THE CRYSTAL STRUCTURES OF α,ω -DIAMINOALKANECADMIUM(II) TETRACYANO-NICKELATE(II)-AROMATIC MOLECULE INCLUSION COMPOUNDS. I. 1,4-DIAMINO-BUTANECADMIUM(II) TETRACYANONICKELATE(II)-2,5-XYLIDINE (1/1): Cd(NH₂(CH₂)₄NH₂)Ni(CN)₄.(CH₃)₂C₆H₃NH₂

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ABSTRACT. The title compound crystallizes in monoclinic space group $P2_1/m$ with a=9.795(2), b=15.010(2), c=7.125(1) Å, β =105.56(1)°, and Z=2. The structure has been refined to the weighted Rw=0.042 for 2742 reflections collected by counter method. Two-dimensionally extended but wavy cyanometal complex layers are bridged by 1,4-diaminobutane (dabn) to give a three-dimensional host structure which provides a channel-like cavity with the guest 2,5-xylidine molecule. The skeleton of the bridging dabn takes a trans-cis conformation to make the packing efficient between the cavity and the guest molecule. The series of Hofmann-dabn-type Cd(NH₂(CH₂)₄NH₂)Ni(CN)₄.nG inclusion compounds are described for several aromatic guest molecules G with various stoichiometric coefficients n.

1. INTRODUCTION

Since Powell and Rayner determined the crystal structure of Hofmann's benzene clathrate Ni(NH₃)₂Ni(CN)₄.2C₆H₆ [1,2], a number of modifications of Hofmann-type and analogous clathrates have been developed by replacing the host moieties such as the six-coordinate and the square-planar Ni(II) and/or the ammine ligands by other metals or amines; the results have been summerized in the reviews [3-5]. As has been reported in the previous communication [6], we have recently developed the metal complex hosts consisting of two-dimensionally extended [CdNi(CN)4]_ sheets and of α , ω -diaminoalkanes bridging adjacent sheets to provide cavities with The novel hosts are aromatic guest molecules. able to accommodate not only small aromatic molecules which have been the guests in the Hofmann-type and analogous hosts already developed but also those with bulky substituents which have never been enclathrated into the previous hosts except Hofmann-dma-type [7-9]. The α, ω -diaminoalkanes which we have attempted to introduce into novel hosts range from 1,4-diaminobutane (dabn) to 1,8-diaminooctane, although ethylenediamine (en: 1,2diaminoethane) was used in our first attempt to develop a three-dimen-

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Journal of Inclusion Phenomena 2, 341–349. 0167–7861/84.15. © 1984 by D. Reidel Publishing Company. sional host structure from the original Hofmann-type host [10]. This paper is related to the crystal structure of the title compound as a representative member of Hofmann-dabn-type series with a general formula $Cd(NH_2(CH_2)_4NH_2)Ni(CN)_4.nG$, and to the preparative results of other members.

2. EXPERIMENTAL

2.1. Preparation

The Hofmann-dabn-type inclusion compounds were prepared by the method described in the previous communication [6]; in Table I the results of elemental analyses and the basal spacings estimated from the powder X-ray diffraction patterns are listed. They are not stable under ambient condition but the rates of decomposition are slow enough to be subjected to the elemental analyses if the specimens are kept in tightly capped vials; some of them, marked with an asterisk in the Table I, are rather unstabe, however.

2.2. Structure Determination

The title compound was chosen as the representative member of the series because of its clear stoichiometry and acceptable stability of single crystal. A single crystal of the dimensions $0.18 \times 0.18 \times 0.20$ mm was coated with epoxy resin and subjected to the intensity data collection on a Rigaku AFC-6A automated four-circle diffractometer using MoK α radiation; 2742 independent reflections with the intensities larger than 3σ (Fo), collected by the ω -2 θ scan technique in the 2 θ range from 2° to 70°, were used for the structure analysis; Lp-corrected but no absorption corrections. The crystal data are:

CdNiC₁₆H₂₃N₇, F.W.=484.51, monoclinic, P2₁/m, a=9.795(2), b=15.010(2), c=7.125(1) Å, β =105.56(1)°, U=1009.2(3) Å³, Z=2, Dx=1.59 g/cm³, Dm=1.62 g/cm³, μ (MoK α)=19.8/cm. Systematic absences: 0k0 with odd k.

