer of the respective guest species in a refrigerator for a few days. Colorless crystals of the respective inclusion compounds were obtained.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{S}(\text{CH}_3)_3 \cdot n\text{G}]$  (III-11, V-4) - In place of  $\text{N}(\text{CH}_3)_4\text{I}$ , 0.55 g (2.27 mmol) of  $\text{S}(\text{CH}_3)_3\text{I}$  was used in the procedures as above.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{NH}_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2\text{H} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$  (II-2) - The pH of solution 1 was adjusted to 8.5 by adding N,N-dimethyl-1,3-diaminopropane (dmtn) and citric acid monohydrate. The procedures were similar to the above after that.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{NH}_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2\text{H} \cdot 2\text{CH}_2\text{Cl}_2]$  (V-5) - N-methyl-1,3-diaminopropane (mtn) was used in place of dmtn in the above; the pH was adjusted to 8.7.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{NH}_2(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2\text{H} \cdot \text{G}]$  (I-3, II-3) - N,N-diethyl-1,3-diaminopropane (detn) was used in place of dmtn in the above; pH was adjusted to 8.7.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_4 \cdot \text{CH}_2\text{Cl}_2]$  (I-2) - In solution 1 0.2 g (81.2 mmol) of  $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$  was added to form a creamy suspension. The mixture became clear by addition of citric acid monohydrate and 2-hydroxyethylamine; the pH was adjusted to 10.0. The procedures were similar to those in the above after that.

$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2(\text{CH}_2)_3\text{N}(\text{CH}_3)_2\text{H} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$  (VI-1) - In solution 1 N,N,N',N'-tetramethyl-1,3-diaminopropane and citric acid monohydrate were dissolved to adjust the pH to 8.7. After a small amount of colorless fine needle-like crystals, once formed at room temperature, was filtered through the plastic membrane, the filtrate was placed over a layer of 1,2-dichloroethane, and kept standing at room temperature.

$[\text{Cd}_3(\text{CN})_7\{\text{N}(\text{CH}_3)_3\}_{1/2}] \cdot [\text{N}(\text{CH}_3)_3\text{H} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$  (IV-1) - In

solution 1 1.55 g of citric acid monohydrate and 5.5 ml of a 30% aqueous solution of trimethylamine were added until the pH became ca. 8.5. After the filtration through the plastic membrane, the solution was placed over a layer of 1,2-dichloroethane, and kept standing at room temperature for a few weeks.

Their analytical results were summarized in Table II. Although those for type IV and type V compounds are suggestive their non-stoichiometric characters with regard to the contents of the neutral guest molecules, details will be discussed on the basis of the crystal structures refined in the following section.

These inclusion compounds are as stable as those of the clay-like structures described in the previous chapter. As a general tendency those compounds of the neutral guest G with the higher boiling point is the more stable, although they decompose gradually under ambient conditions.

#### 4.3. Refined Structures

##### 4.3.1. General Remarks

Each crystal subjected to the X-ray experiments was coated with epoxy resin in order to prevent the decomposition. During the collection of the intensity data on the diffractometer, three representative reflections were measured after every 100 reflections to monitor the stability of the crystal; no significant decay was observed. The crystal and selected experimental data are summarized in Table III.

Generally, Cd atoms were located on the Patterson map at first; the successive Fourier and difference Fourier syntheses were used to locate other atoms. The structures were refined by the least-squares calculation using SHELX76 [2]. Disorder in the orientation and occupancy were observed to a more or less extent for the guest molecules in some cases.

The anionic host  $\text{Cd}_3(\text{CN})_7$  is built of cyanide-bridged octahedral and tetrahedral Cd atoms in a 1:2 ratio; in type IV octahedral, trigonal-bipyramidal, and tetrahedral in a 2:1:3. The octahedral Cd, Cd(o), always takes a  $\text{CdN}_6$  coordination, i.e., Cd(o) is coordinated with six N-ends of NC-Cd(t) and NC-Cd(t'), where Cd(t) and Cd(t') are the tetrahedral Cd atoms. All the space groups applied have the mirror plane as the symmetry element, and a

Table II. Analytical results, found%/calcd%

	C	H	N	Cl	other
I-1	22.99/23.33	3.09/3.13	14.16/14.51		
I-2	25.94/26.16	2.93/3.02	15.51/15.25	9.36/9.65	
I-3	23.34/23.40	2.62/2.62	16.79/16.37	13.35/13.81	
II-1	22.13/22.61	2.17/2.04	16.09/16.23		
II-2	23.15/23.20	2.62/2.65	17.52/17.47		Cd:46.8/46.7
II-3	32.68/32.97	3.47/3.62	17.34/17.30		
III-11	34.75/35.11	3.15/2.81	12.88/13.02		
III-12	33.79/33.80	3.07/2.98	15.54/15.77		
III-21	30.87/31.53	2.91/2.94	16.25/16.34		
III-22	29.95/30.30	2.76/2.99	16.72/16.63		
IV-1	22.24/22.90	2.15/2.63	16.90/16.82		
V-1	21.89/22.76	2.31/2.55	14.08/14.15	15.58/17.92	
V-2	22.22/22.88	2.10/2.05	15.44/14.23	17.25/18.01	
V-3	28.48/29.01	3.00/3.15	20.05/19.90		
V-4	20.89/21.17	2.12/2.16	12.50/12.34	17.06/17.85	S: 5.12/4.04
V-5	20.70/20.06	2.45/2.20	15.72/16.20	17.01/18.21	
VI-1	25.53/25.60	3.10/3.09	16.94/16.82		

Table III-1 Crystall and selected experimental data for I-1

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot [\text{Sn}(\text{CH}_3)_4]$	
Formula	$\text{C}_{15}\text{H}_{24}\text{Cd}_3\text{SnN}_8$	
F.W.	722.4	
Color and habit	colorless plate	
Crystal system	trigonal	
Space group	R3m(No.166)	Hexagonal obverse setting
a/ Å	8.849(1)	
c/ Å	31.086(3)	
V/ Å <sup>3</sup>	2108(1)	
Z	3	
Dm/gcm <sup>-3</sup>	1.84(1)	
Dx/gcm <sup>-3</sup>	1.83	
Crystal size/mm	0.25x0.25x0.20	
Temperature/K	293	
Diffractionmeter	Rigaku AFC5	
Radiation, λ/ Å	Mo K α 0.71069	
μ/cm <sup>-1</sup>	30.5	
Scan type	2 θ - ω	
2 θ range/°	4-60	
Peak scan width	1.470+0.3tan θ	
Reflections measured	1558	
Reflections used	707( >3 σ (Fo) )	
Parameters	40	
Solution program	SHELX76	
Weight scheme	w=1/( σ <sup>2</sup> +0.007F <sup>2</sup> )	
R	0.0816	
Rw	0.1294	
G.O.F.	1.293	
Crystal decay	Not observed	
max shift/esd(Host)	0.174	
max shift/esd(Guest)	0.862	
max & min resid		
e Å <sup>-3</sup>	+1.88(near Sn atom), -5.81	

Table III-2 Crystall and selected experimental data of type 1.2

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_4] \cdot [\text{CH}_2\text{Cl}_2]$
Formula	$\text{C}_{16}\text{H}_{22}\text{Cd}_3\text{Cl}_2\text{N}_8$
F.W.	734.5
Color and habit	colorless plate
Crystal system	trigonal
Space group	$R\bar{3}m(\text{No.}166)$
$a/\text{\AA}$	8.778(4)
$c/\text{\AA}$	30.64(3)
$V/\text{\AA}^3$	2044(2)
$Z$	3
$D_m/\text{gcm}^{-3}$	1.79(2)
$D_x/\text{gcm}^{-3}$	1.79
Crystal size/mm	0.30x0.20x0.15
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	27.00
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-60
Peak scan width	$1.432 + 0.50 \tan \theta$
Reflections measured	1577
Reflections used	669 ( $>3 \sigma(F_o)$ )
Parameters	45
Solution program	SHELX76
Weight scheme	$1/(\sigma^2 + 0.0067F^2)$
$R$	0.0760
$R_w$	0.1349
G.O.F.	1.432
Crystal decay	Not observed
max shift/esd(Host)	0.441
max shift/esd(Guest)	1.438
max & min resid	
$e \text{\AA}^{-3}$	+1.38*, -2.76

\* owing to disordered guest moleculars.

Table III-3 Crystal and selected experimental data of type 1.3

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [\text{CHCl}_3]$
Formula	$\text{C}_{15}\text{H}_{20}\text{N}_9\text{Cd}_3\text{Cl}_3$
F.W.	770.0
Color and habit	colorless plate
Crystal system	trigonal
Space group	$R\bar{3}m$ (No.166) Hexagonal obverse setting
$a/\text{\AA}$	8.850(3)
$c/\text{\AA}$	30.538(4)
$V/\text{\AA}^3$	2071(1)
$Z$	3
$D_m/\text{gcm}^{-3}$	1.83(1)
$D_x/\text{gcm}^{-3}$	1.85
Crystal size/mm	0.40x0.30x0.20
Temperature/K	293
Diffractometer	Rigaku AFC5R
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	5-60
Peak scan width	$1.418 + 0.30 \tan \theta$
Reflections measured	1539
Reflections used	592 ( $>3 \sigma(F_o)$ )
Parameters	21
Solution program	SHELX76
Weight scheme	$1/(\sigma^2 + 0.001223F_2)$
$R$	0.0690
$R_w$	0.1061
G.O.F.	2.232
Crystal decay	Not observed
max shift/esd(Host)	0.003
max shift/esd(Guest)	
max & min resid	
$e \text{\AA}^{-3}$	+1.52, -1.05

Only host has been refined.

Table III-4 Crystal and selected experimental data of type II-1

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot [(\text{E})-\text{ClHC}=\text{CHCl}]$
Formula	$\text{C}_{14}\text{H}_{14}\text{Cd}_3\text{Cl}_2\text{N}_7$
F.W.	690.4
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	$\text{Pnam}(\text{No. } 62)$
$a/\text{\AA}$	11.115(3)
$b/\text{\AA}$	13.287(3)
$c/\text{\AA}$	8.664(3)
$V/\text{\AA}^3$	1280(2)
$Z$	2
$D_m/\text{gcm}^{-3}$	1.80(1)
$D_x/\text{gcm}^{-3}$	1.79
Crystal size/mm	0.25x0.20x0.15
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	26.55
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-60
Peak scan width	$1.234 + 0.50 \tan \theta$
Reflections measured	2241
Reflections used	1744 ( $>4 \sigma(F_o)$ )
Parameters	141
Solution program	SHELX76
Weight scheme	$1/(\sigma^2 + 0.01F^2)$
$R$	0.0509
$R_w$	0.0767
G.O.F.	6.912
Crystal decay	Not observed
max shift/esd(Host)	0.087
max shift/esd(Guest)	0.495
max & min resid $e \text{\AA}^{-3}$	+2.45(near Cd atom), -1.125

Table III-5 Crystal and selected experimental data of type II-2

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [\text{CH}_2\text{ClCH}_2\text{Cl}]$
Formula	$\text{C}_{14}\text{H}_{19}\text{Cd}_3\text{Cl}_2\text{N}_9$
F.W.	721.5
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	$\text{Pn}2_1\text{m}(\text{No.}62)$
a/Å	11.026(5)
b/Å	13.54(1)
c/Å	8.721(2)
V/Å <sup>3</sup>	1302(1)
Z	2
Dm/gcm <sup>-3</sup>	1.84(1)
Dx/gcm <sup>-3</sup>	1.82
Crystal size/mm	0.25x0.25x0.25
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	23.29
Scan type	2θ-ω
2θ range/°	3-70
Peak scan width	1.298+0.5tan θ
Reflections measured	3390
Reflections used	2329( >3 σ(Fo) )
Parameters	156
Solution program	SHELX76
Weight scheme	w=1/( σ <sup>2</sup> +0.0012F <sup>2</sup> )
R	0.0508
Rw	0.0649
G.O.F.	1.260
Crystal decay	Not observed
max shift/esd(Host)	0.493
max shift/esd(Guest)	0.672
max & min resid e Å <sup>-3</sup>	+1.47, -1.21

Table III-6 Crystal and selected experimental data of type II-3

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{C}_2\text{H}_5)_2\text{H}(\text{CH}_2)_3\text{NH}_2] \cdot [\text{C}_6\text{H}_6]$
Formula	$\text{C}_{20}\text{H}_{19}\text{Cd}_3\text{N}_9$
F.W.	728.7
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	$\text{Pnam}(\text{No. } 62)$
$a/\text{\AA}$	11.212(1)
$b/\text{\AA}$	13.483(2)
$c/\text{\AA}$	8.694(2)
$V/\text{\AA}^3$	1314.3(6)
$Z$	2
$D_m/\text{gcm}^{-3}$	1.81(1)
$D_x/\text{gcm}^{-3}$	1.84
Crystal size/mm	0.40x0.20x0.15
Temperature/K	293
Diffractometer	Rigaku AFC5R
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	20.0
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	5-60
Peak scan width	$1.420 + 0.30 \tan \theta$
Reflections measured	2247
Reflections used	2037( $>4 \sigma(F_o)$ )
Parameters	171
Solution program	SHELX76
Weight scheme	$1/(\sigma^2 + 0.002262F^2)$
$R$	0.0271
$R_w$	0.0425
G.O.F.	0.818
Crystal decay	Not observed
max shift/esd(Host)	0.005
max shift/esd(Guest)	0.012
max & min resid	
$e \text{\AA}^{-3}$	+1.19, -1.05

Table III-7 Crystal and selected experimental data of type III-11.

