

THREE-DIMENSIONAL METAL COMPLEX HOSTS BUILT OF  $\alpha, \omega$ -(LONG-CARBON-CHAIN)-  
DIAMINOALKANE LIGAND BRIDGING TWO-DIMENSIONAL CYANOMETAL COMPLEX  
NETWORK: HOFMANN-DIAMINOALKANE-TYPE CLATHRATES

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We have been developing systematically the chemistry of Hofmann-type and related clathrate compounds. Several modifications of the metal complex host structures have been derived from that of the Hofmann-type by replacing the ammine ligands by amines or diamines, and/or the square-planar tetracyanometallate by tetrahedral one [1]. However, their structures were substantially similar to that of the Hofmann-type: the volume of cavity was barely large enough to accommodate such small aromatic molecule as those enclathrated in the Hofmann-type host.

In order to accommodate a variety of guest molecules different in size and shape from those enclathrated in the Hofmann-type and the analogous clathrates previously derived, substitution of the ammine ligands in the Hofmann-type host by lipophilic amines or diamines have been attempted [2-6]. One of those attempts by us [6] and another group [4] was achieved by introducing  $\alpha, \omega$ -(long-carbon-chain)-diaminoalkanes into the host structures, where the diamine behaved as an ambidentate ligand to make a bridge between adjacent two dimensional cyanometal complex layers; the three-dimensional metal complex hosts thus derived may be called Hofmann-diam-type.

As listed in Table I more than 150 kinds of Hofmann-diam-type inclusion compounds have been prepared with the general formula  $\text{Cd}[\text{NH}_2(\text{CH}_2)_n\text{NH}_2]\text{Ni}(\text{CN})_4 \cdot x\text{G}$  for the hosts with  $n = 4 - 9$  and the guests with  $x = 0.5 - 2$ . They were characterized by chemical analyses, thermogravimetry, powder X-ray diffractometry, and vibrational (IR and Raman) spectroscopy; single crystal X-ray structure analyses have been carried out for the eight of them to demonstrate the characteristic features of the host structures [7-10]. In Table I the coefficient  $x$ , i. e., the number of guest molecule per a formal unit of the host metal complex, the basal spacing  $d$  determined from the powder x-ray diffraction pattern, and the crystalline appearance are summarized; for some of them it was difficult to determine  $x$  and/or  $d$  as reproducible values but the formation of something comprised of the metal complex and the aromatic species was affirmed by the infrared spectrum. Those with the  $x$  of about 1 but not larger than 1 have probably the structures similar to those of the Hofmann-dabn-type (dabn = 1,4-diaminobutane) [10] or the

	Table I. Hofmann-diam-type	
<u>n</u>	4	5
Pyrrole	1.0; 7.84; A+	2.0; nd; C
Thiophene	F	F
Benzene	1.5; 9.73; B	1.0; 8.51; B
Phenol	F	NE
Aniline	1.5; 9.70; A+	1.0; nd; C
Toluene	1.5; 9.75; B	-----
Fluorobenzene	0.8; nd; C	1.0; nd; C
Chlorobenzene	1.5; 9.93; B	-----
Bromobenzene	1.3; nd; C	-----
Iodobenzene	1.3; nd; C	-----
Phenylacetylene	1.5; 9.69; B	1.5; 9.43; B
Styrene	1.5; 9.54; B	1.5; nd; B
Ethylbenzene	-----	-----
N,N-Dimethylaniline	1.0; 9.01; A+	1.45; 11.2; B
n-Propylbenzene	NE	NE
i-Propylbenzene	-----	-----
dl-1-Phenylethanol	-----	-----
o-Toluidine	1.5; 9.78; A	1.5; 10.2; A
m-Toluidine	1.28; 9.89; B	1.0; nd; C
p-Toluidine	1.5; 9.50; A	1.5; 11.0; C
o-Xylene	F	-----
m-Xylene	-----	-----
p-Xylene	-----	-----
o-Dichlorobenzene	1.5; 9.93; C	-----
m-Dichlorobenzene	-----	-----
p-Dichlorobenzene	-----	-----
m-Dibromobenzene	-----	-----
2,3-Xylidine	1.28; 10.0; A	1.29; 10.5; A
2,4-Xylidine	1.22; 9.45; A	-----
2,5-Xylidine	1.0; 9.48; A+	1.0; 10.2; A
2,6-Xylidine	1.25; nd; B	1.25; nd; C
3,4-Xylidine	1.25; nd; A	-----
3,5-Xylidine	1.18; 9.93; B	1.0; 10.8; B
1,2,3-Trimethylbenzene	-----	-----
1,2,4-Trimethylbenzene	-----	-----
1,3,5-Trimethylbenzene	-----	-----
2,4,6-Trimethylaniline	1.45; 10.3; B	1.34; 11.1; B
1,2,3,4-Tetramethylbenzene	NE	-----
1,2,3,5-Tetramethylbenzene	NE	NE
1,2,4,5-Tetramethylbenzene	NE	NE
Pentamethylbenzene	NE	NE
Hexamethylbenzene	NE	NE
Indene	2.0; 10.3; A	1.38; 10.5; B
Naphthalene	NE	NE
Phenanthrene	NE	NE

\*  $\text{Cd}[\text{NH}_2(\text{CH}_2)_n\text{NH}_2]\text{Ni}(\text{CN})_4 \cdot x$ . The values of  $x$  and basal spacing  $d$  in guest  $G$  and the host of the  $n = 4, 5, 6, 7, 8, \text{ or } 9$ . F: evidence of -----; examined but not yet obtained; nd: not determined; A+: single crystalline powder; D: fine powder; E: poor or unstable.