The ordinary heavy-atom method was used for the structure refine-All the calculations were carried out on a HITAC computer system ment. M-280H/200H in the computation center of this University using the programs in UNICSIII [11] and their local versions. The atomic scattering factors used are those in the International Tables [12]. Between the two possible space groups $P2_1$ and $P2_1/m$ from the systematic absences, the latter was adopted, because the least-squares calculation at the intermediate stage of refinement diverged for the former one. The positions of Cd and Ni atoms were located on the Patterson map at first; other non-hydrogen atoms were located by the successive Fourier and difference Fourier syntheses and the block-diagonal least-squares calcula-At the final stage, the hydrogen atoms except those of the amino tions. and methyl groups of the guest molecule were located at calculated positions with the isotropic thermal parameter fixed at 5.0 $Å^2$. The refined parameters were the positional and anisotropic thermal ones for all the non-hydrogen atoms; those of the hydrogen atoms were not adjusted but included in the calculation of Fc values. The weighting scheme used

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spacing; those very	unstable	under a	mbient	conditi	ion are	marked	l with *.	
G	n	Cd	N1	С	H	N	d/Å	
pyrrole	1.00	$\tfrac{25.6}{26.11}$	$\frac{13.5}{13.63}$	$\frac{33.2}{33.48}$	<u>3.85</u> 3.98	$\frac{22.8}{22.77}$	7.84	
benzene	1.50	$\frac{23.5}{23.38}$	$\tfrac{12.5}{12.21}$	$\frac{37.9}{42.49}$	$\frac{4.00}{4.40}$	$\frac{19.00}{17.49}$	9.73 *	
toluene	1.50	$\frac{22.5}{22.41}$	$\frac{11.9}{11.70}$	$\frac{41.3}{44.30}$	$\frac{4.37}{4.82}$	$\frac{17.1}{16.75}$	9.75 *	
aniline	1.50	$\frac{22.2}{22.34}$	$\tfrac{11.8}{11.66}$	$\frac{40.5}{40.59}$	$\frac{4.35}{4.50}$	$\frac{20.9}{20.88}$	9.83	
chlorobenzene	1.50	$\frac{21.1}{21.12}$	$\tfrac{11.2}{11.02}$	$\frac{35.6}{38.36}$	$\frac{3.55}{3.69}$	$\tfrac{15.9}{15.79}$	9.93	
0-toluidine	1.50	$\frac{21.4}{21.45}$	$\frac{11.2}{11.19}$	$\frac{42.4}{42.40}$	$\frac{4.88}{4.90}$	$\frac{20.0}{20.04}$	9.78	
<i>m</i> -toluidine	1.28	$\frac{22.3}{22.46}$	$\frac{11.7}{11.72}$	$\frac{40.6}{40.70}$	$\frac{4.53}{4.73}$	$\frac{20.3}{20.37}$	9.89	
p-toluidine	1.50	$\frac{21.4}{21.45}$	$\frac{11.2}{11.19}$	$\frac{42.3}{42.40}$	$\frac{4.71}{4.90}$	$\frac{20.2}{20.04}$	9.50	
0-dichlorobenzene	1.50	$\tfrac{19.1}{19.25}$	$\tfrac{10.0}{10.05}$	$\frac{34.4}{34.97}$	$\frac{3.07}{3.10}$	$\frac{14.5}{14.39}$	9.93	
2,3-xylidine	1.28	$\tfrac{21.5}{19.25}$	$\frac{11.3}{10.05}$	$\frac{42.4}{42.25}$	$\frac{5.02}{5.07}$	$\frac{19.6}{19.66}$	10.0	
2,4-xylidine	1.22	$\frac{21.9}{21.99}$	$\frac{11.5}{11.48}$	$\frac{41.7}{41.73}$	$\tfrac{5.26}{5.01}$	$\frac{18.8}{19.78}$	9.45	
2,5-xylidine	1.00	$\frac{23.0}{23.20}$	$\tfrac{12.3}{12.11}$	$\frac{39.4}{39.66}$	$\frac{4.72}{4.78}$	$\frac{20.2}{20.23}$	9.48	
3,5-xylidine	1.18	$\frac{22.2}{22.20}$	$\frac{11.7}{11.59}$	$\frac{40.9}{41.37}$	$\frac{4.85}{4.97}$	$\frac{19.6}{19.86}$	9.93	
2,4,6-trimethylanilin	ne 1.45	$\frac{20.0}{20.09}$	$\tfrac{10.5}{10.49}$	$\frac{43.5}{45.19}$	$\frac{5.66}{5.55}$	$\frac{18.6}{18.65}$	10.3	
styrene	1.50	$\tfrac{21.0}{21.63}$	$\tfrac{11.0}{11.29}$	$\frac{43.2}{46.23}$	$\frac{4.36}{4.65}$	$\frac{16.4}{16.17}$	9.54 *	
phenylacetylene	1.50	$\frac{21.8}{21.76}$	$\tfrac{11.5}{11.36}$	$\frac{44.0}{46.50}$	$\frac{3.92}{4.09}$	$\tfrac{16.2}{16.27}$	9.69 *	
N,N-dimethylaniline	1.00	$\frac{22.7}{23.20}$	$\frac{12.0}{12.11}$	$\frac{39.2}{39.66}$	$\frac{5.05}{4.78}$	$\frac{19.9}{20.23}$	9.06	
indene	2.00	$\frac{18.7}{18.87}$	<u>9.80</u> 9.85	$\frac{50.5}{52.42}$	$\frac{4.43}{4.73}$	$\frac{14.2}{14.10}$	10.3 *	