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{S}(\text{CH}_3)_3] \cdot 2[\text{C}_6\text{H}_6]$
Formula	$\text{C}_{22}\text{H}_{21}\text{Cd}_3\text{SN}_7$
F.W.	752.8
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	$\text{Pnam}(\text{No. } 62)$
$a/\text{\AA}$	21.934(7)
$b/\text{\AA}$	13.858(4)
$c/\text{\AA}$	8.875(3)
$V/\text{\AA}^3$	2698(2)
Z	4
$D_m/\text{gcm}^{-3}$	1.82(1)
$D_x/\text{gcm}^{-3}$	1.85
Crystal size/mm	0.20x0.20x0.20
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	$\text{Mo K}\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	24.10
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-60
Peak scan width	$1.300 + 0.14 \tan \theta$
Reflections measured	4557
Reflections used	1422( $>4 \sigma(F_o)$ )
Parameters	185
Solution program	SHELX76
Weight scheme	unit weight
R	0.0809
$R_w$	0.0984
G.O.F.	9.391
Crystal decay	Not observed
max shift/esd(Host)	0.361
max shift/esd(Guest)	0.418
max & min resid $e \text{\AA}^{-3}$	+1.48, -1.47

Table III-8 Crystal and selected experimental data of type III-12

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_3] \cdot 1.5[\text{C}_6\text{H}_6]$
Formula	$\text{C}_{20}\text{H}_{21}\text{Cd}_3\text{SN}_8$
F.W.	716.1
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	Pnam(No.62)
a/Å	21.628(3)
b/Å	13.998(3)
c/Å	8.945(1)
V/Å <sup>3</sup>	2708(1)
Z	4
Dm/gcm <sup>-3</sup>	1.77(1)
Dx/gcm <sup>-3</sup>	1.76
Crystal size/mm	0.45x0.20x0.20
Temperature/K	293
Diffractionmeter	Rigaku AFC5R
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	23.29
Scan type	2θ-ω
2θ range/°	5-60
Peak scan width	0.798+0.3tan θ
Reflections measured	10852
Reflections used	2918( >4 σ(Fo) )
Parameters	182
Solution program	SHELX76
Weight scheme	w=1/σ <sup>2</sup>
R	0.0550
Rw	0.0626
G.O.F.	1.175
Crystal decay	Not observed
max shift/esd(Host)	0.059
max shift/esd(Guest)	0.672
max & min resid	
e Å <sup>-3</sup>	+0.94, -1.87

Table III-9 Crystal and selected experimental data of type III-21.

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot [\text{C}_6\text{H}_5\text{CH}_3]$
Formula	$\text{C}_{18}\text{H}_{20}\text{Cd}_3\text{N}_8$
F.W.	685.6
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	Pnam(No.62)
a/Å	22.33(2)
b/Å	13.297(6)
c/Å	8.846(4)
V/Å <sup>3</sup>	2627(2)
Z	4
D <sub>m</sub> /gcm <sup>-3</sup>	1.69(1)
D <sub>x</sub> /gcm <sup>-3</sup>	1.68
Crystal size/mm	0.30x0.35x0.45
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	
Scan type	2θ - ω
2θ range/°	3-65
Peak scan width	0.996+0.50tan θ
Reflections measured	4480
Reflections used	3406( >3 σ (Fo) )
Parameters	148
Solution program	SHELX76
Weight scheme	unit weight
R	0.0555
R <sub>w</sub>	0.0700
G.O.F.	4.278
Crystal decay	Not observed
max shift/esd(Host)	0.058
max shift/esd(Guest)	0.764
max & min resid	
e Å <sup>-3</sup>	+1.47, -1.85

Table III-10 Crystal and selected experimental data of type III-22.

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot 2/3[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]$
Formula	$\text{C}_{17}\text{H}_{20}\text{Cd}_3\text{N}_8$
F.W.	673.6
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	Pnam(No. 62)
a/Å	22.256(4)
b/Å	13.489(4)
c/Å	8.868(3)
V/Å <sup>3</sup>	2662(1)
Z	4
D <sub>m</sub> /gcm <sup>-3</sup>	1.81(2)
D <sub>x</sub> /gcm <sup>-3</sup>	1.80
Crystal size/mm	0.15x0.15x0.20
Temperature/K	293
Diffractionmeter	Rigaku AFC5
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	
Scan type	2θ-ω
2θ range/°	4-60
Peak scan width	0.892+0.30tan θ
Reflections measured	4467
Reflections used	1798( >3 σ(F <sub>o</sub> ) )
Parameters	197
Solution program	SHELX76
Weight scheme	w=1/( σ <sup>2</sup> +0.00126F <sup>2</sup> )
R	0.0634
R <sub>w</sub>	0.0748
G.O.F.	1.255
Crystal decay	Not observed
max shift/esd(Host)	0.249
max shift/esd(Guest)	0.648
max & min residuals	
e Å <sup>-3</sup>	+1.43, -1.03

Table III-11 Crystal and selected experimental data of type IV-1.

Compound[1]	$[\text{Cd}_3(\text{CN})_7 \cdot 0.5\text{N}(\text{CH}_3)_3] \cdot [\text{N}(\text{CH}_3)_3\text{H}] \cdot [\text{CH}_2\text{ClCH}_2\text{Cl}]$
Formula	$\text{C}_{13.5}\text{H}_{18.5}\text{Cd}_3\text{Cl}_2\text{N}_{8.5}$
F.W.	707.99
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	Pnam(No.62)
a/Å	43.39(1).
b/Å	13.602(5)
c/Å	8.773(3)
V/Å <sup>3</sup>	5177(3)
Z	8
Dm/gcm <sup>-3</sup>	1.74-1.86
Dx/gcm <sup>-3</sup>	1.85
Crystal size/mm	0.25x0.13x0.08
Temperature/K	293
Diffractionmeter	Rigaku AFC5R
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	25.25
Scan type	ω
2θ range/°	4-60
Peak scan width	0.966+0.3tan θ
Reflections measured	8636
Reflections used	3636( >4 σ (Fo) )
Parameters	301
Solution program	SHELX76
Weight scheme	w=1/( σ <sup>2</sup> +0.0027F <sup>2</sup> )
R	0.0749
Rw	0.0906
G.O.F.	1.646
Crystal decay	Not observed
max shift/esd(Host)	0.327
max shift/esd(Guest)	0.914
max & min resid	
e Å <sup>-3</sup>	+2.29(in the cavity)*, -1.67

Note [1]  $[\text{Cd}_6(\text{CN})_{14} \cdot \text{N}(\text{CH}_3)_3] \cdot 2[\text{N}(\text{CH}_3)_3] \cdot [\text{CH}_2\text{ClCH}_2\text{Cl}]$  in the asymmetric unit

\* residue owing to the disordered guest atoms

Table III-12 Crystal and selected experimental data of type V-1

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot 2[\text{CHCl}_2\text{CHCl}_2]$
Formula	$\text{C}_{15}\text{H}_{16}\text{Cd}_3\text{Cl}_4\text{N}_8$
F.W.	791.4
Color and habit	hexagonal plate
Crystal system	hexagonal
Space group	$P6_3/\text{mmc}$
a/Å	8.787(2)
c/Å	20.97(3)
V/Å <sup>3</sup>	1404(1)
Z	2
Dm/gcm <sup>-3</sup>	1.87(1)
Dx/gcm <sup>-3</sup>	1.87
Crystal size/mm	0.25x0.25x0.20
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	26.26
Scan type	2θ - ω
2θ range/°	3-60
Peak scan width	1.170+0.5tan θ
Reflections measured	2440
Reflections used	562( >3 σ(Fo) )
Parameters	45
Solution program	SHELX76
Weight scheme	w=1/(σ <sup>2</sup> +0.001119F <sup>2</sup> )
R	0.0678
Rw	0.0815
G.O.F.	1.686
Crystal decay	Not observed
max shift/esd(Host)	0.139
max shift/esd(Guest)	0.691
max & min resid e Å <sup>-3</sup>	+1.57(near Cn atom), -1.35

Table III-13 Crystal and selected experimental data of type V-2

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot 2[\text{CL}_2\text{C}=\text{CH}_2]$
Formula	$\text{C}_{15}\text{H}_{16}\text{Cd}_3\text{Cl}_4\text{N}_8$
F.W.	787.4
Color and habit	hexagonal plate
Crystal system	hexagonal
Space group	$\text{P6}_3/\text{mmc}$
$a/\text{\AA}$	8.775(5)
$c/\text{\AA}$	20.546(8)
$V/\text{\AA}^3$	1370(1)
Z	2
$D_m/\text{gcm}^{-3}$	1.90(2)
$D_x/\text{gcm}^{-3}$	1.91
Crystal size/mm	0.20x0.15x0.10
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, $\lambda/\text{\AA}$	Mo K $\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	26.26
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-60
Peak scan width	$1.245 + 0.5 \tan \theta$
Reflections measured	2410
Reflections used	680 ( $>3 \sigma (F_o)$ )
Parameters	35
Solution program	SHELX76
Weight scheme	$w = 1/(\sigma^2 + 0.012F^2)$
R	0.0680
R <sub>w</sub>	0.0705
G.O.F.	1.889
Crystal decay	Not observed
max shift/esd(Host)	0.339
max shift/esd(Guest)	0.891
max & min resid	
$e \text{\AA}^{-3}$	1.55, -0.55

Table III-14 Crystal and selected experimental data of type V-3

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4] \cdot 2[\text{C}_2\text{H}_5\text{CN}]$
Formula	$\text{C}_{16}\text{H}_{25}\text{Cd}_3\text{N}_{10}$
F.W.	703.7
Color and habit	hexagonal plate
Crystal system	hexagonal
Space group	$\text{P6}_3/\text{mmc}$
$a/\text{\AA}$	8.714(5)
$c/\text{\AA}$	20.437(8)
$V/\text{\AA}^3$	1344(1)
Z	2
$D_m/\text{gcm}^{-3}$	1.72(2)
$D_x/\text{gcm}^{-3}$	1.74
Crystal size/mm	0.20x0.20x0.10
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	Mo K $\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	23.28
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-60
Peak scan width	$1.3 + 0.30 \tan \theta$
Reflections measured	924
Reflections used	588( $>3 \sigma(F_o)$ )
Parameters	44
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.006F^2)$
R	0.0444
Rw	0.0666
G.O.F.	0.767
Crystal decay	Not observed
max shift/esd(Host)	0.313
max shift/esd(Guest)	0.508
max & min resid	
$e \text{\AA}^{-3}$	0.59 -1.36

Table III-15 Crystal and selected experimental data of type V-4

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{S}(\text{CH}_3)_3] \cdot 2[\text{CHCl}_2\text{CHCl}_2]$
Formula	$\text{C}_{14}\text{H}_{13}\text{Cd}_3\text{Cl}_4\text{SN}_7$
F.W.	794.4
Color and habit	hexagonal plate
Crystal system	hexagonal
Space group	$P6_3/\text{mmc}$
$a/\text{\AA}$	8.814(4)
$c/\text{\AA}$	20.567(3)
$V/\text{\AA}^3$	1384(1)
Z	2
$D_m/\text{gcm}^{-3}$	1.89(2)
$D_x/\text{gcm}^{-3}$	1.91
Crystal size/mm	0.30x0.25x0.15
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, $\lambda/\text{\AA}$	Mo K $\alpha$ 0.71069
$\mu/\text{cm}^{-1}$	27.10
Scan type	$2\theta - \omega$
$2\theta$ range/ $^\circ$	3-60
Peak scan width	$1.245 + 0.5 \tan \theta$
Reflections measured	3213
Reflections used	595( $>4 \sigma(F_o)$ )
Parameters	35
Solution program	SHELX76
Weight scheme	$w=1/(\sigma^2 + 0.001119F^2)$
R	0.0728
Rw	0.0705
G.O.F.	1.889
Crystal decay	Not observed
max shift/esd(Host)	0.339
max shift/esd(Guest)	0.891
max & min resid $e \text{\AA}^{-3}$	+1.57(near Cl atom), -1.35

Table III-16 Crystal and selected experimental data of type V-5

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{mtnH}] \cdot 2[\text{CH}_2\text{Cl}_2]$
Formula	$\text{C}_{13}\text{H}_{15}\text{Cd}_3\text{Cl}_4\text{N}_9$
F.W.	778.4
Color and habit	hexagonal plate
Crystal system	hexagonal
Space group	$P6_3/\text{mmc}$
a/Å	8.775(2)
c/Å	20.546(8)
V/Å <sup>3</sup>	1370(1)
Z	2
Dm/gcm <sup>-3</sup>	1.87(1)
Dx/gcm <sup>-3</sup>	1.88
Crystal size/mm	0.25x0.20x0.10
Temperature/K	293
Diffractometer	Rigaku AFC6A
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	26.46
Scan type	2θ - ω
2θ range/°	3-60
Peak scan width	1.340+0.5tan θ
Reflections measured	2339
Reflections used	645( >3 σ (Fo) )
Parameters	29
Solution program	SHELX76
Weight scheme	w=1/( σ <sup>2</sup> +0.001119F <sup>2</sup> )
R	0.11
Rw	0.11
G.O.F.	
Crystal decay	Not observed
max shift/esd(Host)	0.02
max shift/esd(Guest)	1.55
max & min resid e Å <sup>-3</sup>	+1.57(near Cd atom), -1.35

Table III-17 Crystal and selected experimental data of type VI-1

Compound	$[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_2\text{H}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2] \cdot [\text{CH}_2\text{ClCH}_2\text{Cl}]$
Formula	$\text{C}_{16}\text{H}_{23}\text{CdCl}_2\text{N}_9$
F.W.	749.6
Color and habit	colorless plate
Crystal system	orthorhombic
Space group	$\text{Pn}2_1\text{m}(\text{No. 62})$
a/Å	10.817(5)
b/Å	27.553(1)
c/Å	9.048(2)
V/Å <sup>3</sup>	2697(2)
Z	4
Dm/gcm <sup>-3</sup>	1.86(2)
Dx/gcm <sup>-3</sup>	1.85
Crystal size/mm	0.10x0.10x0.07
Temperature/K	293
Diffractometer	Rigaku AFC5
Radiation, λ/Å	Mo Kα 0.71069
μ/cm <sup>-1</sup>	25.25
Scan type	2θ-ω
2θ range/°	4-60
Peak scan width	0.756+0.3tan θ
Reflections measured	4545
Reflections used	1996( >4 σ(Fo) )
Parameters	176
Solution program	SHELX76
Weight scheme	w=1/(σ <sup>2</sup> +0.0027F <sup>2</sup> )
R	0.0859
Rw	0.1089
G.O.F.	1.473
Crystal decay	Not observed
max shift/esd(Host)	0.190
max shift/esd(Guest)	0.697
max & min resid e Å <sup>-3</sup>	+2.17(in the cavity)*, -1.78

Note \* residue owing to the disordered guest atoms

sequence of  $-(NC)-Cd(t)-CN-Cd(o)-NC-Cd(t' \text{ or } t)-$  (T-O-T unit) is found running on the mirror plane periodically for all the structures. The cyanide groups out of the mirror plane always bridge between  $Cd(o)$  and  $Cd(t \text{ or } t')$  respectively on the plane and the adjacent planes.

