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# The Coextraction of Water into Nitrobenzene with Alkali and Alkaline Earth Metal Salts of 2,2′,4,4′,6,6′-Hexanitrodiphenylamine in the Presence of Several Crown Ethers and Cryptands

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Alkali and alkaline earth metal salts of 2,2′,4,4′,6,6′-hexanitrodiphenylamine (HND) were extracted into nitrobenzene in the absence or presence of several crown ethers or cryptands which differ from one another in hole size. The quantity of water transferred to the nitrobenzene phase was determined by means of the Karl-Fischer method. The NMR and near-infrared spectra show that the coextraction of water is caused by the hydration of the cations. The number of water molecules attached to the cations increases upon going from $Cs^+$ (0.6) to $Li^+$ (5.6) and from $Ba^{2+}$ (10.5) to $Ca^{2+}$ (13.0). The complexation between these cations and the crown ethers causes a clear decrease in the hydration number; *e.g.*, in the 1:1 metal-crown ether complexes, more than half of the water molecules are removed, and in the 1:1 metal-cryptand complexes, less than one water molecule remains unremoved. The complexes of a 1:2 stoichiometry are also found; some are stable and carry virtually no water molecules. The number and type of donor atoms have no significant effect on the coextraction of water. The presence of fused benzo rings on the crown ether also has no influence on the number of water molecules.

Recently, interest in the coextraction of water into organic solvents with ion-pairs has been increasing.[1-5] In a previous paper,[6] it was shown that, when aqueous solutions containing alkali metal salts of 2,2′,4,4′,6,6′-hexanitrodiphenylamine (HND) are shaken with nitrobenzene, the water molecules strongly associated with the salts are transferred to the nitrobenzene phase.

It is well known that crown ethers and cryptands combine stoichiometrically with alkali and alkaline earth metal cations to form complexes, in which the cation is accommodated into the molecular hole of the ligand. Depending on the relative size of the hole and the metal ion, 1:1, 1:2, and 2:3 complexes are formed. In some complexes of small crown ethers, the cation lies in or slightly above the donor plane in the solid state;[7,8] a few of them are known to have the same structure in solution as well.[9] This 'metal in the hole' structure does not require a stripping of the entire hydration shell of the ion, since the contact of water molecules with the cation is still possible in the direction perpendicular to the plane of the donor ring. With regard to some solid cryptates, the cation has been found to be enclosed in the molecular cage of the ligand.[10] The cation, therefore, can be expected to exist as an unhydrated or only slightly hydrated state.

In the present study, the number of water molecules attached to alkali and alkaline earth metal complexes with several crown ethers and cryptands has been determined in order to make clear the effect of the ligands on the cation hydration. The number of the water of crystallization was also determined with the alkaline earth metal salts of HND and their complexes with dibenzo-18-crown-6 by means of thermogravimetric analysis.

## Experimental

*Materials.* Commercial HND was purified by repeated recrystallizations from acetone. *N*-(2,4,6-trinitrophenyl)-2,4-dinitro-1-naphthylamine (TDN) was obtained by the reaction between 2-chloro-1,3,5-trinitrobenzene and 1-naphthylamine, followed by nitration.[11] 1,3,7,9-Tetranitrophenothiazine 5-oxide (TPO) was prepared by the nitration of phenothiazine.[12,13] The TDN and TPO thus obtained were recrystallized from acetic acid; their alkali and alkaline earth metal salts were prepared by treating these amines with the corresponding metal carbonate or hydroxide.

The crown ethers used were benzo-12-crown-4 (B12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-24-crown-8 (DB24C8), and 5,6-benzo-4,7,13,16-tetraoxa-1,10-diaza-5-cyclooctadecene (2.2B). 15C5, 18C6, and DB24C8 were obtained from the Nisso Co., Ltd. The first two were used without further purification. DB24C8 was recrystallized from chloroform and then ethanol. B12C4, B15C5, B18C6, and DB18C6 were synthesized and purified by the method of Pedersen.[14] 2.2B was obtained from 3,6-dioxa-1,8-octanediamine and 1,2-bis(chloroformylmethoxy)benzene by the method of Dietrich *et al.*;[15] the product obtained was recrystallized from 4-methyl-2-pentanone. 2.2B was found to be a monohydrate by measuring the weight loss on heating.