Table I. Hofmann-dabn-type inclusion compounds: $Cd(C_4H_{12}N_2)Ni(CN)_4.nG$. Elemental analyses are given as Found/Calcd in %; d refers to the basal spacing; those very unstable under ambient condition are marked with *.

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atom	x/a	y/b	z/c	$B_{eq}/Å^2$
Cd	0.05696(5)	0.25	0.04309(6)	2.12(1)
Ni	0.0	0.0	0.5	2.19(2)
C(1)	0.0752(4)	0.0825(3)	0.3626(6)	2.6(1)
C(2)	-0.0086(4)	0.0883(3)	0.6808(6)	2.7(1)
C(3)	0.4022(8)	0.25	0.179(1)	5.4(4)
C(4)	0.5421(7)	0.25	0.143(1)	4.7(3)
C(5)	0.6689(8)	0.2266(7)	0.301(1)	3.8(5)
C(6)	0.8095(7)	0.25	0.276(1)	4.4(3)
C(7)	0.3865(8)	0.0297(5)	-0.1477(9)	6.2(3)
C(8)	0.5219(9)	0.0461(4)	-0.164(1)	6.5(3)
C (9)	0.6352(8)	0.0168(5)	-0.011(1)	6.4(3)
C(10)	0.548(1)	0.0973(6)	-0.337(1)	9.5(5)
N(1)	0.1184(4)	0.1349(2)	0.2759(6)	3.6(2)
N(2)	-0.0079(5)	0.1409(3)	0.7954(6)	3.8(2)
N(3)	0.2812(6)	0.25	0.0062(9)	4.5(3)
N(4)	0.8328(6)	0.25	0.0838(7)	3.8(2)
N(5)	0.7555(9)	0.0398(7)	-0.021(2)	4.9(4)
				$B_{iso}/Å^2$
H(1)*	0.291	0.191	-0.077	5.0
H(2)	0.394	0.191	0.263	5.0
H(3)	0.538	0.204	0.026	5.0
H(4)	0.559	0.316	0.095	5.0
H(5)	0.667	0.155	0.322	5.0
H(6)	0.659	0.259	0.432	5.0
H(7)	0.834	0.316	0.334	5.0
H(8)	0.885	0.204	0.363	5.0
H(9)	0.780	0.191	0.010	5.0
H(10)	0.296	0.053	-0.260	5.0
H(11)	0.742	0.031	-0.016	5.0