Serious problems in the structure refinements were on the discrimination between the C and N in the cyanide group linking a pair of tetrahedral Cd atoms on the mirror plane; the corresponding cyanide group is shown in the parentheses for the sequence cited above. First, the space group  $R\bar{3}m$  and  $P6_3/mmc$  applied respectively for type I and type II predicted the discrimination impossible. An inversion center intermediate between the C and N makes both atoms equivalent each other; in  $P6_3/mmc$  a mirror plane bisecting the  $Cd(t)-(CN)-Cd(t)$  linkage is added. When the space group of lower symmetry was selected, i.e.,  $C2/m$  in place of  $R\bar{3}m$  or  $Bbmm$  in place of  $P6_3/mmc$ , the relationship with the symmetry element was unchanged. Secondly, in some cases, although the applied space group allows the discrimination, significant selection was impossible for the X-ray data collected. When the discrimination was impossible theoretically or practically, both C and N atoms were refined as an atom with 50 % each probability of C and N atoms. When the  $Cd(t')-N$  distance longer than  $Cd(t)-C$  was observed with the difference greater than the sum of three times their e.s.d.'s was observed under the acceptable convergence of the final refinement, the C and N were described to be discriminated each other. The atomic parameters refined are listed for type I through VI in Table IV-IX respectively.

#### 4.3.2. Type I structures (Fig. 1)

For type I compounds the reflection data supported the Laue class of  $\bar{3}m$ . Based on the obverse setting of the hexagonal axes, the observed reflections satisfied the conditions  $-h+k+l = 3n$ . Among three possible space groups  $R\bar{3}m$ ,  $R32$ , and  $R\bar{3}m$ , the best convergence was given for the  $R\bar{3}m$ , although the substantially identical results were obtained for all the three.  $Cd(o)$  was located at the origin with the  $\bar{3}$  site symmetry;  $Cd(t)$  at  $0,0,z$  with the  $3m$  symmetry. Because of the space group  $R\bar{3}m$  the discrim-

Table IV. Atomic parameters for type I  
for I-1

Host [Cd <sub>3</sub> (CN) <sub>7</sub> ] <sup>-</sup>					
Atom	x	Y	z	Beq/ Å <sup>2</sup>	
Cd(o)	0.0	=X	0.0	2.36(4)	
Cd(t)	0.0	=X	0.40985(4)	2.69(3)	
CN(1)	0.0	=X	0.4801(4)	3.7(3)	
N(1)	0.1276(7)	=-X	0.0412(4)	4.8(3)	
C(1)	0.1963(8)	=-X	0.0553(4)	4.0(3)	
neutral guest Sn(CH <sub>3</sub> ) <sub>4</sub>					
Atom	x	Y	z		occupancy
Sn	0.0	=X	0.2217(2)	6.9(1)	0.5
C(2)	0.0	=X	0.2902(6)	7.1(3)	0.5
C(3)	0.136(2)	=-X	0.205(2)	12.2(6)	0.5
onium guest N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>					
N(2)	0.0	=X	0.246(1)	3.3(5)	0.5
C(4)	0.0	=X	0.293(1)	7.8(6)	0.5
C(5)	0.083(2)	=-X	0.223(2)	9.7(6)	0.5

for I-2

Host [Cd <sub>3</sub> (CN) <sub>7</sub> ] <sup>-</sup>					
Atom	x	Y	z	Beq/ Å <sup>2</sup>	
Cd(o)	0.0	=X	0.0	3.81(5)	
Cd(t)	0.0	=X	0.40822(4)	3.70(4)	
CN(1)	0.0	=X	0.4820(6)	4.7(4)	
N(1)	0.1271(8)	=-X	0.0436(4)	6.6(2)	
C(1)	0.1934(9)	=-X	0.0550(4)	5.3(2)	
Guest					
CN(2)	0.0	=X	0.194(2)	14.5(4)	
Cl(1)	0.0	=X	0.137(2)	22.7(4)	0.25
Cl(2)	0.097(2)	=-X	0.224(1)	15.5(4)	0.25
C(2)	0.043(4)	=-X	0.238(2)	18.5(4)	0.167
C(3)	0.0	=X	0.284(2)	9.3(4)	0.5
C(4)	-0.080(3)	=-X	0.166(2)	18.5(4)	0.5
C(5)	0.099(4)	=2X	0.144(3)	21.6(4)	0.5

for I-3

Host [Cd <sub>3</sub> (CN) <sub>7</sub> ] <sup>-</sup>					
Atom	x	Y	z	Beq/ Å <sup>2</sup>	
Cd(o)	0.0	=X	0.0	3.81(4)	
Cd(t)	0.0	=X	0.40985(4)	3.91(3)	
CN(1)	0.0	=X	0.4801(4)	5.6(4)	
N(1)	0.1271(8)	=-X	0.0436(4)	6.6(4)	
C(1)	0.1934(9)	=-X	0.0550(4)	4.8(4)	

Table V-1 Atomic parameters for II-1

Host $[\text{Cd}_3(\text{CN})_7]^-$				
Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(o)	0.22899(9)	0.0	0.0	2.36(3)
Cd(t)	0.0740(1)	0.4032(1)	0.0	2.70(4)
Cd(t')	0.4933(1)	0.6350(1)	0.0	2.85(4)
N(1)	0.096(1)	-0.0481(9)	0.191(1)	4.1(2)
N(2)	0.361(1)	0.058(1)	0.190(1)	4.5(2)
N(3)	0.139(2)	0.161(1)	0.0	4.7(2)
N(4)	0.333(2)	0.849(1)	0.0	4.3(2)
C(1)	0.035(1)	-0.0628(9)	0.293(1)	3.0(2)
C(2)	0.413(1)	0.089((6)	0.289(2)	4.0(2)
C(3)	0.117(1)	0.240(1)	0.0	3.4(2)
C(4)	0.390(1)	0.776(1)	0.0	3.4(2)
CN(1)*	0.243(1)	0.486(1)	0.0	4.2(2)
CN(2)*	0.328(2)	0.535(2)	0.0	5.1(2)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

## neutral guest (E)-ClHC=CClH

Atom	x	y	z	occupancy
Cl(1)	-0.045(1)	0.183(1))	0.5	10.4(2)
Cl(2)	0.295(1)	0.324(2)	0.436(2)	11.7(2)
C(5)	0.103(2)	0.214(2)	0.5	9.8(2)
C(6)	0.150(2)	0.304(2)	0.5	8.4(2)

onium guest  $\text{N}(\text{CH}_3)_4^+$ 

Atom	x	y	z	occupancy
N(5)	0.260(2)	0.669(2)	0.5	7.3(2)
C(7)	0.364(2)	0.600(2)	0.5	9.2(2)
C(8)	0.354(2)	0.749(2)	0.5	9.0(2)
C(9)	0.199(2)	0.709(2)	0.366(2)	9.9(2)

Table V-2 Atomic parameters for II-2  
 $[\text{Cd}_3(\text{CN})_7] \cdot [\text{dmtnH} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$

Host $[\text{Cd}_3(\text{CN})_7]^-$				
Atom	x	y	z	Beq/ Å <sup>2</sup>
Cd(o)	0.23232(6)	0.0	0.0	2.24(2)
Cd(t)	0.06947(7)	0.39749(8)	0.0	2.85(2)
Cd(t')	0.48663(7)	0.63535(8)	0.0	3.21(3)
N(1)	0.1002(6)	-0.0460(5)	0.1907(7)	4.01(8)
N(2)	0.3653(6)	0.0583(6)	0.1913(7)	4.52(8)
N(3)	0.1493(8)	0.1615(6)	0.0	4.30(8)
N(4)	0.3337(7)	0.8508(7)	0.0	4.03(8)
C(1)	0.0412(6)	-0.0656(6)	0.2915(7)	3.57(8)
C(2)	0.4182(6)	0.0873(6)	0.2914(8)	3.78(8)
C(3)	0.1189(8)	0.2406(7)	0.0	3.86(8)
C(4)	0.3839(8)	0.7770(7)	0.0	3.76(8)
CN(1)*	0.2440(9)	0.4821(8)	0.0	4.59(9)
CN(2)*	0.3259(7)	0.5318(8)	0.0	4.39(9)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest  $\text{CH}_2\text{ClCH}_2\text{Cl}$

Atom	x	y	z	occupancy
Cl(1)	-0.0416(6)	0.1751(6)	0.5	12.5(1)
Cl(2)	0.2984(6)	0.3138(6)	0.4417(9)	12.0(1)
C(5)	0.107(1)	0.237(1)	0.427(1)	13.3(1)
C(6)	0.169(1)	0.280(1)	0.447(1)	9.6(1)

onium guest  $(\text{CH}_3)_2\text{NH}(\text{CH}_2)_3\text{NH}_2^+$

Atom	x	y	z	occupancy
N(5)	0.299(1)	0.863(1)	0.5	7.6(1)
N(6)	0.553(1)	0.855(1)	0.5	12.8(1)
C(7)	0.4250(9)	0.821(1)	0.5	16.5(1)
C(8)	0.513(1)	0.735(1)	0.5	12.7(1)
C(9)	0.302(1)	0.840(1)	0.423(1)	6.7(1)
C(10)	0.380(1)	0.713(1)	0.467(1)	18.1(1)
C(11)	0.297(1)	0.730(1)	0.378(1)	11.5(1)
N(7)	0.2579(9)	0.667(1)	0.5	13.3(1)
C(12)	0.193(1)	0.663(1)	0.350(1)	8.8(1)
C(13)	0.213(1)	0.587(1)	0.404(1)	15.3(1)

Table V-3 Atomic parameters for II-3  
[Cd<sub>3</sub>(CN)<sub>7</sub>] · [detnH · C<sub>6</sub>H<sub>6</sub>]

Host [Cd <sub>3</sub> (CN) <sub>7</sub> ] <sup>-</sup>				
Atom	x	y	z	Beg/ Å <sup>2</sup>
Cd(o)	0.23376(4)	0.0	0.0	1.79(2)
Cd(t)	0.06788(4)	0.39923(5)	0.0	2.01(2)
Cd(t')	0.48572(4)	0.63246(5)	0.0	2.04(2)
N(1)	0.1008(4)	-0.0419(4)	0.1923(6)	3.2(2)
N(2)	0.3679(4)	0.0507(4)	0.1925(5)	3.1(2)
N(3)	0.1579(7)	0.1617(5)	0.0	3.2(3)
N(4)	0.3225(6)	0.8417(5)	0.0	2.9(2)
C(1)	0.0392(5)	-0.0612(4)	0.2927(6)	2.8(2)
C(2)	0.4200(4)	0.0817(4)	0.2933(6)	2.5(2)
C(3)	0.1235(6)	0.2420(6)	0.0	2.5(3)
C(4)	0.3765(7)	0.7691(6)	0.0	2.5(2)
CN(1)*	0.2391(6)	0.4827(6)	0.0	3.4(3)
CN(2)*	0.3272(6)	0.5243(6)	0.0	2.8(2)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest C<sub>6</sub>H<sub>6</sub>

Atom	x	y	z	occupancy
C(5)	0.3607(8)	0.3760(6)	0.422(1)	5.5(4)
C(6)	0.2799(8)	0.3157(9)	0.341(1)	5.8(4)
C(7)	0.2070(9)	0.259(1)	0.415(2)	6.8(5)

onium guest (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub><sup>+</sup>

Atom	x	y	z	occupancy
N(5)	0.2860(7)	0.8671(7)	0.5	4.4(4)
C(8)	0.407(1)	0.842(1)	0.459(2)	4.3(6)
C(9)	0.4458(8)	0.7440(9)	0.5	4.3(3)
C(10)	0.3682(9)	0.660(1)	0.461(1)	3.7(5)
N(6)	0.2419(6)	0.6660(5)	0.5	3.1(3)
C(11)	0.2292(2)	0.632(1)	0.320(2)	3.6(4)
C(12)	0.158(1)	0.6153(8)	0.407(2)	3.3(4)
C(13)	0.1293(7)	0.6716(6)	0.253(1)	4.1(3)

Table VI-1 Atomic parameters for III-11  
 $[\text{Cd}_3(\text{CN})_7] \cdot [\text{S}(\text{CH}_3)_3 \cdot 2\text{C}_6\text{H}_6]$

Host $[\text{Cd}_3(\text{CN})_7]^-$				
Atom	x	y	z	Beq/Å <sup>2</sup>
Cd(o)	0.1307(1)	0.3145(2)	0.25	2.7(1)
Cd(t)	0.2272(1)	0.9339(2)	0.25	3.0(1)
Cd(t')	0.0236(1)	0.6836(2)	0.25	3.1(1)
N(1)	0.0628(9)	0.282(2)	0.046(3)	4.1(6)
C(1)	0.0313(1)	0.291(2)	-0.050(3)	3.5(6)
N(2)	0.203(1)	0.360(2)	0.056(3)	4.1(6)
C(2)	0.226(1)	0.387(2)	-0.047(3)	3.5(6)
N(3)	0.092(1)	0.472(2)	0.25	3.2(6)
C(3)	0.066(2)	0.542(3)	0.25	4.7(6)
N(4)	0.170(1)	0.153(2)	0.25	3.3(6)
C(4)	0.192(2)	0.082(3)	0.25	3.7(6)
CN(1)*	0.111(2)	0.783(3)	0.25	5.2(6)
CN(2)*	0.149(2)	0.833(3)	0.25	3.8(6)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest 2 C <sub>6</sub> H <sub>6</sub>				
Atom	x	y	z	Beq/Å <sup>2</sup>
C(5)	0.399(2)	0.054(3)	0.178(4)	9.8(6)
C(6)	0.364(2)	0.122(2)	0.101(3)	7.8(6)
C(7)	0.334(2)	0.194(3)	0.178(4)	8.9(6)
C(8)	0.493(4)	0.490(5)	0.25	16.9(6)
C(9)	0.470(3)	0.473(4)	0.104(4)	20.9(6)
C(10)	0.438(4)	0.390(3)	0.146(5)	18.3(6)
C(11)	0.428(4)	0.315(4)	0.25	18.1(6)

onium guest S(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>				
Atom	x	y	z	occupancy
S	0.316(2)	0.561(3)	0.25	21.5(6)
C(12)	0.350(3)	0.678(3)	0.25	9.9(6)
C(13)	0.242(2)	0.619(4)	0.25	14.7(6)
C(14)	0.375(3)	0.614(5)	0.138(6)	11.2(6)

