Inclusion Compounds Formed Between α,ω-(Long-Carbon-Chain)-Diaminecadmium(II) Tetracyanonickelate(II) Host and Aromatic Guest Molecules

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Abstract. Inclusion compounds with the general formula $Cd(NH_2(CH_2)_nNH_2)Ni(CN)_4 \cdot xG$ were prepared for $n = 4$ to 8, and for G of such an aromatic guest molecule as pyrrole, benzene, aniline, toluene, toluidine, xylene, xylidine, dichlorobenzene, trimethylbenzene, tetramethylbenzene, ethylbenzene, styrene, or isopropylbenzene, with varying x. Generally, longer chain lengths of α,ω-diamine in the host permit the inclusion of bulkier guest molecules. However, the presence of an amino group on the phenyl ring of the guest appears to impart a special affinity with the hosts.

Key words: Hofmann-type clathrate, pyrrole, benzene, aniline, substituted benzene, substituted aniline, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, cadmium tetracyanonickelate.

One of our strategies to develop novel three-dimensional metal complex host structures from the two-dimensional Hofmann-type host $Cd(NH_3)_2Ni(CN)_4$ is to replace the pair of ammine ligands opposed to each other between adjacent metal complex sheets of $[CdNi(CN)_4]_\infty$ by a diaminoalkane which bridges the adjacent sheets. Examples have been seen for the Hofmann en-type $Cd(en)Ni(CN)_4 \cdot 2G$ and the Hofmann pn-type $Cd(pn)Ni(CN)_4 \cdot \frac{3}{2}G$ clathrates $(G = C_4H_5N, C_4H_4S, C_6H_6)$ [1–6]. Although these hosts exhibit guest selectivity similar to that of the Hofmann-type, the span of en or pn is not long enough to enclathrate an aniline molecule. Our recent preparation of Hofmann dma-type clathrates $Cd(dma)_2Ni(CN)_4 \cdot xG$ $(dma = NH(CH_3)_2; x = \frac{1}{2}$ for $G = C_6H_6$, and $x = 1$ for $G = C_6H_5X, C_6H_4X_2$ (X = Cl, Br), $C_6H_5CH_3, C_6H_4(CH_3)_2$ $(x \simeq 1), CH_3C_6H_4NH_2$, etc.) [7–9] suggested that α,ω-diamines $NH_2(CH_2)_nNH_2$ with values of n larger than 2 may produce novel three-dimensional hosts with a hydrophobic character favorable to the inclusion of aromatic guest molecules with bulky substituents. Such an attempt has recently been reported briefly by Davies and Maver [10]. In this communication we report preliminary results of systematic investigations of three-dimensional hosts $Cd(NH_2(CH_2)_nNH_2)Ni(CN)_4$ with n varying from 4 to 8.

The inclusion compounds were prepared by the following general procedure. To an aqueous solution containing an equimolar mixture of $CdCl_2$ and $K_2[Ni(CN)_4]$, a two-fold molar amount of α,ω-diamine was added and mixed vigorously by a magnetic stirrer for a few hours. After the pH of the aqueous phase was adjusted to about 9.5, the mixture was filtered with a plastic membrane (Millipore filter with a pore size 0.45 μm). An organic phase of pure guest

species, or the guest in an appropriate solvent, was layered over the filtrate in a stoppered flask, and the flask was left for a few days at room temperature or in a refrigerator. Crystalline or massive product of the inclusion compound formed at the interface between the aqueous and the organic phases and the bottom of the former phase.

The novel inclusion compounds thus prepared are listed in Table I. All the compounds give a strong infrared absorption band with a split structure at about 2140 cm^{-1} which supports the bridging coordination of the CN$^-$ ligand between the Cd and Ni atoms in a two-dimensional metal complex network similar to those observed for Hofmann-type clathrates. A few bands due to the guest species shift by 5–20 cm^{-1} to higher frequency; a similar shift has been observed for the guest species enclathrated in the Hofmann-type and analogous clathrates. In the powder X-ray diffraction patterns, systematic reflection peaks assigned to a layered structure have been observed for the crystalline products. The basal spacings calculated are listed in Table I.