Table II. Positional and isotropic thermal parameters with estimated standard deviations in the least significant digits in parentheses

* H(1) at N(3), H(2) at C(3), H(3) and H(4) at C(4) with the weight of 0.5, H(5) and H(6) at C(5) with the weight of 0.5, H(7) and H(8) at C(6) with the weight of 0.5, H(9) at N(4), H(10) at C(7), and H(11) at C(9) with the weight of 0.5.

were as follows: $w=(70/|Fo|)^2$ for $|Fo|\geq 70$, w=1 for 70>|Fo|>30, and w=0.25 for 30>|Fo|. The final R and Rw were 0.052 and 0.042, respectively [13].

3. RESULTS AND DISCUSSION

3.1. Structure Description



Fig. 1. Projection along the b-axis. Hydrogen atoms are omitted.



Fig. 2. Projection along the a-axis. Hydrogen atoms are omitted.

			0	
Å		<u></u>		
2.358(4)	$Cd-N(2)*^{1}$	2.366(4)	Cd-N(3)	2.281(6)
2.291(6)	C(1) - N(1)	1.149(6)	C(2) - N(2)	1,135(6)
1.850(4)	Ni-C(2)	1.866(4)	N(3) - C(3)	1.461(9)
1.46(1)	C(4)-C(5)	1,48(1)	C(5)-C(6)	1.48(1)
1.45(1)	C(7)-C(8)	1.38(1)	C(8)-C(9)	1.40(1)
1.39(1)	C(8)-C(10)	1.53(1)	C(9)-N(5)	1.25(1)
_	3.28(1)	N(3)N(5)	* 3	4.37(1)
)* ⁶	4.58(1)	C(10)C(1	0)*5	3.69(1)
<u>*</u> 6	3.67(1)	C(5)* ⁴ C(10)* ⁶	4.08(1)
* 4	94.2(1)	N(2)* ² -Cd-N	(2)* ⁷	87.6(1)
* 1	89.1(1)	N(1)-Cd-N(3))	90.5(2)
3)	89.3(2)	N(1)-Cd-N(4))* ⁸	89.1(2)
4)	91.1(2)	C(1)-Ni-C(2)	89.3(2)
*9	90.7(2)	Ni-C(1)-N(1))	178.1(4)
	177.0(4)	Cd-N(1)-C(1)	144.9(3)
2)	165.2(4)	Cd-N(3)-C(3)	119.5(5)
4)	116.2(7)	C(3)-C(4)-C	(5)	120.2(7)
6)	118.0(7)	C(5)-C(6)-N	(4)	120.3(6)
$C(6) - N(4) - Cd^{*2}$		C(7)-C(8)-C(9)		117.3(7)
$C(8) - C(9) - C(7) *^{3}$		C(8)-C(7)-C(9)* ³		120.9(7)
C(7)-C(8)-C(10)		C(9)-C(8)-C(10)		121.0(8)
5)	115.5(8)	C(7)*°-C(9)	-N(5)	122.6(7)
	2.358(4) 2.291(6) 1.850(4) 1.46(1) 1.45(1) 1.39(1))* ⁶ * ⁶ * ⁴ * ¹ 3) 4) * ² 2) 4) 5) * ² 7)* ³ 10) 5)	A 2.358(4) $Cd-N(2)*^1$ 2.291(6) $C(1)-N(1)$ 1.850(4) $Ni-C(2)$ 1.46(1) $C(4)-C(5)$ 1.45(1) $C(7)-C(8)$ 1.39(1) $C(8)-C(10)$ 3.28(1) $*^6$ $4.58(1)$ $*^6$ $3.67(1)$ $*^4$ $94.2(1)$ $*^4$ $94.2(1)$ $*^6$ $3.67(1)$ $*^4$ $94.2(1)$ $*^6$ $3.67(1)$ $*^4$ $94.2(1)$ $*^5$ $3.67(1)$ $*^4$ $94.2(1)$ $*^1$ $89.1(1)$ $3)$ $89.3(2)$ $4)$ $91.1(2)$ $*^9$ $90.7(2)$ $177.0(4)$ $2)$ $165.2(4)$ $116.2(7)$ $5)$ $118.0(7)$ $*^2$ $121.3(4)$ $7)*^3$ $121.6(7)$ $10)$ $121.6(7)$ $5)$ $115.5(8)$	$2.358(4)$ $Cd-N(2)*^1$ $2.366(4)$ $2.291(6)$ $C(1)-N(1)$ $1.149(6)$ $1.850(4)$ $Ni-C(2)$ $1.866(4)$ $1.46(1)$ $C(4)-C(5)$ $1.48(1)$ $1.46(1)$ $C(4)-C(5)$ $1.48(1)$ $1.45(1)$ $C(7)-C(8)$ $1.38(1)$ $1.39(1)$ $C(8)-C(10)$ $1.53(1)$ $3.28(1)$ $N(3)N(5)$ $3.28(1)$ $N(3)N(5)$ $3.28(1)$ $N(3)N(5)$ $3.28(1)$ $N(3)N(5)$ $3.28(1)$ $N(3)N(5)$ $3.28(1)$ $N(3)N(5)$ $3.67(1)$ $C(5)*^4C(1)$ $89.3(2)$ $N(1)-Cd-N(3)$ 4.5 $90.7(2)$ $N1-C(1)-N(1)$ 3.3 $89.3(2)$ $N(1)-Cd-N(4)$ 4.4 $91.1(2)$ $C(1)-Ni-C(2)$ k^9 $90.7(2)$ $Ni-C(1)-N(1)$ $177.0(4)$ $Cd-N(3)-C(3)$ 4.4 $116.2(7)$ $C(3)-C(4)-C$ 4.4 $116.2(7)$ $C(3)-C(6)-N$ 4.4 $116.2(7)$ $C(3)-C(6)-N$ 4.4 <td>$\begin{array}{c} \begin{array}{c} 2.358(4) & \text{Cd-N}(2)^{\pm 1} & 2.366(4) & \text{Cd-N}(3) \\ 2.291(6) & \text{C}(1)-\text{N}(1) & 1.149(6) & \text{C}(2)-\text{N}(2) \\ 1.850(4) & \text{Ni-C}(2) & 1.866(4) & \text{N}(3)-\text{C}(3) \\ 1.46(1) & \text{C}(4)-\text{C}(5) & 1.48(1) & \text{C}(5)-\text{C}(6) \\ 1.45(1) & \text{C}(7)-\text{C}(8) & 1.38(1) & \text{C}(8)^{\pm}\text{C}(9) \\ 1.39(1) & \text{C}(8)-\text{C}(10) & 1.53(1) & \text{C}(9)-\text{N}(5) \\ & & 3.28(1) & \text{N}(3)\text{N}(5)^{\pm 3} \\ 3.28(1) & \text{N}(3)\text{N}(5)^{\pm 3} \\ 3.28(1) & \text{N}(3)\text{N}(5)^{\pm 3} \\ 3.28(1) & \text{C}(10)\text{C}(10)^{\pm 5} \\ & & 3.67(1) & \text{C}(5)^{\pm 4}\text{C}(10)^{\pm 6} \\ \end{array}$</td>	$ \begin{array}{c} \begin{array}{c} 2.358(4) & \text{Cd-N}(2)^{\pm 1} & 2.366(4) & \text{Cd-N}(3) \\ 2.291(6) & \text{C}(1)-\text{N}(1) & 1.149(6) & \text{C}(2)-\text{N}(2) \\ 1.850(4) & \text{Ni-C}(2) & 1.866(4) & \text{N}(3)-\text{C}(3) \\ 1.46(1) & \text{C}(4)-\text{C}(5) & 1.48(1) & \text{C}(5)-\text{C}(6) \\ 1.45(1) & \text{C}(7)-\text{C}(8) & 1.38(1) & \text{C}(8)^{\pm}\text{C}(9) \\ 1.39(1) & \text{C}(8)-\text{C}(10) & 1.53(1) & \text{C}(9)-\text{N}(5) \\ & & 3.28(1) & \text{N}(3)\text{N}(5)^{\pm 3} \\ 3.28(1) & \text{N}(3)\text{N}(5)^{\pm 3} \\ 3.28(1) & \text{N}(3)\text{N}(5)^{\pm 3} \\ 3.28(1) & \text{C}(10)\text{C}(10)^{\pm 5} \\ & & 3.67(1) & \text{C}(5)^{\pm 4}\text{C}(10)^{\pm 6} \\ \end{array} $