0.5

Table VI-2 Atomic parameters for type III-12

Host  $[\text{Cd}_3(\text{CN})_7]^-$

Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(o)	0.13000(3)	0.31264(5)	0.25	2.24(3)
Cd(t)	0.22861(3)	0.93390(5)	0.25	2.64(3)
Cd(t')	0.02490(3)	0.68011(6)	0.25	2.50(3)
N(1)	0.0632(3)	0.2846(5)	0.0530(7)	3.8(2)
C(1)	0.0326(3)	0.2946(6)	-0.0474(9)	3.3(2)
N(2)	0.2018(3)	0.3581(5)	0.0628(7)	3.5(2)
C(2)	0.2252(3)	0.3871(5)	-0.0432(8)	2.9(2)
N(3)	0.0949(5)	0.4691(7)	0.25	4.1(3)
C(3)	0.0695(5)	0.5385(8)	0.25	3.5(3)
N(4)	0.1678(4)	0.1542(6)	0.25	3.1(3)
C(4)	0.1877(5)	0.0785(8)	0.25	3.0(3)
CN(1)*	0.1057(5)	0.7809(8)	0.25	3.8(3)
CN(2)*	0.1469(5)	0.8321(8)	0.25	3.7(3)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest  $1.57\text{C}_6\text{H}_6$

Atom	x	y	z	Beq	occupancy
C(5)	0.3934(6)	0.0533(9)	0.325(2)	9.0(3)	
C(6)	0.3639(5)	0.120(1)	0.402(1)	8.0(3)	
C(7)	0.3329(5)	0.1931(8)	0.330(2)	8.8(3)	
C(8)	0.518(2)	0.514(3)	0.25	11.9(3)	0.574(4)
C(9)	0.504(2)	0.494(2)	0.403(3)	15.6(3)	0.574(4)
C(10)	0.461(1)	0.410(2)	0.405(2)	13.8(3)	0.574(4)
C(11)	0.467(2)	0.367(2)	0.25	9.1(3)	0.574(4)

onium guest

Atom	x	y	z	Beq	occupancy
N(5)	0.3141(7)	0.5961(9)	0.25	7.0(3)	
C(12)	0.356(1)	0.661(2)	0.173(2)	13.1(3)	0.6666
C(13)	0.265(1)	0.614(2)	0.134(2)	14.1(3)	0.6666
C(14)	0.332(1)	0.516(1)	0.162(2)	13.8(3)	0.6666

Table VI-3 Atomic parameters for III-21  
[Cd<sub>3</sub>(CN)<sub>7</sub>] · [N(CH<sub>3</sub>)<sub>4</sub> · C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)]

Host [Cd <sub>3</sub> (CN) <sub>7</sub> ] <sup>-</sup>				
Atom	x	y	z	Beq/ Å <sup>2</sup>
Cd(o)	0.14605(2)	0.34057(5)	0.25	2.64(2)
Cd(t)	0.20682(3)	0.92918(5)	0.25	2.77(2)
Cd(t')	0.00437(3)	0.69339(5)	0.25	2.95(2)
N(1)	0.0776(3)	0.3023(6)	0.0617(7)	5.0(1)
C(1)	0.0483(3)	0.3000(6)	-0.0421(7)	4.2(1)
N(2)	0.2145(3)	0.3783(5)	0.0614(6)	4.5(1)
C(2)	0.2419(3)	0.3931(5)	-0.0424(7)	3.6(1)
N(3)	0.0994(5)	0.4992(6)	0.25	4.6(1)
C(3)	0.0664(5)	0.5602(7)	0.25	4.3(1)
N(4)	0.1789(4)	0.1757(6)	0.25	4.1(1)
C(4)	0.1877(4)	0.0934(6)	0.25	3.1(1)
CN(1)*,N	0.0759(4)	0.8075(6)	0.25	5.2(1)
CN(2)*,C	0.1204(4)	0.8494(6)	0.25	3.4(1)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )				
Atom	x	y	z	Beq/ Å <sup>2</sup>
C(5)	0.4763(9)	0.423(1)	0.25	10.7(1)
C(6)	0.4483(7)	0.462(1)	0.375(1)	10.2(1)
C(7)	0.3958(7)	0.5204(9)	0.390(1)	9.3(1)
C(8)	0.3707(8)	0.559(1)	0.25	9.5(1)
C(9)	0.3164(9)	0.622(1)	0.25	12.7(1)

onium guest N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>				
Atom	x	y	z	Beq/ Å <sup>2</sup>
N(5)	0.3761(5)	0.160(1)	0.25	8.3(1)
C(10)	0.4430(8)	0.163(1)	0.25	12.0(1)
C(11)	0.3561(9)	0.047(1)	0.25	15.4(1)
C(12)	0.3464(8)	0.166(1)	0.112(1)	11.6(1)

Table VI-4 Atomic parameters for III-22  
 $[\text{Cd}_3(\text{CN})_7] \cdot [\text{N}(\text{CH}_3)_4 \cdot 1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]$

Host $[\text{Cd}_3(\text{CN})_7]^-$				
Atom	x	y	z	Beq/ Å <sup>2</sup>
Cd(o)	0.14225(6)	0.3369(1)	0.25	3.00(5)
Cd(t)	0.21181(6)	0.93381(9)	0.25	3.09(6)
Cd(t')	0.00835(6)	0.6937(1)	0.25	3.35(6)
N(1)	0.0722(5)	0.2971(9)	0.063(1)	5.2(3)
C(1)	0.0443(6)	0.298(1)	-0.042(2)	4.7(3)
N(2)	0.2094(5)	0.3796(8)	0.061(1)	4.8(3)
C(2)	0.2371(6)	0.3992(9)	-0.043(2)	4.2(3)
N(3)	0.0979(8)	0.494(1)	0.25	5.5(3)
C(3)	0.067(1)	0.556(1)	0.25	4.6(3)
N(4)	0.1774(8)	0.175(1)	0.25	4.8(3)
C(4)	0.1897(9)	0.095(1)	0.25	4.1(3)
CN(1)*,N	0.0871(8)	0.804(1)	0.25	5.5(3)
CN(2)*,C	0.1298(7)	0.848(1)	0.25	3.4(3)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest 1,3,5- $\text{C}_6\text{H}_3(\text{CH}_3)_3$				
Atom	x	y	z	Beq/ Å <sup>2</sup>
C(5)	0.5	0.5	0.0	11.3(3)
C(6)	0.498(2)	0.489(3)	0.25	8.1(3)
C(7)	0.372(2)	0.571(3)	0.25	7.6(3)
C(8)	0.461(1)	0.512(2)	0.130(2)	8.8(3)
C(9)	0.403(1)	0.549(2)	0.116(2)	9.7(3)
C(10)	0.315(2)	0.626(3)	0.25	9.7(3)
C(11)	0.246(2)	0.646(4)	0.25	8.6(3)
C(12)	0.435(3)	0.530(4)	0.25	8.6(3)
C(13)	0.342(2)	0.566(3)	0.143(3)	8.5(3)
C(14)	0.459(2)	0.556(3)	0.015(4)	8.3(3)
onium guest $\text{N}(\text{CH}_3)_4^+$				
N(5)	0.3756(8)	0.186(2)	0.25	7.3(3)
C(15)	0.419(2)	0.267(2)	0.25	13.7(3)
C(16)	0.427(2)	0.117(2)	0.25	13.1(3)
C(17)	0.342(1)	0.164(2)	0.117(2)	12.5(3)

Table VII Atomic parameters for IV

Host $\text{Cd}_6(\text{CN})_{14}\text{N}(\text{CH}_3)_3$				
Atom	x	y	z	Beq/Å <sup>2</sup>
Cd(o)	0.06455(4)	0.3146(1)	0.25	2.78(7)
Cd(t1)	0.01291(4)	0.6948(1)	0.25	2.91(7)
Cd(t2)	0.11654(4)	0.9347(1)	0.25	2.83(7)
Cd(o')	0.19273(4)	0.8363(1)	0.75	2.43(6)
Cd(t1')	0.23129(4)	0.2380(1)	0.75	2.82(7)
Cd(p)	0.11966(4)	0.4967(1)	0.75	3.44(8)
N(1)	0.0873(5)	0.158(1)	0.25	3.8(3)
C(1)	0.0972(5)	0.082(2)	0.25	3.6(3)
N(2)	0.0450(5)	0.471(1)	0.25	5.0(3)
C(2)	0.0335(6)	0.545(2)	0.25	3.7(3)
N(3)	0.1682(5)	0.681(1)	0.75	4.2(3)
C(3)	0.1535(6)	0.616(2)	0.75	4.3(3)
N(4)	0.2117(5)	0.000(2)	0.75	4.2(3)
C(4)	0.2200(5)	0.079(2)	0.75	3.5(3)
CN(1)*	0.0548(6)	0.791(2)	0.25	4.2(4)
CN(2)*	0.0762(6)	0.832(2)	0.25	4.3(4)
N(5)	0.1668(6)	0.360(2)	0.75	6.3(3)
C(5)	0.1853(6)	0.319(2)	0.75	3.7(3)
N(6)	0.0310(3)	0.275(1)	0.442(2)	4.5(3)
C(6)	0.0150(3)	0.280(1)	0.543(2)	3.4(3)
N(7)	0.0986(3)	0.375(1)	0.439(2)	4.7(3)
C(7)	0.1076(4)	0.417(1)	0.539(2)	4.8(3)
N(8)	0.1591(3)	0.882(1)	0.560(2)	4.3(3)
C(8)	0.1445(3)	0.901(1)	0.457(2)	3.2(3)
N(9)	0.2270(3)	0.794(1)	0.558(2)	4.4(3)
C(9)	0.2415(4)	0.772(1)	0.457(2)	3.5(3)
N(10)	0.0752(5)	0.599(2)	0.75	5.1(3)
C(10)	0.0495(9)	0.538(3)	0.75	9.9(4)
C(11)	0.0760(6)	0.661(2)	0.895(3)	7.6(4)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

## neutral guest

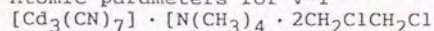
Atom	x	y	z	Beq/Å <sup>2</sup>	occupancy
Cl(1)	0.2632(3)	0.0054(8)	0.25	10.7(4)	
Cl(2)	0.1744(2)	0.133(1)	0.25	10.9(4)	
C(12)	0.2230(7)	0.038(3)	0.25	13.1(4)	
C(13)	0.2122(8)	0.097(3)	0.312(4)	11.4(4)	0.5
C(14)	0.4550(8)	0.440(2)	0.112(3)	7.7(4)	0.5
Cl(4)	0.472(1)	0.509(3)	0.033(4)	8.2(4)	0.5
Cl(3)	0.433(1)	0.427(3)	0.25	12.6(4)	
C(15)	0.478(1)	0.449(3)	0.25	15.0(4)	

## onium guest

Atom	x	y	z	Beq/Å <sup>2</sup>
N(16)	0.1784(9)	0.511(3)	0.25	12.0(4)
C(16)	0.177(1)	0.412(4)	0.25	17.3(4)
C(17)	0.1945(9)	0.518(3)	0.387(3)	17.0(4)
N(17)	0.3811(5)	0.686(1)	0.25	3.9(4)
C(18)	0.4149(7)	0.694(2)	0.25	7.2(4)
C(19)	0.3689(6)	0.637(2)	0.393(2)	8.1(4)

Table VIII-1

Atomic parameters for V-1



Host	$\text{Cd}_3(\text{CN})_7$			
Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(o)	0.0	=X	=X	2.45(6)
Cd(t)	1/3	2/3	0.1161(1)	2.76(5)
CN*	1/3	2/3	0.2223(9)	4.2(5)
N(1)	0.1284(9)	=2X	0.0604(5)	4.5(4)
C(1)	0.1959(9)	=2X	0.0810(6)	3.7(4)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest  $\text{CH}_2\text{ClCH}_2\text{Cl}$ 

Atom	x	y	z	Beq/ $\text{\AA}^2$	occupancy
Cl	0.5538(9)	=2X	0.1706(7)	15.5(5)	2/3
C(2)	0.618(2)	=2X	0.097(1)	11.0(6)	2/3

onium guest  $\text{N}(\text{CH}_3)_4$ 

N(3)	0.0	=X	0.25	6.6(6)	
C(4)	0.0	=X	0.320(1)	9.0(6)	1/2
C(5)	0.085(2)	=2X	0.218(2)	10.9(6)	1/2

Table VIII-2 Atomic parameters for V-2

Host	$\text{Cd}_3(\text{CN})_7$			
Atom	x	y	z	Beq/ $\text{\AA}^2$
Cd(o)	0.0	=X	=X	2.73(3)
Cd(t)	1/3	2/3	0.11476(7)	3.02(4)
CN*	1/3	2/3	0.222(1)	3.9(5)
N(1)	0.1277(7)	=2X	0.0606(5)	4.0(3)
C(1)	0.1944(9)	=2X	0.0811(5)	3.6(3)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest  $\text{Cl}_2\text{C}=\text{CH}_2$ 

Atom	x	y	z	occupancy
Cl	0.57106(4)	=2X	0.1709(7)	15.7(7) 2/3

onium guest  $\text{N}(\text{CH}_3)_4$ 

N	0.0	=X	1/4	11(2)
C(2)	0.0	=X	0.301(6)	13(2)
C(3)	0.103(2)	=2X	0.208(2)	15(2)