## Compounds\*

6	7	8	9
0.9; nd; E	F	1.2; nd; C	NE
0.9; nd; C	0.3; nd; E	1.2; nd; D	NE
1.0; 9.19; E	1.0; 13.27; E	0.25; 10.73; D	0.45; nd; C
1.0; nd; D	NE	0.5?; 10.78; D	NE
1.0; nd; C	1.0; nd; C	1.2; nd; D	1.0; nd; C
1.0; 9.40; B	1.0; nd; B	0.5?; 11.05; A	0.5; 10.2; D
1.0; nd; C	0.8; nd; E	0.75; nd; C	NE
1.0; 9.21; C	1.0; 10.96; A	0.8?; nd; C	F
1.0; 9.49; C	1.0; nd; B	1.0; nd; C	NE
1.0; nd; C	1.0; nd; D	1.0; nd; D	NE
1.0; 9.59; B	1.0; nd; D	F	1.0; nd; B
0.9; 9.48; B	1.0; nd; C	F; 10.83; B	0.6; nd; D
0.7; 9.42; A	-----	1.0; 10.98; C	NE
0.8; 9.60; B	1.0; 10.64; C	F	2.5; nd; E
-----	-----	0.8; 10.96; C	NE
-----	-----	0.9; 11.33; C	NE
F	-----	F	NE
1.0; 9.42; A+	1.0; 9.63; A	2.5?; 10.92; B	2.8?; nd; C
1.0; 9.62; A+	1.0; nd; B	1.0; 11.01; C	2.3; nd; B
0.9; 10.56; A+	1.0; nd; B	1.0; 10.96; C	2.5; nd; B
F	1.0; nd; D	1.0; nd; C	NE
F	-----	1.0; 11.1; C	2.0; nd; C
0.7; 9.40; C	1.0; nd; C	1.0; 10.50; C	2.0; nd; C
1.0; nd; C	1.0; nd; B	1.0; nd; B	F
0.75; 9.45; B	-----	1.0; nd; C	F
0.8; 9.65; C	-----	1.0; nd; C	F
F	1.0; nd; C	F	NE
1.0; 9.82; A	1.0; nd; B	0.9; 10.81; A	3.0; nd; A
1.0; 9.47; A+	1.0; nd; C	0.9; 10.86; A	3.0; nd; A
1.0; 9.60; B	1.0; 10.35; B	0.9; 10.73; A	3.0; 13.78; A
0.7; nd; A	3.0?; nd; B	0.85; nd; A	0.5; 13.60; A
0.6; nd; B	0.5; nd; B	1.0; nd; A	2.5; nd; C
0.75; 9.61; B	0.8; nd; D	0.9; nd; A	2.5; nd; C
0.9; 9.98; C	-----	0.9; nd; C	2.0; nd; C
0.7; 9.98; C	-----	F	2.0; nd; C
-----	-----	1.0?; 11.14; D	2.0; nd; C
1.0; nd; B	0.9; nd; C	1.0; nd; C	2.5; nd; C
F	-----	0.6; nd; C	0.6?; nd; C
-----	-----	0.8; nd; D	0.6?; nd; C
0.7; 9.73; C	-----	0.5?; nd; D	NE
-----	-----	3.0; nd; C	NE
-----	-----	-----	-----
1.0; nd; A	1.0; nd; B	1.0; nd; B	2.5; nd; B
F	1.0; nd; C	F	F
2.22?; nd; E	F	NE	NE

d/A, and apparent crystalline state are shown for each compound with the formation has been obtained; NE: synthesis has not yet been examined; crystal data are available; A: good crystals; B: acceptable ones; C:

Hofmann-dahxn-type (dahxn = 1,6-diaminohexane) [8,9] ; their three-dimensional host structures are built of the stacking of two-dimensional cyanometal complex layers bridged by diaminoalkane ligands. Although the structure of the Hofmann-dabn-type aniline clathrate with  $\bar{x} = 1.5$  has been determined, it is rather unprobable that those with  $1 < \bar{x} < 1.5$  are isostructural to the aniline one: the guests bulkier than aniline cannot be accommodated in the host with the ratio larger than 1 [10]. The products with the value of  $\bar{x}$  larger than 1 are assumed to have structures considerably different from those already determined.

During the research work on these clathrate compounds we discovered a rare case of conversion from an apparently more stable coordination complex to a less stable clathrate compound for the Hofmann-dahxn-type series. The p-toluidine compound obtained under the experimental conditions similar to those for the o- and the m-toluidine clathrates was not a clathrate but a coordination complex  $[\text{Cd}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NH}_2)_2(\text{dahxn})][\text{Ni}(\text{CN})_4]$ , which turned to a clathrate  $\text{Cd}(\text{dahxn})\text{Ni}(\text{CN})_4 \cdot \text{p-CH}_3\text{C}_6\text{H}_4\text{NH}_2$  isostructural to the o- and the m-toluidine clathrates on heating under ambient atmosphere: one mol of the p-toluidine ligand was thermally liberated from the complex but the retained 1 mol was converted from a ligand to a guest in the solid state reaction [11].

Another notable fact is the accommodation of an aliphatic guest molecule in the Hofmann-daotn-type host (daotn = 1,8-diaminooctane). After screening more than thirty kinds of aliphatic molecules against the Hofmann-diam-type hosts, the Hofmann-daotn-type n-hexanol clathrate was obtained. The guest is accommodated with the orientation of the aliphatic chain parallel to the all-trans daotn bridge in the host. The structure can be seen as a model of pillared intercalation compound for which few single crystal data have been available.

A phase transition probably to a superlattice structure has been observed for Hofmann-dahxn-type o-toluidine clathrate at 200 K. Above this temperature the atomic temperature factors of the guest molecule increase steeply to suggest that the librational motion of the guest molecule is excited thermally. The details of the phase transition is still unknown, although it should be related to motion of the guest molecule.

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