The cryptands, 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]-eicosane (2.1.1), 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-[8.8.5]tricosane (2.2.1), 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2.2.2), and 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacos-5-ene (2.2.2B), were purchased from Merck and well used without further purification.

Some crown ether complexes were crystallized from methanol-water mixtures.

The nitrobenzene was treated with an aqueous sodium carbonate solution and washed with water several times prior to use.

*Measurements.* A nitrobenzene solution (20 $cm^3$ for crown ethers and 5 $cm^3$ for cryptands) containing the ligands (0—0.03 mol $dm^{-3}$) and HND or the other polynitro-substituted amines (0—0.01 mol $dm^{-3}$) was shaken with an equal volume of an aqueous alkali or alkaline earth metal chloride solution for 1 h at $(25\pm0.01)$ °C in a thermostated water bath, the ionic strength being adjusted to 0.1 mol $dm^{-3}$, and the pH, to about 12, with the corresponding metal chloride (or sulfate) and hydroxide (or carbonate).

Table 1. The number of water molecules coextracted with $M^{n+}$, $h(M^{n+})$

| Anion | $M^{n+}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cs<br>0.59$^{a)}$ | Rb<br>0.66$^{a)}$ | K<br>0.75$^{a)}$ | Na<br>1.03$^{a)}$ | Li<br>1.47$^{a)}$ | Ba<br>2.49$^{a)}$ | Sr<br>3.58$^{a)}$ | Ca<br>4.04$^{a)}$ |
| HND | 0.6 | 0.9 | 1.3 | 3.5 | 5.6 | 10.5 | 12.1 | 13.0 |
| TDN | 0.1 | 0.8 | 1.4 | 3.8 | 5.5 | 8.6 | 10.4 | 13.8 |
| TPO | — | — | — | 2 | 5 | 13 | 14 | 13 |

a) $z^2/r_c$ values.

The water-content in the nitrobenzene phase was determined by the use of a Mitsubishi Kasei CA-01 Karl-Fischer titrator. Nitrobenzene was treated with an aqueous solution under the same conditions, and the water-content increments, $\Delta s$, were obtained. The total metal concentration in the nitrobenzene phase, $[M(t)]_o$, was calculated from the difference between the total quantity of HND and the quantity of HND anions found in the aqueous phase by the use of Hitachi 124 spectrophotometer. The total concentration of the ligand, L, in the nitrobenzene phase, $[L(t)]_o$, was obtained by measuring the quantity of L left unextracted in the aqueous phase in the following manner: to the aqueous phase, a large excess of potassium chloride (sodium chloride for 15C5 and B15C5; lithium chloride for B12C4) and an excess of HND were added. L was then extracted as the potassium complex into benzene (1,2-dichlorobenzene for B12C4, 15C5, and B15C5). The concentration of the complex in the benzene phase was determined spectrophotometrically. From the total quantity of L and the concentration of the complex thus obtained, $[L(t)]_o$ was calculated.

The conductance measurements in nitrobenzene were carried out at (25±0.005) °C by the use of a universal bridge (Ando Electric Co., Ltd., LCR 10) equipped with platinized platinum electrodes.

The thermogravimetric curves were obtained on a Rigaku Denki TG unit under a nitrogen flow of about 30 cm$^3$/min. The temperature rise was 0.625 °C/min.

## Results and Discussion

*Hydration of the Uncomplexed Cations.* Nitrobenzene dissolves water at a concentration of 0.178 mol dm$^{-3}$ at 25 °C, while a nitrobenzene solution containing the alkali or alkaline earth metals dissolves a slightly greater quantity of water. The quantity of water coextracted increases linearly with the increase in the metal concentration, as is shown in Fig. 1. From the slope of each line, the quantity of water coextracted, $h(M^{n+})$, is calculated.