Table VIII-3

Atomic parameters for V-3  
[Cd<sub>3</sub>(CN)<sub>7</sub>] · [N(CH<sub>3</sub>)<sub>4</sub> · 2C<sub>2</sub>H<sub>5</sub>CN]

Host Cd <sub>3</sub> (CN) <sub>7</sub>	x	y	z	Beq/ Å <sup>2</sup>
Atom				
Cd(o)	0.0	=X	=X	2.23(3)
Cd(t)	1/3	2/3	0.11958(5)	2.47(2)
CN(1)*	1/3	2/3	0.2234(7)	4.7(2)
N(1)	0.1275(5)	=2X	0.0618(3)	3.6(2)
C(1)	0.1950(5)	=2X	0.0854(3)	3.0(2)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest C<sub>2</sub>H<sub>5</sub>CN

Atom	x	y	z	occupancy
CN(2)**	0.653(2)	=2X	0.200(2)	17.2(2) 2/3
CN(3)**	0.723(2)	=2X	0.091(2)	22.2(2) 2/3

\*\* The atom has been refined as 3/1=C/N.

onium guest N(CH<sub>3</sub>)<sub>4</sub>

Atom	x	y	z	occupancy
N(2)	0.0	=X	1/4	12.9(3)
C(2)	0.0	=X	0.3222(9)	11.6(3) 0.36
C(3)	0.098(1)	=2X	1/4	11.9(3) 0.36
C(4)	0.075(2)	=2X	0.203(2)	14.7(3) 0.36

Table VIII-4 Atomic coordinate for V-4

[Cd<sub>3</sub>(CN)<sub>7</sub>] · [S(CH<sub>3</sub>)<sub>3</sub> · 2CH<sub>2</sub>ClCH<sub>2</sub>Cl]

Host Cd <sub>3</sub> (CN) <sub>7</sub>	x	y	z	Beq/ Å <sup>2</sup>
Atom				
Cd(o)	0.0	=X	=X	3.84(8)
Cd(t)	1/3	2/3	0.1137(1)	4.03(6)
CN*	1/3	2/3	0.222(1)	5.4(8)
N(1)	0.126(1)	=2X	0.0615(7)	6.3(7)
C(1)	0.194(1)	=2X	0.0798(8)	4.6(6)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest CH<sub>2</sub>ClCH<sub>2</sub>Cl

Atom	x	y	z	Beq/ Å <sup>2</sup>	occupancy
Cl	0.562(1)	=2X	0.1709(7)	19.5(6)	2/3
C(2)	0.717(3)	=2X	0.092(2)	12(1)	2/3

onium guest S(CH<sub>3</sub>)<sub>3</sub>

Atom	x	y	z	Beq/ Å <sup>2</sup>	occupancy
S	0.0	=X	0.216(1)	11.9(8)	1/2
C(3)	0.098(7)	=X	0.233(6)	10(3)	1/4
C(4)	0.19(2)	0.18(2)	0.25	13(3)	1/2

Table VIII-5 Atomic parameterse for V-5  
 $[\text{Cd}_3(\text{CN})_7] \cdot [\text{mtnH} \cdot \text{CH}_2\text{Cl}_2]$

Host  $\text{Cd}_3(\text{CN})_7$

Atom	x	y	z	Beq
Cd(o)	0.0	=X	=X	3.4(1)
Cd(t)	1/3	2/3	0.1136(1)	3.60(9)
CN*	1/3	2/3	0.2250(9)	5.3(9)
N(1)	0.1226(9)	=2X	0.0651(5)	4.3(7)
C(1)	0.1950(9)	=2X	0.0814(6)	3.8(3)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest  $\text{CH}_2\text{Cl}_2$

Atom	x	y	z	occupancy
Cl(1)	0.5762(9)	=2X	0.1706(7)	1/3
Cl(2)	0.702(2)	=2X	0.097(1)	8(1) 1/3

onium guest mtnH

some peaks due to the mtnH after the final difference Fourier.

Table IX Atomic coordinates for VI-1  
 $[\text{Cd}_3(\text{CN})_7] \cdot [\text{dmtdmH} \cdot \text{CH}_2\text{ClCH}_2\text{Cl}]$

Host $\text{Cd}_6(\text{CN})_{14}$				
Atom	x	y	z	Beq
Cd(o)	0.3405(3)	0.0	0.0	2.8(1)
Cd(t1)	0.1621(3)	0.1941(2)	0.0	2.9(1)
Cd(t1')	0.6033(3)	0.3011(2)	0.0	4.7(2)
Cd(o')	0.1353(3)	0.7370(1)	0.5	2.8(1)
Cd(t2)	0.3681(3)	0.5516(2)	0.5	3.4(1)
Cd(t2')	0.0667(3)	0.9397(2)	0.5	2.9(1)
N(1)	0.742(3)	0.580(1)	0.0	4.4(4)
C(1)	0.768(3)	0.618(1)	0.0	3.5(4)
N(2)	0.410(3)	0.920(1)	0.0	3.5(4)
C(2)	0.426(4)	0.881(1)	0.0	4.5(4)
CN(1)*	0.581(3)	0.761(2)	0.0	3.0(4)
CN(2)*	0.673(3)	0.742(2)	0.0	3.3(4)
N(3)	0.790(2)	0.478(1)	0.199(3)	3.9(4)
C(3)	0.840(2)	0.464(1)	0.299(3)	3.7(4)
N(4)	0.525(3)	0.524(1)	0.197(3)	5.3(4)
C(4)	0.474(3)	0.534(1)	0.298(3)	5.5(4)
N(5)	0.218(3)	0.659(1)	0.5	4.4(4)
C(5)	0.267(3)	0.623(2)	0.5	5.1(4)
N(6)	1.060(3)	0.817(1)	0.5	4.5(4)
C(6)	1.058(3)	0.858(1)	0.5	3.3(4)
CN(3)*	0.209(3)	0.498(1)	0.5	2.8(4)
CN(4)*	0.120(3)	0.478(3)	0.5	2.3(4)
N(7)	0.994(3)	0.716(1)	0.319(3)	4.2(4)
C(7)	0.940(2)	0.711(1)	0.211(3)	4.0(4)
N(8)	0.275(3)	0.762(2)	0.342(3)	7.8(4)
C(8)	0.309(3)	0.772(2)	0.228(3)	6.5(4)

\* The atom has been refined as 50% each occupancy of C and N atoms at the coordinates.

neutral guest

Atom	x	y	z	Beq	occupancy
Cl(1)	0.055(2)	0.741(7)	0.5	9.5(4)	
Cl(2)	0.384(3)	0.138(1)	0.374(3)	10.7(4)	0.5
C(9)	0.200(3)	0.106(2)	0.5	8.8(4)	
C(10)	0.246(3)	0.102(2)	0.378(4)	4.8(4)	0.5
Cl(3)	0.100(3)	0.608(1)	0.054(3)	12.2(4)	0.5
Cl(4)	0.385(3)	0.638(1)	0.0	15.2(4)	
C(11)	0.236(3)	0.639(2)	0.114(3)	5.2(4)	0.5
C(12)	0.233(3)	0.615(2)	0.0	6.0(4)	

onium guest

C(13)	0.109(4)	0.355(3)	0.147(4)	8.4(4)	0.5
C(14)	0.207(4)	0.360(2)	0.092(4)	6.8(4)	0.5
N(9)	0.124(4)	0.329(2)	0.0	10.4(4)	
C(15)	-0.018(4)	0.331(2)	0.0	11.4(4)	
C(16)	-0.032(4)	0.387(2)	0.0	10.2(4)	
C(17)	0.065(4)	0.433(2)	0.0	10.5(4)	
N(10)	0.173(4)	0.472(2)	0.0	11.6(4)	
C(11)	0.173(4)	0.537(2)	0.021(5)	8.0(4)	0.5
C(12)	0.254(4)	0.477(3)	0.128(4)	8.4(4)	0.5

C(13)	0.288(4)	0.251(2)	0.5	10.0(4)	
C(14)	0.449(4)	0.264(3)	0.433(4)	7.1(4)	0.5
N(11)	0.357(3)	0.296(2)	0.5	9.4(4)	
C(15)	0.276(4)	0.295(3)	0.362(4)	7.1(4)	0.5
C(16)	0.274(4)	0.323(3)	0.5	10.5(4)	
C(17)	0.356(4)	0.370(2)	0.5	10.3(4)	
N(12)	0.491(3)	0.382(2)	0.5	7.2(4)	
C(18)	0.585(4)	0.401(3)	0.389(4)	7.7(4)	0.5
C(19)	0.460(4)	0.397(3)	0.346(4)	7.8(4)	0.5

ination is impossible between both the tetrahedral Cd atoms and the C and N atoms of the cyanide linking the tetrahedral Cd.

The cross-linking of the  $-(T-O-T)-_{\infty}$  chains produces the cavity surrounded by three each of T-O-T-O tetragons and of chair-formed O-(T-T)<sub>2</sub>-O hexagons, as shown in Fig. 1. The cavity can be seen as the adamantane-like cavity of the cristobalite-like host but capped by a T-(CN)<sub>3</sub> moiety on a chair-formed hexagon.

In I-1, each of the tetrahedral guest  $N(CH_3)_4^+$  and  $Sn(CH_3)_4$  is accommodated in the cavity with 50% each probability, i.e., the distribution is at random. At the final stage of the refinement, the bond lengths of the N-C and the Sn-C in the guest moieties were constrained at 1.46(2) and 2.14(2) Å, respectively. When the space group R3m (No.160) was applied, the discrimination between the C and N of the cyanide and between the cavities accommodating the respective guests were theoretically possible, but the results did not make any progress.

Since only one kind of crystallographically independent cavity formed in type I host structure, the guests in I-2 were also distributed with 50% each probability in the cavity. The bond lengths of the C-C and C-N in  $N(C_2H_5)_4^+$  and C-Cl in  $CH_2Cl_2$  were constrained at 1.54(3), 1.48(3), and 1.76(3) Å, respectively, in the final stage of the refinement, where all the host atoms were refined anisotropically and the non-hydrogen guest atoms isotropically.

Due to the random distribution of the guest species, it was extremely difficult to obtain the significant atomic parameters for the onium and the neutral guests: only the host structure was refined anisotropically.

#### 4.3.3. Type II Structures ( Fig. 2 ) [2]

The observed systematic absences were consistent with the space group  $Pnm2_1$  or  $Pn2_1m$  (No.31) and  $Pnmm$  (No.59); the non-centrosymmetric  $Pn2_1m$  gave uniquely the chemically acceptable results. The discrimination between Cd(t) and Cd(t'), and C and N of the CN linking Cd(t) and Cd(t') was possible in this space group; Cd(t) is in a  $CdC_4$  coordination and Cd(t') in a  $CdC_3N$ . The Cd(t)-C and Cd(t')-N distances on the mirror plane have been observed 2.19(2) and 2.28(2) Å for II-1, 2.21(1) and 2.28(1) Å for

II-2, and 2.214(8) and 2.313(8) Å for II-3. If the criterion is strictly applied, the discrimination is inadequate for II-1.

Crystallographically independent but topologically very similar two kinds of cavities are formed. One cavity, A is surrounded by the  $O-(T-T')_2-O$  hexagon at the top,  $T-O-T'-O$  tetragon at the bottom, and two each of  $T-T'-O-T'-O$  and  $T-O-T'-T-O$  pentagons at sides; the other, B, sharing the  $T-O-T'-O$  tetragon but by  $O-(T'-T)_2-O$  hexagons, and two each of  $T'-T-O-T-O$  and  $T'-O-T-T'-O$  pentagons. With respect to the coordination polyhedra, both are surrounded by seven tetrahedra and four octahedra. In spite of the similarity in topology between cavities A and B, the respective onium guest  $N(CH_3)_4^+$ ,  $dmtnH^+$ , and  $detnH^+$ , always prefer cavity A independent of their molecular geometries. The two trimethylenediamine derivatives appear to form an intramolecular hydrogen bond between the amino group and the substituted amino group in the cavity: the N-N distances are 2.69(2) Å for the  $dmtnH^+$  and 2.76(2) Å for the  $detnH^+$ . When the coiled skeletons are seen from the amino group to the substituted amino group, the orientation of the projection of the coil is clockwise for  $dmtnH^+$  and counter-clockwise for  $detnH^+$  along the c-axis of the given unit cell setting. The refinement with the counter-clockwise orientation of  $dmtnH^+$  gave the reversed  $Cd(t)-C$  and  $Cd(t')-N$  distances, 2.27(1) and 2.24(1) Å, respectively. Although a distribution of the clockwise and counter-clockwise orientation has been adopted as the final conclusion, the problem of the C-N discrimination has not been completely solved.

#### 4.3.4. Type III Structures ( Fig. 3 )

The observed systematic absences were consistent with the space group  $Pna2_1$  (No. 33) and  $Pnam$  (No.62); the latter was chosen because it gave the better convergence. Although the space group allowed theoretically the discrimination between the C and N of the cyanide linking  $Cd(t)$  and  $Cd(t')$ , the  $Cd(t)-C$  and  $Cd(t')-N$  distances were 2.21(4) and 2.35(5) Å for III-1, 2.27(1) and 2.25(1) Å for III-12, 2.209 and 2.204(9) Å for III-1, and 2.16(2) and 2.30(2) Å for III-22. There remains some ambiguities except for the last. At any rate there are three kinds of crystallographical-

ly independent Cd atoms, Cd(o), Cd(t), and Cd(t').

Three kinds of cavities A, B, and C, can be defined in the three-dimensional host structure, although the mutual opening are rather wide. A is surrounded by three O-T-O-T' tetragons, T-T'-O-T-O pentagons, and O-(T-T')<sub>2</sub>-O hexagons; B by four hexagons, three O-(T-T')<sub>2</sub>-O, and a T-(O-T)<sub>2</sub>-T; C by a T-(O-T)<sub>2</sub>-T hexagon, two O-T-T'-O-T pentagons, and a O-T-O-T' tetragon. A share the hexagon with B, and C does the hexagon with B. According to the positions of the respective guests in these cavities, type III compounds are grouped to III-11 and -12 and III-21 and 22. In the former subgroup, the onium guest is accommodated in C, and the benzene molecules are in B and A; in the latter, the onium in A, and the substituted benzene guest places the benzene ring in B and the substituent(s) in C. Hence, the limiting formula is given [Cd<sub>3</sub>(CN)<sub>7</sub>] · [onium · 2G] for the former, and [Cd<sub>3</sub>(CN)<sub>7</sub>] · [onium · G] for the latter, but non-stoichiometric accommodation of the aromatic guests was observed for both sub-groups.

