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AN APPLICATION OF ^{1}H NMR TO THE DETERMINATION OF THE STOICHIOMETRY OF CROWN ETHER COMPLEXES (ML_n (n=1,2): M=Li, Na, K, Rb, Cs, Ca, Sr, AND Ba; L=12-CROWN-4, 15-CROWN-5, AND 18-CROWN-6)

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Alkali and alkaline earth metal salts with 2,2',4,4',6,6'-hexanitrodiphenylamine were titrated stepwise with the crown ethers in nitrobenzene-d_5 in the presence of a small quantity of water. The ^{1}H NMR spectra obtained for each step showed that the water and the ligand signals shift on complexation. The stoichiometries of the crown ether complexes were obtained through analysis of the shift. The water signal was found to be advantageous to the stoichiometry determination for its high sensitivity.

The alkali and alkaline earth metal salts with 2,2',4,4',6,6'-hexanitrodiphenylamine (HND) exist as a strongly dissociated state in nitrobenzene,[1,2] so that, if the solvent contains water, the cations can readily be hydrated. Hydration measurements show that the greater the charge and the smaller the size of the cation, the greater is it tendency to bind the water molecules; the number of water molecules associated with the cation increases on going from Cs (0.6) to Li (5.6) and from Ba (10.5) to Ca (13.0).[1,3] Crown ethers combine stoichiometrically with 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 cation, complexes other than 1:1 stoichiometries are also formed. Our early papers showed that the water molecules associated to the cation are partially or almost fully released when the hydrated cations form crown ether complexes.[3,4] It can, therefore, be expected that useful information about the complex formation will be obtained from the behavior of the water molecules.

The aim of this paper is to prove that the water molecules serve as a useful indication of complex formation. The behavior of the water molecules was followed up by means of ^{1}H NMR spectroscopy. 12C4 (1,4,7,10-tetraoxacyclododecane), 15C5 (1,4,7,10,13-pentaoxacyclopentadecane), and 18C6 (1,4,7,10,13,16-hexaoxacyclooctadecane) were chosen as ligands because these spectra are simple. Nitrobenzene was favorable as the solvent because it dissolves the ligands, the salts, and their complexes to a considerable extent.

12C4, 15C5, and 18C6 were purchased from the Nisso Co., Ltd. 18C6 was dried under vacuum. These ligands were dissolved into nitrobenzene-d_5 (99%, Merck) to

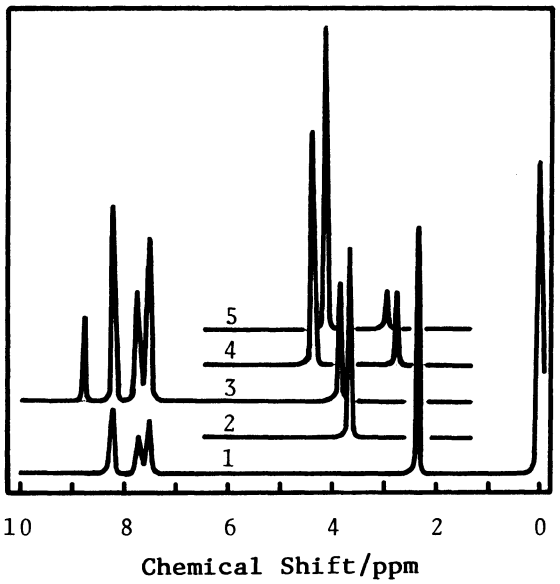

Fig. 1. ^1H NMR spectra.
1: water, 2: 18C6, 3: $Ca(HND)_2 \cdot 11H_2O$
4 and 5: the complexes.