Table 1 shows that the values of $h(M^{n+})$ increase linearly with the ratio of the charge to the ionic radii of the cations, $z^2/r_c$, except for those of the heavy alkali metals ($K^+$, $Rb^+$, and $Cs^+$). The $h(M^{n+})$ values are found not to be dependent on the anion species used. In general, bulky univalent anions are believed not to be hydrated in solution. These values, therefore, are assumed to be identical with the hydration numbers of the cations.

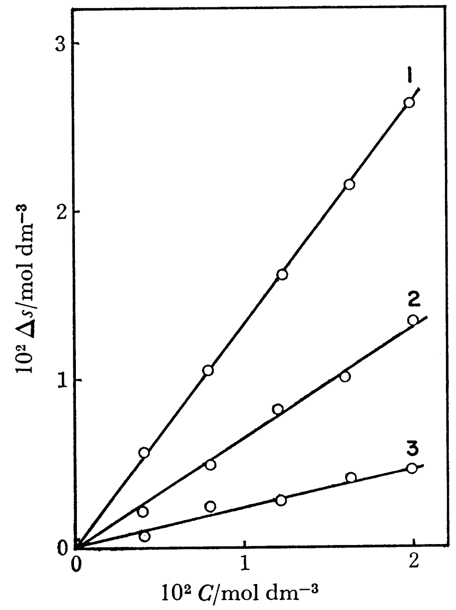

Fig. 1. Coextraction of water with DB18C6, the potassium salt of HND, and the complex.
1: Potassium salt of HND, 2: DB18C6, 3: complex.

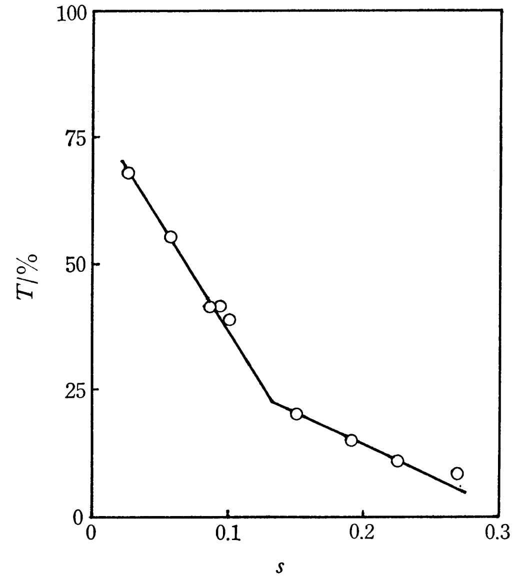

Fig. 2. Plot of $T$ % *vs.* the water content, $s$, in the nitrobenzene phase.
$Ca(HND)_2$: 0.01 mol dm$^{-3}$.

Stokes and Robinson, on the other hand, obtained the hydration numbers of the alkali and alkaline earth metal chlorides in an aqueous solution by means of activity measurements ($Rb^+$ 1.2, $K^+$ 1.9, $Na^+$ 3.5, $Li^+$ 7.1, $Ba^{2+}$ 7.7, $Sr^{2+}$ 10.7, and $Ca^{2+}$ 12.0).[16] These values are similar in magnitude to the corresponding $h(M^{n+})$ values listed in Table 1. This fact suggests that the cations in the aqueous phase carry water into the nitrobenzene phase without being stripped