The structure of III-11 was solved without non-stoichiometric occupation of the benzene molecules, although the sulfonium is distributed statistically with respect to the mirror plane in cavity C. The benzene molecules in B cavities are alternately arranged along the c-axis of crystal with a deviation from the center of cavity to the hexagonal face shared with cavity A; the deviation appears to lessen the steric repulsion between the benzene molecules in the next cavity along the c-axis. It also appears that the repulsion is stronger for III-12 than for III-11, as the benzene in B of III-12 locates at the cavity center with the refined occupancy factor of 0.57 with considerably greater thermal parameters than that in A. The occupancy of ca. 0.5 means that the cavity B is alternately arranged with occupied and vacant. Since the methyl groups of the onium guests in C invade B to a certain extent through the hexagonal opening, the methyl groups of the tetramethylammonium guest with a full occupancy makes the effective volume of B lessen.

In contrast with the former sub-group, the onium is accommodated in cavity A and the aromatic guest in B for III-21 and -22. The aromatic plane of the guest in B takes an orientation rotated

by  $90^\circ$  about the c-axis from that in the former sub-group; the methyl group of the toluene in III-21 locates at the position similar to the onium guest in the former. The mesitylene molecule in III-22 makes one of the methyl groups invade cavity C similarly to that of the toluene, but leaves the remaining two related to the mirror plane in cavity B to bring about great repulsion between the neighboring guests along the c-axis. The occupancy was refined as 0.667: two thirds of the total B cavities should be occupied by the mesitylene molecules. Moreover, the molecule is distributed statistically at two positions with a ratio of 1/3. The deeper position makes the repulsion between the neighboring mesitylenes the less. If neighboring cavity is vacant, the less deep position should be energetically stable. When the arrangement of the both positions were in order, a superlattice structure with at least three times c dimension should have been given from the reflection data. It did not. Hence the occupancies of both the cavity and position should be in disorder in the analyzed crystal.

#### 4.3.5. Type IV structure ( Fig. 4 )

Only one example has been obtained for this type, which has remarkable difference from others. Penta-coordinated Cd atom taking a trigonal-bipyramidal configuration, Cd(p), joins the host structure. The space group Pnam was chosen similarly to the case of type III. There are six crystallographically independent Cd atoms, two Cd(o) three Cd(t1,t2,t3), and one Cd(p) atoms in the unit cell with the extremely long a dimension of 43.39(1) Å. The penta-coordination of Cd(p) is attained by the ligation of the unidentate neutral  $N(CH_3)_3$ . The Cd(t1)-CN-Cd(p) distance of 5.99(2) Å is unusually long, but the Cd(t1)-C and Cd(p)-N distances of 2.28(2) and 2.76(2) Å makes the discrimination between the C and N atoms clear. That for the CN group linking Cd(t2) to Cd(t3) was impossible with the same distance of Cd-C, N: 2.24(2) Å.

Five kinds of cavities IIA, IIB, IIIA, IIIB, and IIIC, similar to but distorted from those in type II and type III are formed in the three-dimensional framework. The ligating  $N(CH_3)_3$  occupies IIIA; IIA and IIIB are accommodated respectively with a  $CH_2ClCH_2Cl$  molecule, and IIB and IIIC with  $N(CH_3)_3H^+$ . Similarly to the case

of type III, the  $\text{CH}_2\text{ClCH}_2\text{Cl}$  molecules in IIIB appears to be non-stoichiometric based on the accuracies of the refined parameters; values of the measured densities were scattered, too.

#### 4.3.6. Type V Structures ( Fig. 5 )

The diffraction data supported the Laue class of  $6/\text{mmm}$ ; the space group  $\text{P}6_3/\text{mmc}$  was chosen as the most reasonable. The host atoms are arranged with the high symmetries, but the guest species are highly disordered in each compound owing to the little correlation of the molecular group with the site symmetry of the cavity center.

#### 4.3.7. Type VI structure ( Fig. 6 )

The space group  $\text{Pb}2_1\text{m}$ (No. 26) was chosen as the most reasonable from those possible from the observed systematic absences, including the  $\text{Pbm}2$ (No. 28) and  $\text{Pbmm}$ (No. 51). Two formula units are crystallographically independent in the unit cell of the long b dimension of  $27.553(3)$  Å. The discrimination between the C and N atoms of the cyanide linking  $\text{Cd}(\text{t})$  and  $\text{Cd}(\text{t}')$  was practically impossible. The 1,2-dichloroethane takes a trans conformation, and the  $\text{dmtdmH}^+$  forms an intramolecular hydrogen bond, in the respective cavities.

#### 4.4. Classification of the host Structures

There have been observed substantially the three ways of bending for the chains on the mirror plane consisting of the periodical sequence of  $-(\text{T-O-T})_\infty$  units in each host structure: (1) E-TOT, E-TT for type I through IV, (2) E-TOT, Z-TT for type V, and (3) Z-TOT, E-TT for type VI, as shown in Fig. 7. The notation E-TOT means that the chain bends oppositely at both end of T-O-T unit; E-TT means that the couple of (T-O-T) units bends at T-T junction oppositely. Hence, Z-TOT and Z-TT are those bending to the same directions, respectively. Z-TOT, Z-TT is impossible to extend an infinite chain.

A chain on a mirror plane is linked with the cyanide groups out of the plane at every Cd atoms to the chains in the adjacent

planes above and beneath: T in one plane is connected to O in the adjacent planes and vice versa. As has been seen in 4.3., the connections make tetra-, penta-, and hexagons cornered by T or O Cd atoms and edged by CN group between the planes. The polyhedral cavities thus formed are surrounded by the polygons whose edges are thick enough to hold a guest inside due to the  $\pi$ -electrons on the CN triple bond.

The relative array of the respective chains on the same and the adjacent planes gives the varieties of the structures from type I to type VI. First in type I, a given E-TOT, E-TT chain on a mirror plane generates with the chain on the adjacent plane by an appropriate parallel translation; a hexagon and a tetragon are formed between the chains. In type II, the selected chain is correlated with that on the adjacent planes by a  $2_1$  screw rotation, i.e., the direction of bending is alternately reversed between the planes. If the chain first selected is called to take an "ortho" arrangement, those on the adjacent planes are in "anti" arrangement. Let this mode denote o-a'; two kinds of pentagons are formed between the chains. In type III, the chains in o and a are alternately arranged on the same plane along the a axis, but the interplane arrangement is o-a'-a-o': between o-a' formed are two pentagons and between a'-a are a tetragon and a hexagon. In type IV, the arrangement is o-a'-o-a'-a-o'-a-o' to make the a dimension longest among type II through type IV, where the penta-coordinated Cd was seen as a T moiety. Approximately, the a dimension is two times that of type II for type III and four times for type IV. In type V, E-TOT, Z-TT chains are arranged in o-o' mode to give a tetragon and a hexagon similar to those in type I. Type VI is only one example of Z-TOT, E-TT with a-o' arrangement to give a tetragon, pentagon, and a hexagon.

#### 4.5. Discussion

Although the number of the structures have been analyzed are still limited to 17 for the zeolite-like  $\text{Cd}_3(\text{CN})_7$  host inclusion compounds, at least six variations of the structural pattern have been found on the basis of the difference in bending and relative arrangement of the (tetrahedral cadmium)-(cyanide)-(octahedral

cadmium)-(cyanide)-(tetrahedral cadmium)-(cyanide) sequential chains ( Fig. 8 ). The non-stoichiometric character of the neutral guest molecules observed for some examples suggests the behavior of the guest similar to those adsorbed in the real zeolite frameworks. The negative charge of the host and the cationic guest inside the framework show also the similarity to the real zeolites. The intracavity chemistry of the guest should be the next problem to be challenged.

As for the chemical crystallography, the discrimination between the N and C atoms in the linking cyanide group is always a problem in solving the crystal structure precisely. In the present series of the structures it depended on case by case either possible or not. The recent progress in  $^{113}\text{Cd}$  solid state NMR will be a great help to solve the problem [3].

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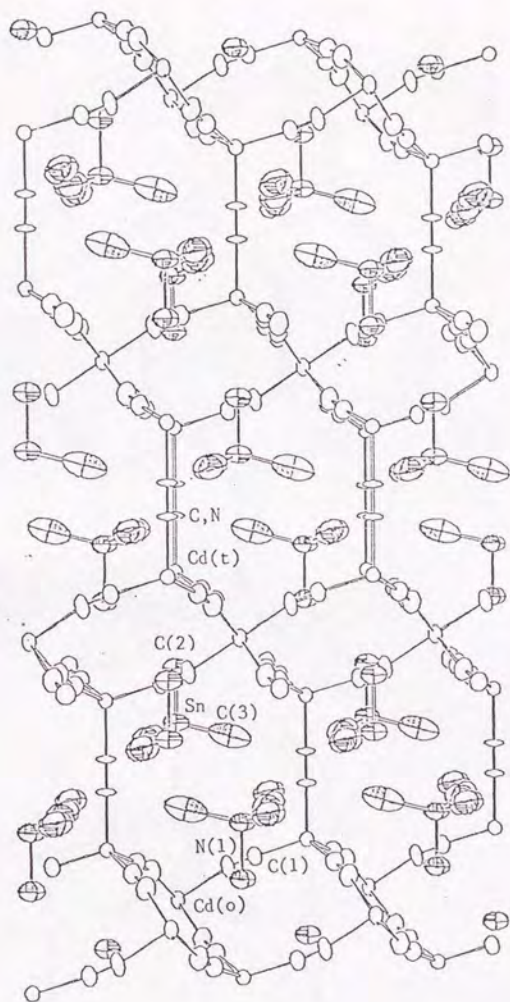
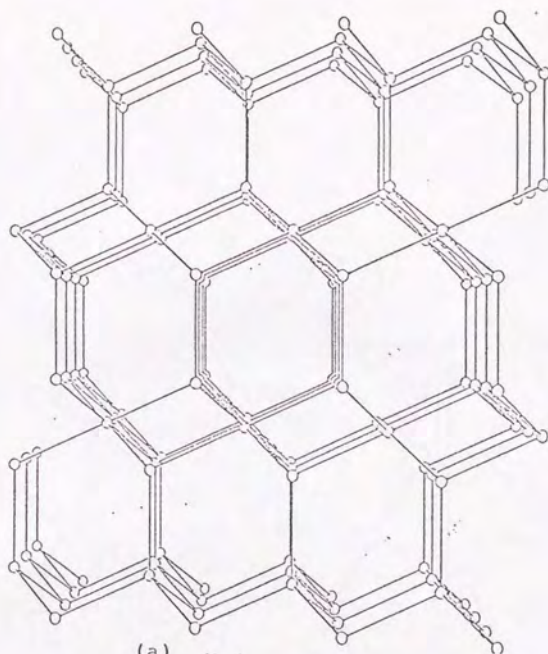
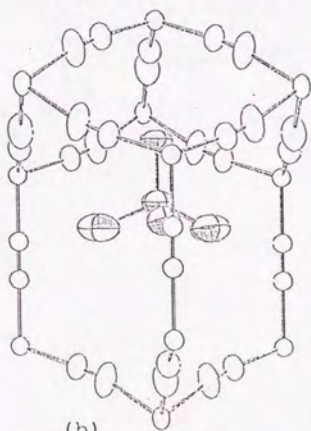


Fig. 1-1 View of the structure of I-1 along the b-axis.



(a)



(b)

Fig. 1-2

(a) View of the host structure of type I along the b-axis.  
 (b) View of the cavity of type I.

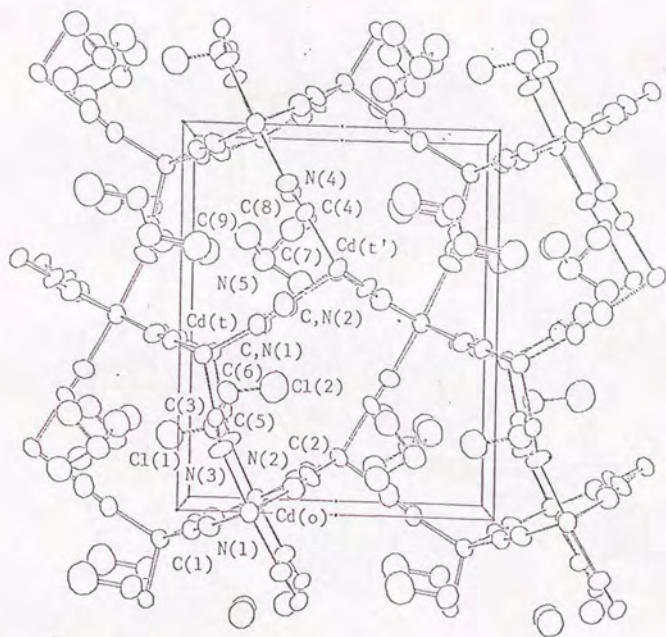


Fig. 2-1 View of the unit cell of II-1 along the c-axis.