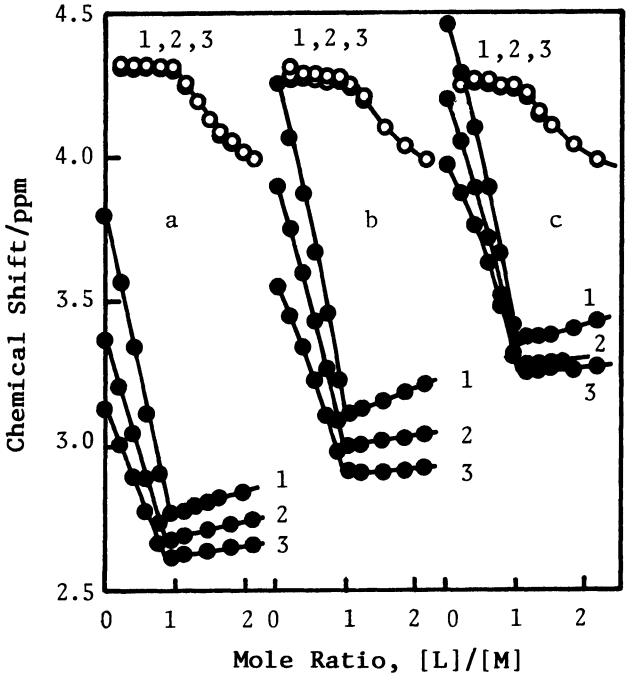

Fig. 2. Influence of the H_2O and 18C6 concentrations on the chemical shifts.
○: Ligand signal, ●: Water signal.
a: [Ca]=0.0022 M; [H_2O] (1) 0.025 M, (2) 0.034 M, (3) 0.063 M.
b: [Ca]=0.013 M; [H_2O] (1) 0.1 M, (2) 0.17 M, (3) 0.28 M.
c: [Ca]=0.03 M; [H_2O] (1) 0.31 M, (2) 0.41 M, (3) 0.62 M.
1 M=1 mol dm^{-3}.

give an about 0.035 M (1 M=1 mol dm^{-3}) solution. Commercial HND (Tokyo Kasei Kogyo Co.,Ltd.) was recrystallized repeatedly from acetone and then treated with an alkali or alkaline earth metal carbonate solution. The resulting crystalline precipitates were dried at room temperature. The Li, Sr, and Ba salts retained 4 water of crystallization, the Ca salt 11, and the others none. These salts were dissolved each into nitrobenzene-d_5 to give a 0.002 M solution. To an NMR tube, 400 μl of the solution were transferred and then a few μl of water were added, if necessary. The NMR spectra were obtained on a Hitachi R600 FT-NMR spectrometer (60 MHz, 0.4 Hz resolution) each time 4 - 5 μl portions of the ligand solution were added. Tetramethylsilane was used as internal standard. All the measurements were carried out at 25°C.

The unsubstituted crown ethers showed quite simple NMR spectra which were sensitive to the complex formation. In Fig. 1 are shown the NMR spectra of the 18C6 complexes and the related compounds. A free water signal appeared at 2.33 ppm. Three signals at about 8 ppm are due to the aromatic protons of the residual ordinary solvent. A proton signal due to the free ligand appeared at 3.67 ppm. The spectrum of $Ca(HND)_2 \cdot 11H_2O$ consists of two singlets, one due to the aromatic protons of an HND anion (8.75 ppm) and the other due to the water protons (3.80 ppm). Spectra (4) and (5) were obtained with solutions containing Ca and the ligand at a Ca:L mole ratios of 1:1 and 1:2 respectively.

The detailed chemical shift changes can be seen from Fig. 2(a - c). For the water signal, the addition of 18C6 to $Ca(HND)_2$ first produced an upfield shift until a minimum at 1:1 (Ca:L) and then a gradual downfield shift. For the ligand