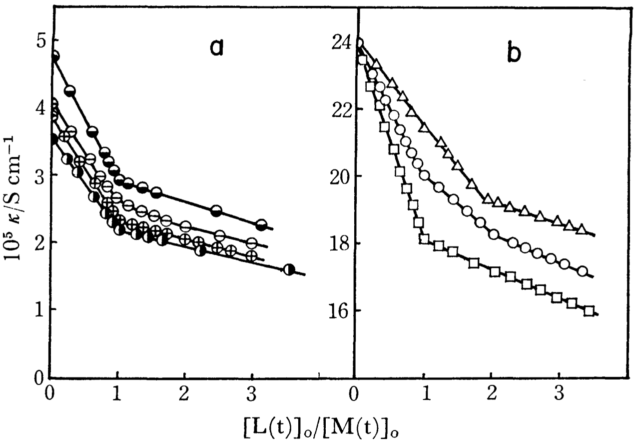

Fig. 3. Conductometric titration curves of the alkali metal and $Ba^{2+}$ salts of HND.
a: DB18C6 complexes with $Na^+$ (⊕), $K^+$ (◒), $Rb^+$ (◑), and $Cs^+$ (⊖). Concentrations of the HND salts: $Na^+$ 0.01, $K^+$ 0.02, $Rb^+$ 0.01, and $Cs^+$ 0.012 mol dm$^{-3}$. b: $Ba^{2+}$ complexes with 15C5 (△), 18C6 (○), and DB24C8 (□). The concentration of $Ba(HND)_2$: 0.005 mol dm$^{-3}$.

of the water molecules attached to them when they pass through the interface.

In a previous paper,[17] it was shown that the NMR and near-infrared spectra gave information concerning the behavior of water in a nitrobenzene solution containing the calcium salt of HND. The infrared spectra were also found to be useful for the investigation of water in the nitrobenzene solution. The transmittance, $T$ %, of a 0.01 mol dm$^{-3}$ solution of anhydrous $Ca(HND)_2$ in dry nitrobenzene was measured in the presence of varying amounts of water at 3660 cm$^{-1}$. The $T$ % decreases with an increase in the water concentration, as is shown in Fig. 2. The curve obtained can be approximated by two line portions; the value of 13.3, which is obtained from the concentration ratio of water to $Ca^{2+}$ at the intersection, agrees quite well with the $h(M^{n+})$ value for $Ca^{2+}$. It can thus be concluded that, when water is added to the nitrobenzene solution of $Ca(HND)_2$, the water binds exclusively to $Ca^{2+}$, and that the excess water then disperses into the solvent.

*Complex Formation.* The stoichiometries of the complexes in nitrobenzene were determined by means of conductometric titration. As an illustration, the conductometric titration curves for alkali metal–DB18C6 complexes and for some $Ba^{2+}$–crown ether complexes are shown in Fig. 3. The addition of ligands to the salts on HND in nitrobenzene results in a decrease in the specific conductance, $\kappa$. All the curves except for $Ba(15C5)^{2+}$ break at the first equivalence point, indicating the formation of stable complexes of a 1:1 stoichiometry. $Cs(DB18C6)^{2+}$ may be less stable than the others, because its titration curve shows no clear change at the equivalence point; this finding does not, however, necessarily mean the absence of the 1:2 complexes, as will be seen later.

The conductivity data of the alkali metal and ammonium–DB18C6 complexes in nitrobenzene were analyzed by means of the method of Schedlovsky.[18]

Table 2. $\Lambda^\circ$ and $\lambda^\circ$ values (S cm$^2$ mol$^{-1}$), together with the ion-pair formation constants, $K$

| $M^+$ | $\Lambda^\circ$(M(L)HND) | $\lambda^\circ(ML^+)$ | $\lambda^\circ(M^+)$ | $K$/mol$^{-1}$ dm$^3$ a) |
|---|---|---|---|---|
| Na | 21.4 | 9.6 | 16.3b) | 10 |
| K | 21.4 | 9.6 | 17.8b) | 7 |
| Rb | 21.5 | 9.7 | — | 8 |
| $NH_4$ | 21.1 | 9.3 | 18.4b) | 5 |

a) $K=[M(L)HND]/[ML^+][HND^-]$. b) From Ref. 19.