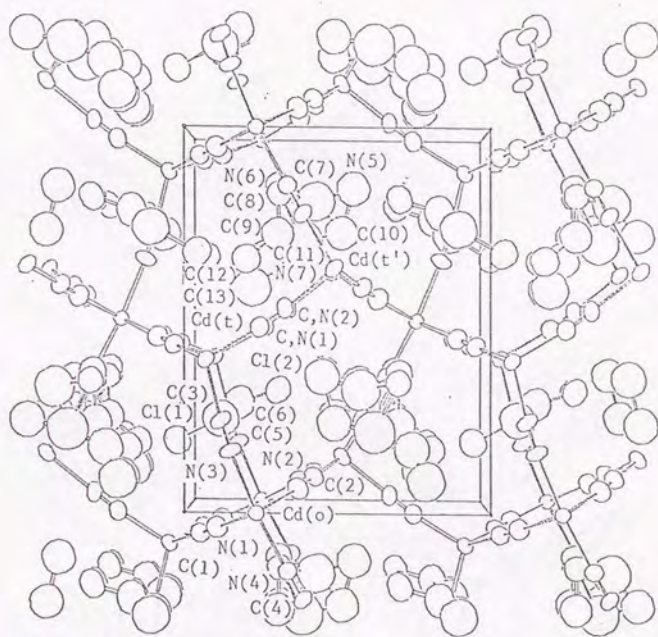


Fig. 2-2 View of the unit cell of II-2 along the c-axis,

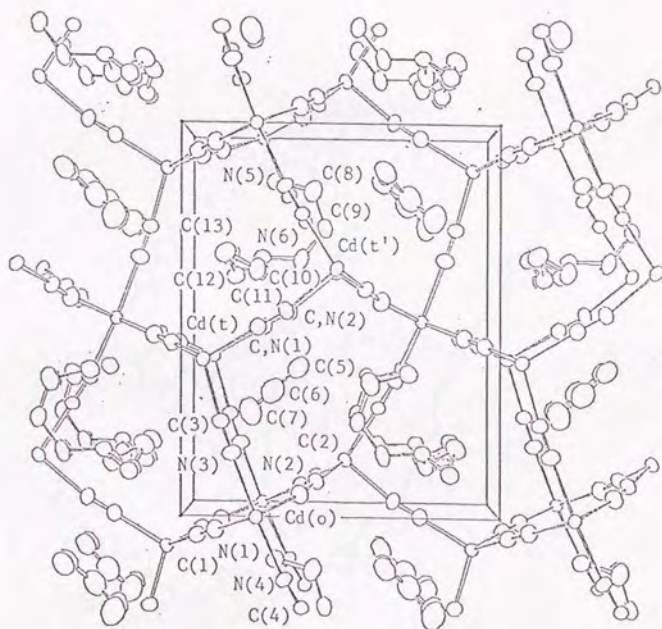


Fig. 2-3 View of the unit cell of II-3 along the c-axis.

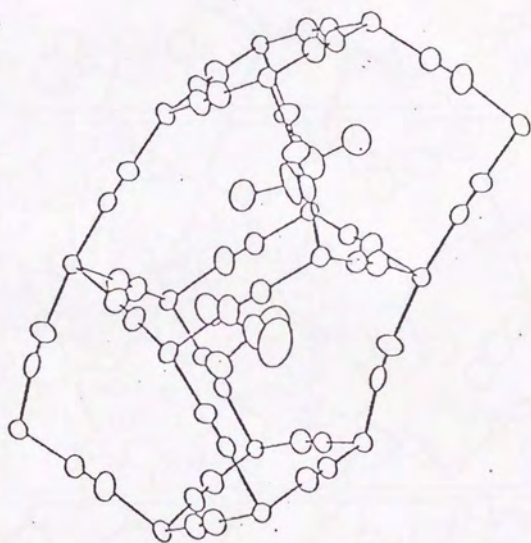


Fig. 2-4 View of the cavity of type II.

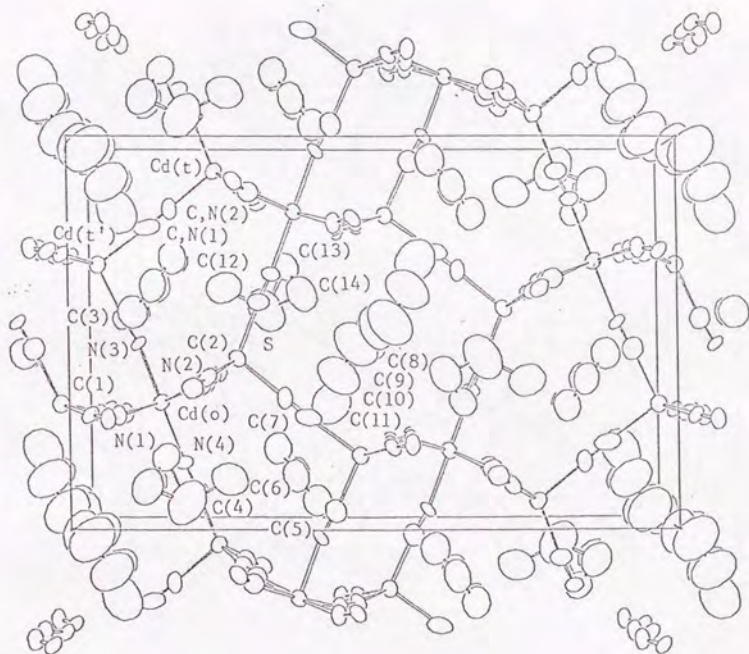


Fig. 3-1 View of the unit cell of III-11 along the c-axis,

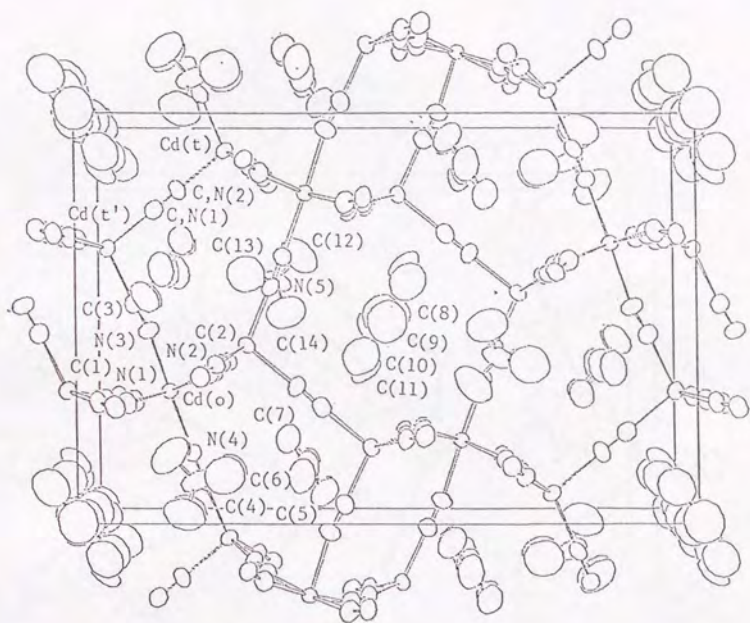


Fig. 3-2 View of the unit cell of III-12 along the c-axis,

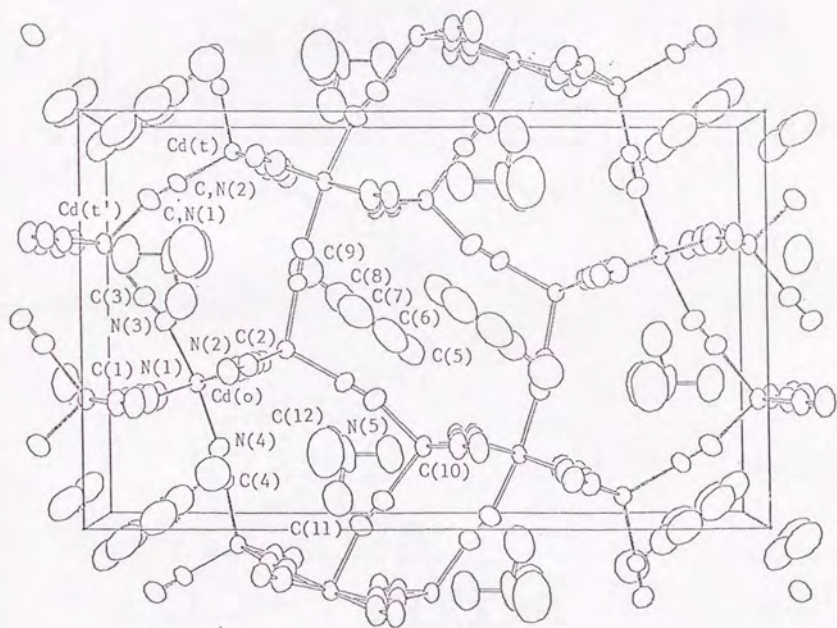
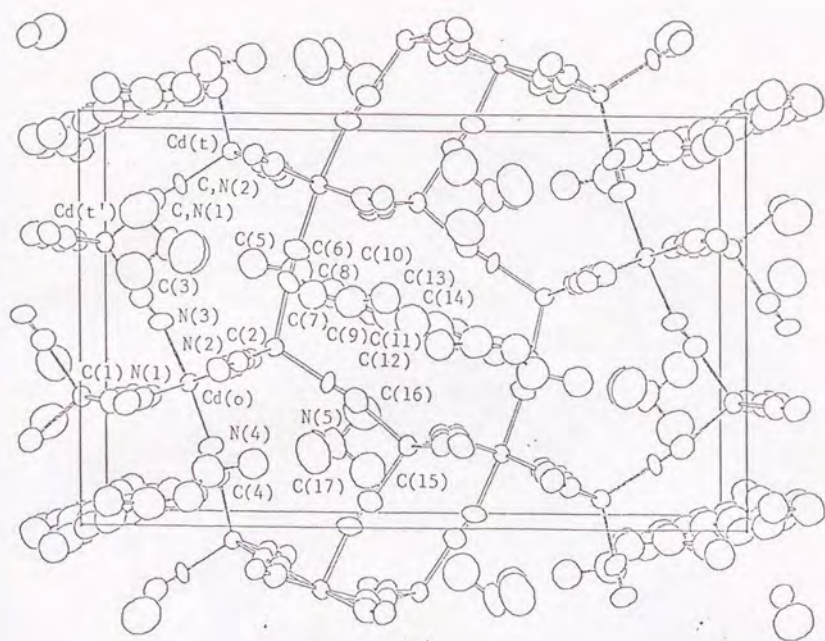
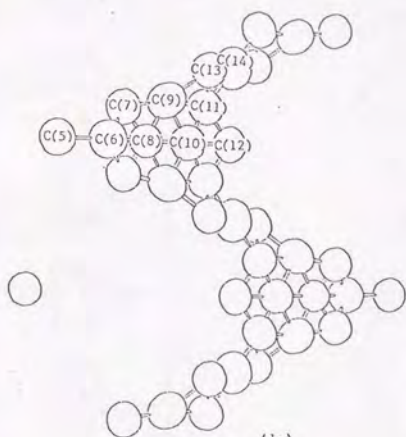


Fig. 3-3 View of the unit cell of III-21 along the *c*-axis.



(a)



(b)

Fig. 3-4 (a) View of the unit cell of III-22 along the c-axis.  
(b) View of the distributed guest molecules.

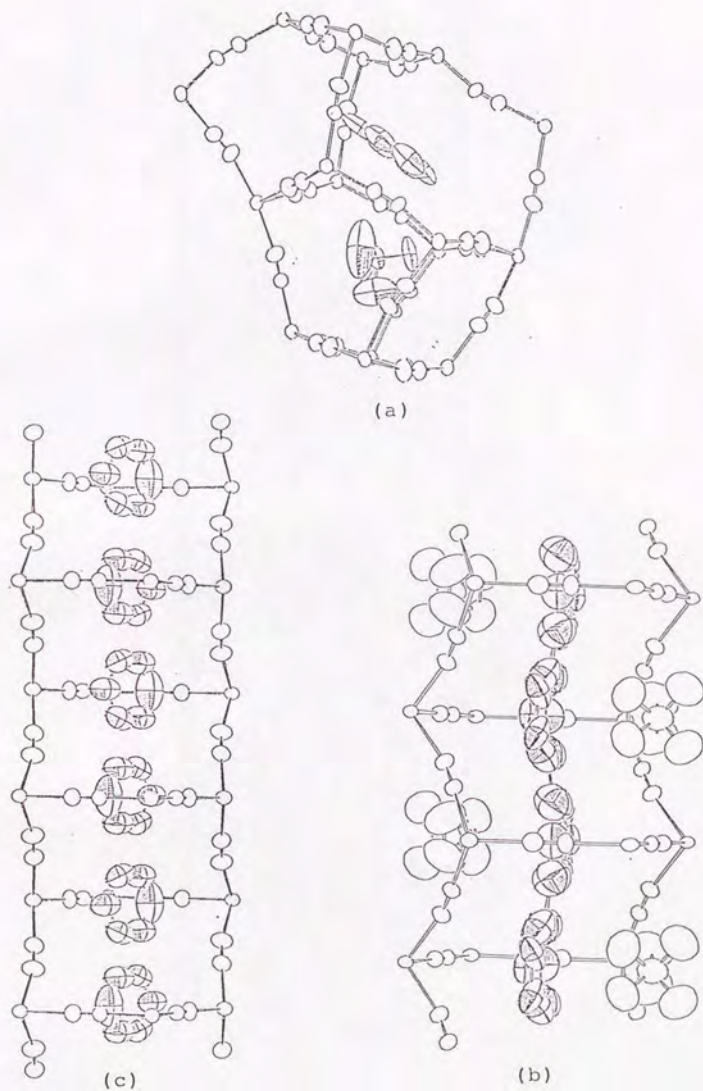


Fig. 3.5 (a) View of the cavity of III-21 along the c-axis.  
 (b) View of the cavity of III-11.  
 (c) view of the cavity of III-21.

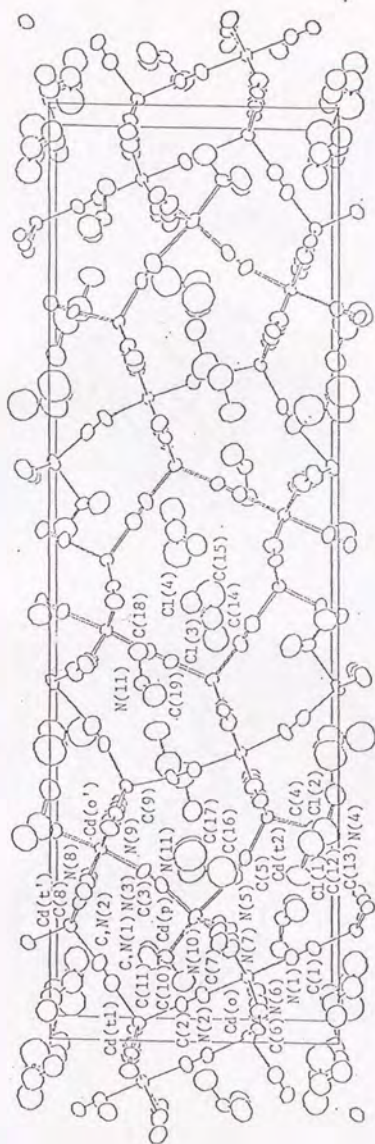


Fig. 4 View of the unit cell of IV along the c-axis.