Figure 1 displays the thermal decomposition of an ethylbenzene-guest compound $Cd(NH_2(CH_2)_6NH_2)Ni(CN)_4 \cdot \simeq 1C_2H_5C_6H_5$. The TG curve shows that the guest molecule is released in two steps: about 40% of the guest was lost at the first step by 140°C, the remaining 60% was lost at the second step with a plateau beginning at 190°C. The residual host complex $Cd(NH_2(CH_2)_6NH_2)Ni(CN)_4$ burns at 260°C prior to dissociation of the

Table I.   Inclusion compounds $Cd(NH_2(CH_2)_nNH_2)Ni(CN)_4 \cdot xG$

G	n				
	4	5	6	7	8
C_4H_5N	8.66 : ?[a]	–[b]	–	–	–
C_6H_6	? : ≃1.3	–	9.19 : ≃1	–	10.7 : ?
$C_6H_5NH_2$	0[c]	–	0	–	0
$CH_3C_6H_5$	? : ≃1.5	–	9.40 : 1.0	–	11.0 : ?
$o\text{-}CH_3C_6H_4NH_2$	9.78 : ≃1.3	0	9.42 : 1.0	0	10.9 : ≃0.3
$m\text{-}CH_3C_6H_4NH_2$	9.89 : ≃1.3	0	9.62 : 1.0	0	11.0 : ≃0.4
$p\text{-}CH_3C_6H_4NH_2$	9.50 : ≃1.5	0	9.71 : ≃2	0	10.9 : ≃1.5
$2,3\text{-}(CH_3)_2C_6H_3NH_2$	10.0 : ≃1.3	–	–	–	–
$2,4\text{-}(CH_3)_2C_6H_3NH_2$	9.45 : ≃1.3	–	–	–	–
$2,5\text{-}(CH_3)_2C_6H_3NH_2$	9.48 : 1.0	–	–	–	–
$2,4,6\text{-}(CH_3)_3C_6H_2NH_2$	10.5 : ≃1.5	–	–	–	–
$o\text{-}(CH_3)_2C_6H_4$	×[d]	×	9.55 : ≃1	0	10.9 : ?
$m\text{-}(CH_3)_2C_6H_4$	×	×	9.54 : ≃1	0	11.1 : ≃1
$p\text{-}(CH_3)_2C_6H_4$	×	×	9.40 : ≃1	0	10.5 : ?
$o\text{-}Cl_2C_6H_4$	9.93 : ?	–	–	–	–
$p\text{-}Cl_2C_6H_4$	–	–	9.61 : ≃1	–	–
$1,2,3\text{-}(CH_3)_3C_6H_3$	×	–	0	–	0
$C_2H_5C_6H_5$	×	×	9.42 : ≃1	–	11.0 : ≃1
$CH_2 = CHC_6H_5$	–	–	–	–	10.8 : ?
$CH(CH_3)_2C_6H_5$	×	×	×	×	11.3 : ≃1
$1,2,4\text{-}(CH_3)_3C_6H_3$	–	–	–	–	10.8 :.?
$1,3,5\text{-}(CH_3)_3C_6H_3$	×	×	×	×	11.2 : ≃1
$1,2,3,4\text{-}(CH_3)_4C_6H_2$	–	×	×	×	0

[a] The numerals are *basal spacing*/Å : x ; ?, basal spacing unidentified or too nonstoichiometric.

[b] Preparation has not been tried.

[c] Evidence of formation has been obtained.