The limiting equivalent conductivities, $\Lambda^\circ$, were found to differ not all from one another. The limiting ionic equivalent conductivity for the anion of HND could be determined to be $\lambda^\circ(HND)=11.8$ S cm$^2$ mol$^{-1}$. The values of $\lambda^\circ(ML^+)$, therefore, were determined by using the $\lambda^\circ(M^+)$ values reported by Witschonke and Kraus.[19] Table 2 shows that the $\lambda^\circ(ML^+)$ values are not affected by the size of the central cation and are smaller than the $\lambda^\circ$ values for the uncomplexed cations. The $K$ values in Table 2 show that virtually no ion-pairs are formed between $ML^+$ and the anion of HND. It is clear that $ML^+$ is much bulkier than $M^+$ and that the effective size of $ML^+$ is exclusively determined by the ligand size. These findings strongly support the view that $ML^+$ exists as a complex with the 'metal in the hole' structure, even in a dissolved state.

*Hydration of the Free Ligands.* As can be seen from Fig. 1, water is also coextracted with uncomplexed DB18C6. The $\Delta s$ values for L were measured by means of the extraction method in the absence of HND. Under such conditions, the transfer of ligand as complexes was neglected. The number of water molecules attached to a molecule of a ligand, $h$(L), can be calculated from the slope of the plot. The data thus obtained, together with the hole diameters,[20,21] are summarized in Table 3.

Table 3 shows that the free ligands exist in a slightly hydrated form in the nitrobenzene phase. The benzo derivatives seem to be less hydrated. It should be noted that 2.2B exists as a monohydrate not only in the nitrobenzene phase, but also in the solid state. 18C6 and the uncomplexed potassium ion have 1.6 and 1.3 water molecules respectively, while the complex has only 0.3 water molecule. From these data, it is possible to assume that 1.6 water molecules are bound inside the ligand hole.

*Hydration of the Complexed Cations, $ML^{n+}$.* The number of water molecules attached to the complexed cations, $h(ML^{n+})$, is obtained from the slope of the $\Delta s$-$[M(t)]_\circ$ plot (Fig. 1) when 1:1 complexes alone are known to exist in the nitrobenzene phase. The $h(ML^{n+})$ values can also be obtained from an $h$-$a$ plot, as is shown in Fig. 4, where $h=\Delta s/[M(t)]_\circ$ and $a=[L(t)]_\circ/[M(t)]_\circ$.

For a given metal cation, the $h$ value at $a=0$ in Fig. 4, for example, is identical with the $h(M^{n+})$ value. Since $ML^{n+}$ is less hydrated than $M^{n+}$, the $h$ values decrease with the addition of L to a solution containing $M^{n+}$ and HND anions ($a<1$). The intensity of the orange-red color of the aqueous phase, which shows the presence of HND anions, also decreases upon the addition of L. At the first equivalence point ($a=1$),

Table 3. The number of water molecules coextracted with the ligands, $h$(L)

| L | B12C4 | 15C5 | B15C5 | 18C6 | B18C6 | DB18C6 | 2.2B[a] | DB24C8 | 2.1.1 | 2.2.1 | 2.2.2 | 2.2.2B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hole diameter (nm) | 0.10—0.13 | 0.17 — 0.22 | | 0.26 — 0.32 | | | | 0.4 | 0.16 | 0.22 | 0.28 | |
| $h$(L) | 0.2 | 0.7 | 0.5 | 1.6 | 0.8 | 0.6 | 1.0 | 0.5 | 0.5 | 0.8 | 0.8 | 0.5 |

a) $pK_1=7.9$, $pK_2=8.7$.