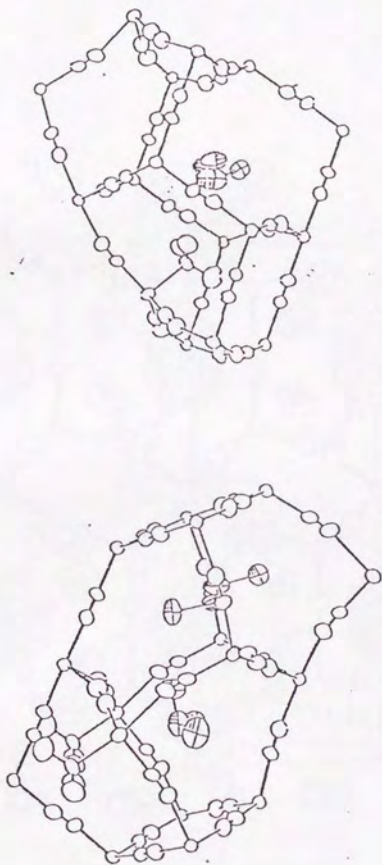


Fig. 4-1 View of the cavities of IV.

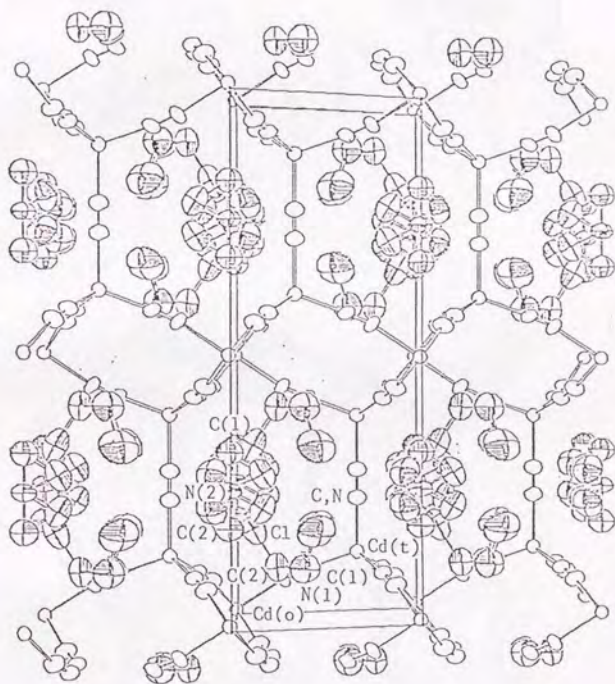
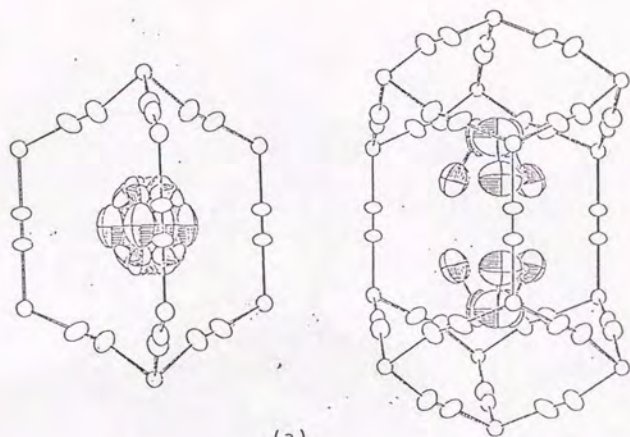
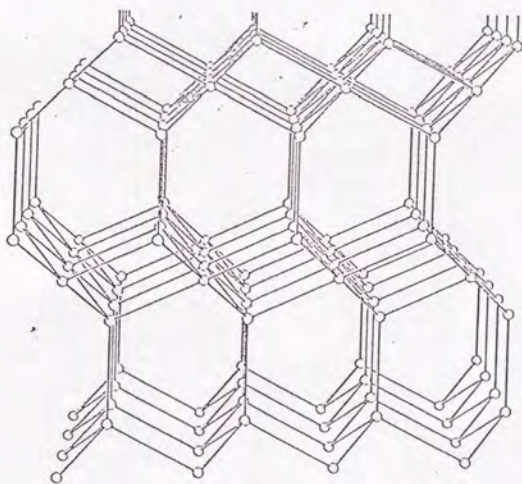


Fig. 5-1 View of the unit cell of V-1 along the c-axis.



(a)



(b)

Fig. 5-2 (a) View of the cavities of type V.  
(b) View of the host structure of type V.

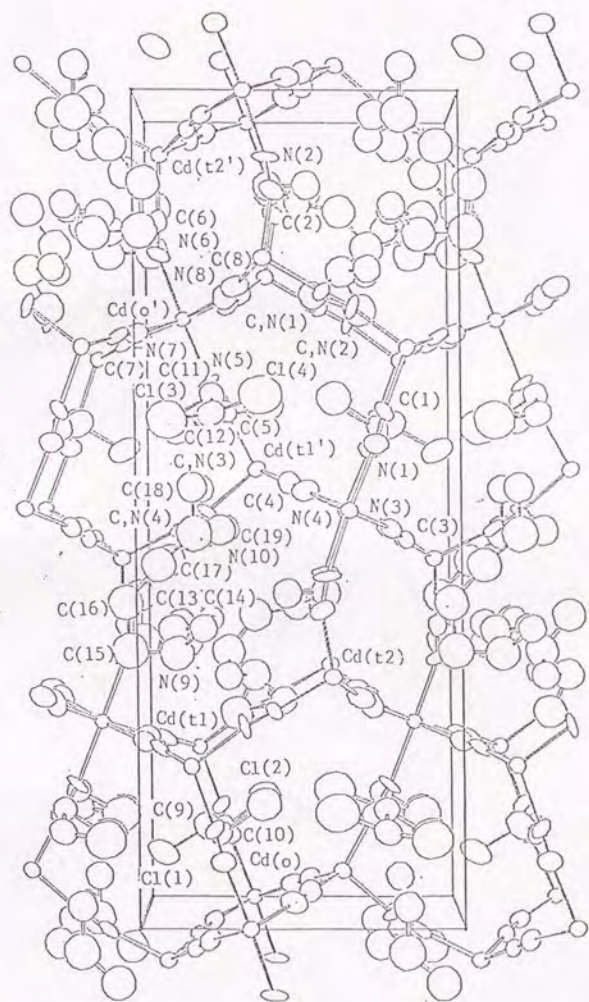


Fig. 6-1 View of the unit cell of VI-1 along the c-axis.

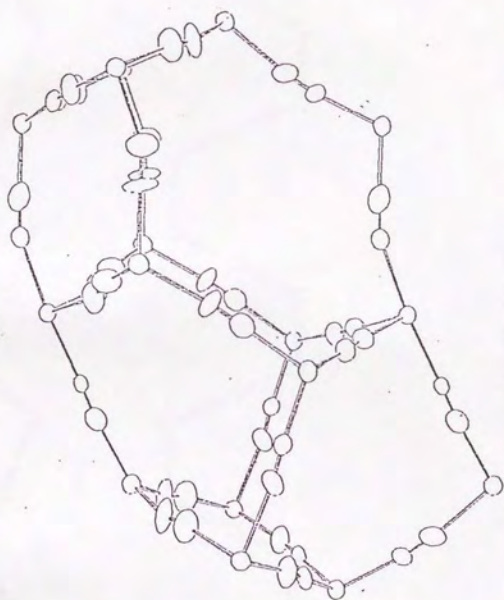


Fig. 6-2 View of the cavity of VI-1 along the c-axis.



Fig. 7-1 Chains on the mirror plane consisting of the periodical sequence of  $-(T-O-T)_{\infty}^-$   
 (1) E-TOT, E-TT (2) E-TOT, Z-TT (3) Z-TOT, E-TT

Chain A (E-TOT, E-TT)

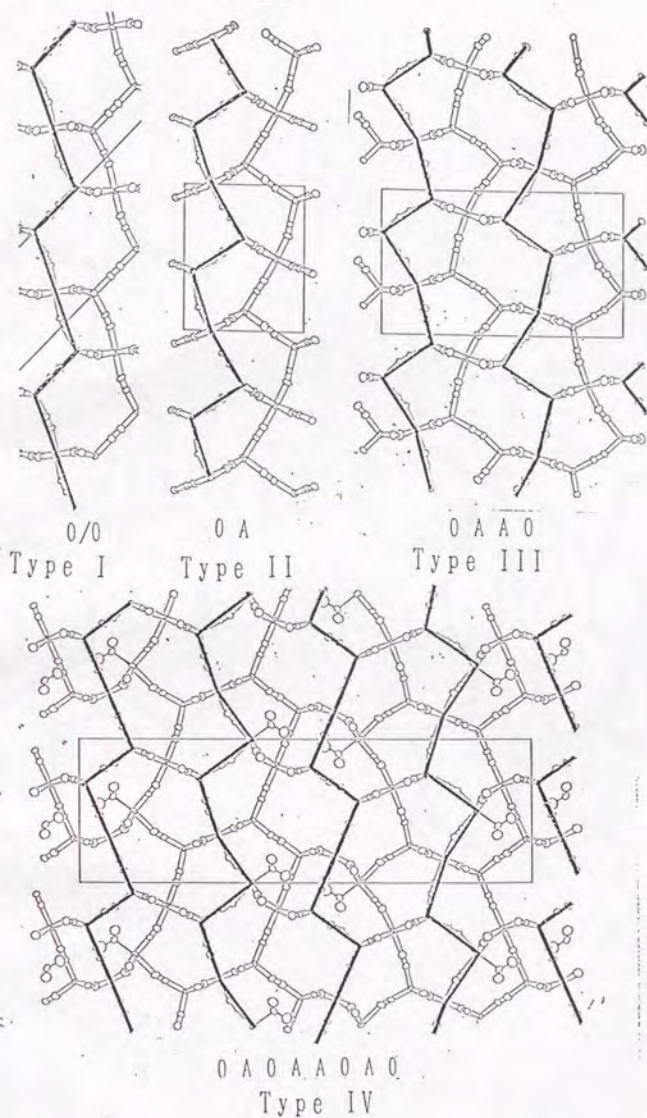
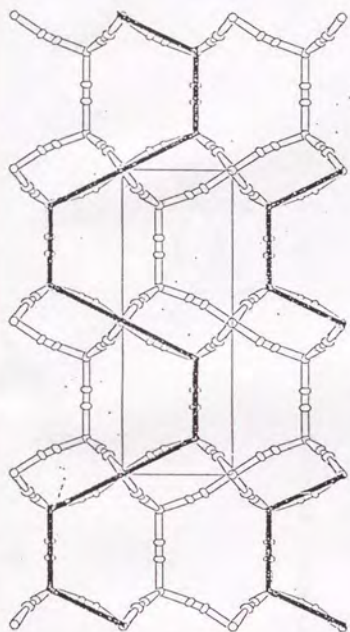
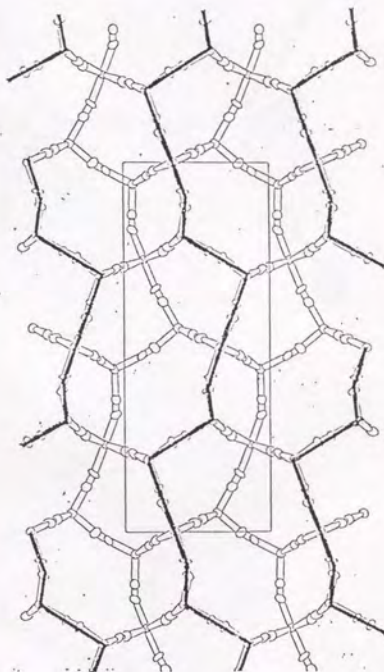


Fig. 7-2 Chains of Type I, II, III, and IV.  
(1) E-TOT, E-TT



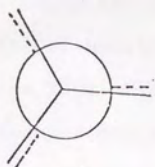
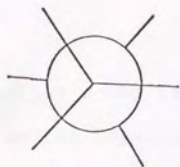
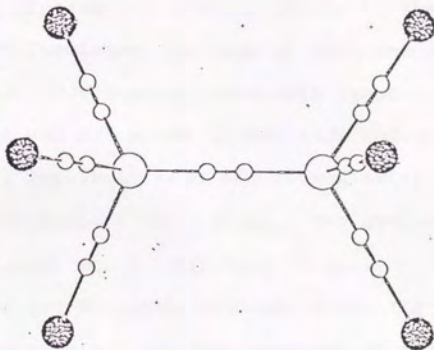
0/0  
Chain B (E-TOT, Z-TT)  
Type V



0 A  
Chain C (Z-TOT, E-TT)  
Type VI

Fig. 7-3 Chains of type V and VI; (2) E-TOT, Z-TT,  
(3) Z-TOT, E-TT.

Subunit of  $[\text{Cd}(\text{Oh})-\text{NC}]_3-\text{Cd}(\text{Td})-\text{CN}-\text{Cd}(\text{Td})-\text{CN}-\text{Cd}(\text{Oh})]_3$



Subunit of  $[\text{Cd}(\text{Td})-\text{CN}]_3-\text{Cd}(\text{Oh})-[\text{NC}-\text{Cd}(\text{Td})]_3$

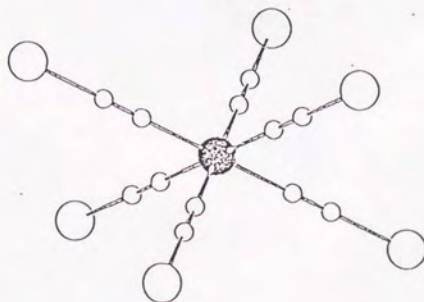


Fig. 8 Subunit of the Zeolite-like host structures.

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