Table III. Selected atomic distances and angles

Key to symmetry: normal, x, y, z; with $*^1$, x, y, -1+z; with $*^2$, 1+x, y, z; with $*^3$, 1-x, -y, -z; with $*^4$, x, 1/2-y, z; with $*^5$, 1-x, -y, -1-z; with $*^6$, x, y, 1+z; with $*^7$, x, 1/2-y, -1+z; with $*^8$, -1+x, y, z; with $*^9$, -x, -y, 1-z.

The atomic parameters determined are listed in Table II; the anisotropic thermal parameters have been deposited along with the table of structure factors [13]. The structure is illustrated in Figs. 1 and 2 along with the atomic notations. Selected atomic distances and angles are listed in Table III.

The host metal complex has the three-dimensional structure consisting of the two-dimensionally extended cyanometal complex sheets and of the 1,4-diaminobutane ligands bridging adjacent sheets at the respective Cd atoms in the sheets. The Cd atoms are alternately linked with the square-planar Ni(CN)₄ moieties at the N-ends; at each Cd-N junction the metal complex network bends to give a wavy structure of the sheet similar to those observed for Hofmann-mea-type pyrrole clathrate [14] and Hofmann-dma-type ones [8,9]. 1,4-Diaminobutane takes a trans-cis conformation of its N(3)-C(3)-C(4)-C(5)-C(6)-N(4) skeleton on the mirror plane at y=1/4 except the C(5) which is distributed statistically at both sides of the mirror plane; the positions of hydrogen atoms attached to C(4) and C(6) atoms have been calculated in relation to both the positions of C(5). The large thermal parameters, the short bond distnaces, and the wide bond angles for the dabn skeletal atoms suggest that their atomic coordinates, except those of C(5), should be read as averaged ones, or potential minima, in the time scale of X-ray diffraction measurement.

The guest 2,5-xylidine molecule is trapped in the channel-like cavity extended along the c-axis of crystal but its aromatic plane is clipped by the columns of dabn ligands. Since the center of the phenyl ring is located at the center of inversion, the amino nitrogen, N(5), is also distributed statistically at the top and the bottom sides along the a-axis in the orientations shown in Fig. 1 with the weight of 0.5; H(11) is also distributed in the similar way. The thermal parameters are considerably large for the phenyl and methyl carbons. The largest 9.5 \mathbb{A}^2 of the methyl carbon C(10) suggests a freedom of motion of the guest molecule in the cavity. The nearest distance between the host and the guest atoms is 3.28(1) Å for N(4)...N(5) if the hydrogen atom is omit-This distance suggests the presence of a hydrogen bond between the ted. amino groups of the dabn and the guest accompanied with H(9) atom attached to the former amino group. The shortest interguest distance is observed between the respective methyl groups as 3.69(1) Å, the value which shows the guest molecules being in contact with each other in the channel-like cavity.