Table 4. The number of water molecules coextracted with the 1:1 crown ether complexes, $h(ML^{n+})$

| $M^{n+}$ | Cation diameter (nm) | L | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | None | B12C4 | 15C5 | B15C5 | 18C6 | B18C6 | DB18C6 | 2.2B | DB24C8 |
| Li | 0.136 | 5.6 | 2.9 | 2.0 | 1.4 | 2.5 | 2.6 | 2.9 | 2.5 | 2.4 |
| Na | 0.196 | 3.5 | — | 0.9 | 0.8 | 1.2 | 1.1 | 1.2 | 1.3 | 0.2 |
| K | 0.266 | 1.3 | — | 0.3 | 0.5 | 0.3 | 0.4 | 0.1 | 0.6 | 0.3 |
| Rb | 0.298 | 0.9 | — | 0.5 | 0.3 | 0.3 | 0.2 | 0.1 | 0.5 | 0.2 |
| Cs | 0.336 | 0.6 | — | 0.2 | 0.4 | 0.1 | 0.2 | 0.1 | — | 0.3 |
| Ca | 0.198 | 13.0 | — | 5.3 | 6.5 | 4.7 | 5.5 | 5.1 | 4.8 | 5.3 |
| Sr | 0.226 | 12.1 | — | 0.4[a] | 0.5[a] | 4.6 | 4.6 | 4.9 | 4.3 | 4.1 |
| Ba | 0.270 | 10.5 | — | 0.2[a] | 0.2[a] | 3.4 | 4.2 | 4.4 | 3.7 | 2.9 |

a) M:L=1:2.

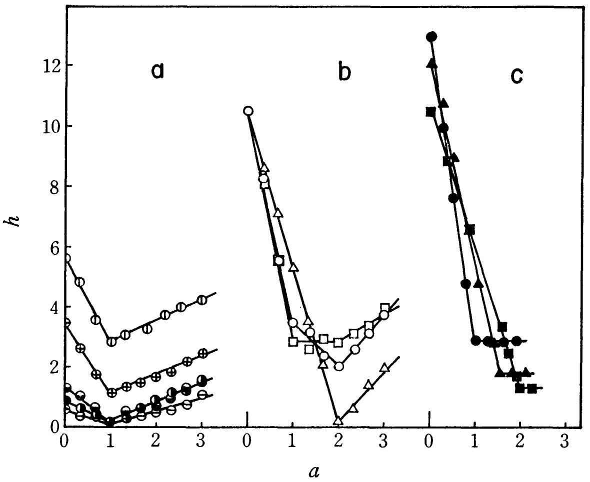

Fig. 4. Effect of the ligands on the coextraction of water.
a: Alkali metal complexes with DB18C6, $Li^+$ (⦶), $Na^+$ (⊕), $K^+$ (◒), $Rb^+$ (◑), and $Cs^+$ (⊖). b: $Ba^{2+}$ complexes with 15C5 (△), 18C6 (○), and DB24C8 (□) c: Alkaline earth metal complexes with 2.1.1, $Ca^{2+}$ (●), $Sr^{2+}$ (▲), and $Ba^{2+}$ (■).

the aqueous phase becomes colorless, indicating the complete transfer of the HND anions as ion-pairs, M(L)HND or M(L)$HND_2$, from the aqueous to the nitrobenzene phases. As regards the $Ba^{2+}$ complex with 15C5, the curve in Fig. 4(b) shows no change at $a=1$. This is also the case for the other 1:2 complexes listed in Table 4. The conductometric titration curves (Fig. 3) for these complexes also fall off smoothly until $a=2$, indicating that the 1:1 complexes do not exist or are not so stable as the 1:2 complexes. Figure 4(b) shows that the alkaline earth metals form 1:2 complexes with the crown ethers, whereas, in some instances, the formation of the 1:2 complexes is not clear from the conductometric titration curves. In the crown ether complexes, the $h$ values calculated from the slopes of the third line portions ($a>2$) are identical with the $h$(L) values; this indicates that no 1:2 complexes undergo further complexation.

The cryptands used form stable 1:1 complexes with the alkali and alkaline earth metals. It must be noted that 2.1.1 forms the 1:2 complex with $Ba^{2+}$ and the 2:3 complex with $Sr^{2+}$ (Fig. 4(c)). The fact that these 1:1 complexes are not formed between these cations and the cryptand is evident from the observation of the color change in the aqueous phase.