[d] Preparation was attempted but inclusion compounds have not yet been obtained.
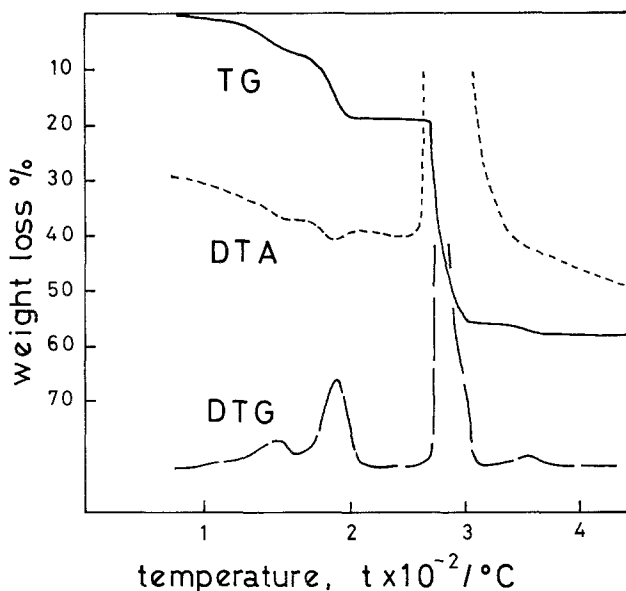
Fig. 1. The TG, DTA, and DTG curves of Cd(NH$_2$(CH$_2$)$_6$NH$_2$)Ni(CN)$_4 \cdot \simeq$ 1C$_2$H$_5$C$_6$H$_5$. Instrument: Daini-Seikosha SSC/560GH; heating rate: 20°/min; sample amount: 10.7 mg. The scale of temperature is not linear owing to the extremely exothermic reaction of the sample. The scale of the ordinate for DTA (up: exothermic; down: endothermic) and DTA is arbitrary.

diamine ligand; the behavior is not similar to that observed for Hofmann-type benzene clathrates with more volatile ammine ligands in their hosts [11].

The relationship between the chain length of α,ω-diamine and the guest selectivity appears to be rather complex. As listed in Table I, the 1,4-diaminobutane (1,4-dabn) host can include three of the toluidine isomers, three of the xylidine isomers, and even 2,4,6-trimethylaniline, whereas none of the xylene isomers are included in the same host. The 1,6-diaminohexane (1,6-dahxn) host appears to be the smallest which is able to include the xylene isomers. These observations suggest that the amino group on the phenyl ring has a special affinity with the long chain α,ω-diamine host.

As a general trend, a longer chain length of the α,ω-diamine results in a longer basal spacing, but the order is reversed in the case of o- and m-toluidines for $n = 4$ and 6. Contrary to the previous observation [10], the 1,6-dahxn host can include the p-isomers of xylene and dichlorobenzene. Ethylbenzene, which has never been enclathrated in a Hofmann dma-type host, forms inclusion compounds with the 1,6-dahxn and the 1,8-diaminooctane (1,8-daon) hosts, whereas isopropylbenzene, 1,3,5-trimethylbenzene, and 1,2,3,4-tetramethylbenzene are included only in the 1,8-daon host.

A problem in the analysis and characterization of these inclusion compounds is that they rarely give good crystalline products. The analytical results indicate non-stoichiometry for several products, and sometimes composition varied from sample to sample. Typical examples are as follows: For Cd(1,6-dahxn)Ni(CN)$_4 \cdot$ CH$_3$C$_6$H$_5$ ($=$ C$_{17}$H$_{24}$N$_6$CdNi) found(calcd)% : C 41.81(42.22), H 4.81(5.00), N 17.34(17.38), Cd 23.54(23.24), Ni 12.05(12.14). For Cd(1,6-dahxn)Ni(CN)$_4 \cdot xp$-CH$_3$C$_6$H$_4$NH$_2$ ($=$ C$_{24}$H$_{34}$N$_8$CdNi for $x = 2.0$) found(calcd for $x = 2.0$; $= 1.9$)% : C 47.19(47.59; 47.04), H 5.47(5.66; 5.61), N 18.59(18.50; 18.60)

Cd 19.0(18.56;18.89),   Ni 10.0(9.69;9.86).   For $Cd(1,6\text{-dahxn})Ni(CN)_4 \cdot p\text{-}C_6H_4Cl_2$ $(= C_{16}H_{20}N_6Cl_2CdNi)$ found(calcd)%: C 35.69(37.37), H 3.74(4.33), N 15.61(16.54), Cd 20.88(22.23), Ni 10.90(11.61). The first appears to be acceptable for the stoichiometric composition, the second can be seen as a case of imperfect enclathration with a 95% occupancy factor, but the last appears to be rather non-stoichiometric although the ratio C : H : N : Cd : Ni $\simeq$ 16 : 22 : 6 : 1 : 1 has been observed. At present the detailed compositions and structures cannot be given. Among these inclusion compounds, those of the toluidine guest give relatively good crystals and single crystal X-ray diffraction experiments are in progress.

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