3.2. Comparison with Hofmann-en-type Host

The Hofmann-en-type Cd(en)Ni(CN)4.2G clathrates (G=C6H6, C4H4S, or C_4H_5N) are the prototype of the series of three-dimensional host inclusion compounds derived from Hofmann-type host using α, ω -diaminoalkane as the ligand bridging adjacent two-dimensional cyanometal complex sheets. The cavity formed in Hofmann-en-type host is essentially similar to that formed in Hofmann-type host; the planar cyanometal complex sheets are stacked completely parallel to keep the tetragonal symmetry [15], Davies and Maver proposed the structure similar to that of Hofmann-en-type for the inclusion compounds of Hofmann-dahxn-type host [16]. Although the crystal structure of the Hofmann-dahxn-type O-toluidine inclusion compound will be reported in the following paper [17], the structure of the host with a long-carbon-chain α, ω -diaminoalkane ligand is remarkably different from Hofmann-en-type host in the points as follows: (i) the cyanometal complex network is not planar but bent at each Cd-N junction to give a waved sheet, (ii) the sheets are stacked with shift leading to distortion from a tetragonal symmetry to a monoclinic one, and (iii) the column of α, ω -diaminoalkane ligand bridges the shifted sheets slantwise. These flexible features in structure make the novel hosts favorable to accommodate the guest molecules with bulky substituents, the molecules which have never been enclathrated into the rigid Hofmann-type and Hofmann-en-type hosts. Although the skeletal length of en limits the guest species in Hofmann-en-type host to those not larger than benzene molecule, the longer carbon chain contributes not only to the enlargement of spacing between the sheets but also, and mainly, to making host structure flexible enough to accommodate guest molecules with various shapes and sizes.

3.3. Stoichiometry and Guest Selectivity

As shown in Table I, the stoichiometric coefficient of the guest, n, which has been estimated by putting a great confidence on the values of Cd and Ni contents determined on our bench-top immediately after the preparation, varies from 1.0 to 2.0 depending on the guest species. The basal spacing, which may be the measure of distance between adjacent cyanometal complex sheets bridged by dabn, ranges from the shortest 7.84 Å for the smallest pyrrole guest to the longest 10.3 Å for the bulkier guests such as 2,4,6-trimethylaniline and indene. However, there is no direct relationship between the basal spacing and the size of guest molecule to support a hypothesis that the bulkier guest gives the longer basal spacing. Furthermore, the stoichiometric coefficient does not show any systematic dependency on both the size of guest and the basal spacing.

Assuming that these Hofmann-dabn-type inclusion compounds have the host structure substantially similar to the present 2,5-xylidine guest compound, i.e., the three-dimensional host is built of the waved cyanometal complex sheets bridged by the dabn ligands, the cavity may have the channel-like character similar to that observed for the present compound. Other factors to be considered are the conformation of the dabn skeleton and the degree of shift in the cyanometal complex sheets. If the substantial host structure is flexible enough to accommodate all of the guests listed in Table I into the channel-like cavity, the variation in the stoichiometric coefficient and the basal spacing may be due to the optimal accommodation of each guest with an efficient packing for the respective inclusion compound.

It is a curious observation that the Hofmann-dabn-type host appears not to accommodate xylene molecule in spite that four kinds of xylidines and other guests bulkier than xylene have been accommodated into the host. As far as the comparison with the xylidines is concerned, the presence of hydrogen bond between the amino groups of 2,5-xylidine and dabn suggests the preference of the amino group over the hydrogen atom on the phenyl ring. However, there is no reasoning to interpret the preference of the guests such as styrene, phenylacetylene, N,N-dimethylaniline, or indene over xylene in terms of hydrogen bonding. The problem should be solved by the structural analyses of the respective inclusion compounds.

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