The $h$ values obtained with the 1:1 complexes, together with those for the 1:2 and 2:3 complexes, are listed in Table 4. If the 1:2 alkaline earth metal–crown ether complexes are sufficiently stable, the $h(ML_2^{2+})$ values can be determined from $h$ values at $a=2$, but they are omitted from Table 4 because the stability data are lacking.

Table 4 shows that the number of water molecules attached to the metal cations decreases on complexation; roughly speaking, the $h(ML^{n+})$ values are reduced to less than one-half the $h(M^{n+})$ values. The number of water molecules released, for example, amounts roughly to as much as 6—8 for the alkaline earth metals. The heavy alkali metal complexes lose virtually all the water molecules on complexation. It is noteworthy that $Sr^{2+}$ and $Ba^{2+}$ complexes with 15C5 and B15C5 have no water molecules. B12C4 forms no stable complex with any of the cations tested except for $Li^+$, as can be expected from its small hole size (*cf.* Table 3). 2.2B also forms no complex with $Cs^+$, though the reason for this is not known.

The $h$ values for the metal–cryptand complexes (cryptates) are listed in Table 5. It is clear that the cryptates are much less hydrated than the crown ether complexes. Two important features are that the cryptates always have about one water molecule and

Table 5. The number of water molecules coextracted with the 1:1 cryptands, $h(\mathrm{ML}^{n+})$

| $\mathrm{M}^{n+}$ | L |  |  |  |
|---|---|---|---|---|
|  | 2.1.1 | 2.2.1 | 2.2.2 | 2.2.2B |
| Li | 0.7 | 0.9 | 1.0 | 1.2 |
| Na | 0.4 | 0.8 | 0.5 | 0.5 |
| Ca | 2.9 | 0.6 | 1.0 | 1.3 |
| Sr | 1.8[a)] | 0.7 | 1.2 | 1.2 |
| Ba | 1.3[b)] | 0.8 | 1.2 | 1.0 |

a) M:L=2:3. b) M:L=1:2.

the $h$ values are not affected by the cation size.

*Complex Structures.* For some crown ether complexes, the 'metal in the hole' structure is proved in the crystalline state and in solution. The complex formation, therefore, does not necessarily require a stripping of the entire hydration shell of the cation. The molecular holes of 15C5 and B15C5 are so small that $\mathrm{Sr}^{2+}$ and $\mathrm{Ca}^{2+}$ can not be well accommodated. Hence, these crown ethers form 1:2 complexes of a sandwich-type structure, in which the metal cation is located between the two parallel rings consisting of five donor atoms. In the complexes of this type, the number of donor atoms is twice as many as that in the 'metal in the hole' structure. It is, therefore, not likely that no binding sites of the metal cation are left for the further coordination of water molecules. In the alkaline earth metal–crown ether complexes, it can also be noted that the number of water molecules released by complexation is roughly equal to that of the donor atoms.

Table 5 shows that all the 1:1 cryptates except for $\mathrm{Ca}(2.1.1)^{2+}$ are associated with only 0.4—1.3 water molecules; this finding is in striking contrast to the results obtained with the crown ether complexes. Such a marked decrease in the $h$ values strongly supports the 'metal in the cage' structure. In solid complexes of 2.2.2 with $\mathrm{CaBr_2}$[22)] and $\mathrm{BaSCN_2}$,[23)] the cations are known to be coordinated by one water molecule in each case. It, therefore, likely seems that the 0.4—1.3 water molecules are attached to the central cation by coordination, even in the nitrobenzene phase.

As can be seen from Table 5, $\mathrm{Ca}(2.1.1)^{2+}$ is highly hydrated; the fact may suggest that $\mathrm{Ca}^{2+}$ is surrounded by the ligand, as in typical crown ether complexes. $\mathrm{Ba}^{2+}$ is much larger than the hole size of 2.1.1 and forms 1:2 complexes with it. From analogy with potassium B15C5,[24)] a sandwich structure is inferred for the cryptate. A 'club sandwich' structure is postulated for a 2:3 crown ether complex, in which three ligands are arranged as planes in three tires, each separated from the next by a metal cation.[20)] With regard to the cryptate formed between $\mathrm{Sr}^{2+}$ and 2.1.1, however, such a structure is unlikely, because 2.1.1 is not a planar molecule like crown ethers.

*Thermogravimetric Analysis.* $\mathrm{Li}^+$, $\mathrm{Ca}^{2+}$, $\mathrm{Sr}^{2+}$, and $\mathrm{Ba}^{2+}$ salts of HND were found to have 4, 11, 4, and 4 molecules of water of crystallization respectively. For the $\mathrm{Ba}^{2+}$ salt, a crystal with two molecules of water of crystallization was found. The stoichiometries of the crystalline solids of the alkaline earth metal–crown ether complexes were determined from the thermogravimetric curves by the help of the spectrophotometric method ($\mathrm{Ca(DB18C6)_2HND_2 \cdot 6H_2O}$, $\mathrm{Sr(DB18C6)_2HND_2 \cdot 6H_2O}$, and $\mathrm{Ba(DB18C6)_2HND_2 \cdot 5.5H_2O}$).

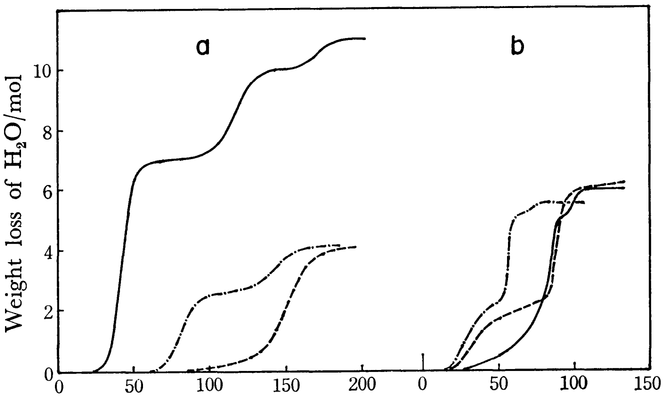

Fig. 5. Thermogravimetric analysis of water of crystallization.
a: $\mathrm{Ca(HND)_2 \cdot 11H_2O}$ (—), $\mathrm{Sr(HND)_2 \cdot 4H_2O}$ (----), and $\mathrm{Ba(HND)_2 \cdot 4H_2O}$ (——–—). b: $\mathrm{Ca(DB18C6)_2HND_2 \cdot 6H_2O}$ (——), $\mathrm{Sr(DB18C6)_2HND_2 \cdot 6H_2O}$ (— — —), $\mathrm{Ba(DB18C6)_2HND_2 \cdot 5.5H_2O}$ (——–—).

As an illustration, the thermogravimetric curves are shown in Fig. 5. In most cases, the thermal dehydration occurs in multistages in the range from about 30 to 180 °C. The DB18C6 complexes are found to lose their water of crystallization completely below about 100 °C; such is the case with 18C6. The uncomplexed salts still have some molecules of water of crystallization above 100 °C. It can be concluded that alkaline earth metal cation–water molecule bonds are much weaker in the complexes than in the uncomplexed salts. There are some instances in which $h$ values are closely related to the number of water of crystallization. For example, Yamamoto *et al.* found that the ion-pairs formed between $\mathrm{Fe(phen)_3}^{2+}$ (where phen refers to 1,10-phenanthroline) and $\mathrm{ClO_4}^-$, $\mathrm{SCN}^-$, $\mathrm{I}^-$, and $\mathrm{Br}^-$ are accompanied by 1, 2, 2, and 6 water molecules respectively in the solid state and in the nitrobenzene phase as well.[25)] In the present investigation, however, no such fine correlation was found. It can be recognized that large cations are at least less hydrated than smaller ones, both in the solid state and in the nitrobenzene phase.

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