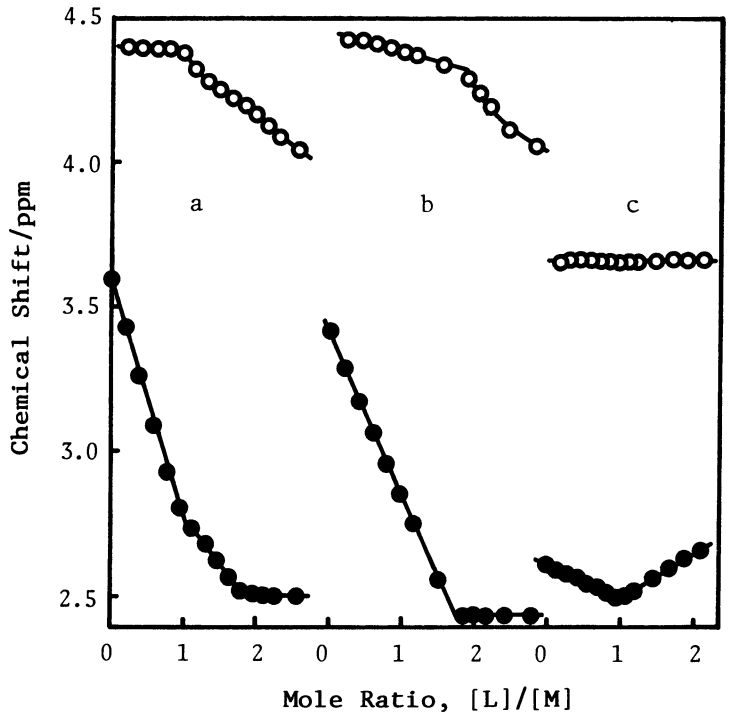

Fig. 3. Typical plots of the Chemical shifts vs. [L]/[M].
○: Ligand signal, ●: Water signal.
a: L=15C5, [Ca]=0.0022 M.
b: L=12C4, [Sr]=0.0023 M.
c: L=18C6, [K]=0.0417 M.
1 M=1 mol dm^{-3}.

signal, on the other hand, the addition of the ligand first showed virtually no shift until a mole ratio of 1:1; the further addition resulted in an upfield shift. The chemical shift of water was also dependent on both the Ca and the water concentrations but the ligand signal was not. It is noted that the curves in Fig. 2 (a - c) all break at the same ligand concentration. The molar ratio determined graphically from the breaks agreed with the stoichiometry of the complex. Typical plots are shown in Fig. 3(a - c). Each of the water and the ligand curves in Fig. 3(a) clearly shows two breaks, indicating that 15C5 forms both 1:1 and 1:2 complexes with Ca. It is clear from Fig. 3(b) that 12C4 forms only a 1:2 complex with Sr. This was also the case for a 12C4-Ca complex. A complex of 18C6 with K showed a different pattern; no breaks were found in both the water and 18C6 curves under the conditions used. The V-shaped water curve in Fig. 3(c) was obtained when an about 20 times concentrated solution of K(HND) was titrated; no break, however, was found in the ligand curve.

The M:L ratios obtained from the breaks are summarized in Table 1. Most values in Table 1 can be regarded as an integer; an M:L ratio of 1:1.7 may be taken as 1:2 rather than 1:1.5, taking into account the experimental error. Complexes with a 1:1 stoichiometry were commonly observed for all the cases except for 12C4 mentioned above. The formation of a 1:1 complex between 15C5 and Ba[5] was not clear. In a few cases, both 1:1 and 1:2 complexes were detected (e.g., 12C4-Na,Ba; 15C5-Ca,Ba). A 1:2 complex of 18C6 with Cs[6] was not detected in the present experiments. The

Table 1. Molar ratios, [L]/[M], at the breaks

Ligand	Signal	Li	Na	K	Rb	Cs	Ca	Sr	Ba
12C4	L[a]	0.9	1.0, 1.9	1.0	1.0	0.9	- 1.8	- 1.8	0.9, 1.9
	W[b]	0.9	1.0, 1.8	1.2	1.0	0.9	- 1.7	- 1.8	1.0, 1.8
15C5	L	1.0	1.0 -[c]	0.9	0.9	1.0	0.9, 1.9	- -	- -
	W	0.9	1.0 -	1.0	1.0	1.0	0.9, 1.8	0.8, 1.7	- 1.7
18C6	L	0.9	1.0 -	-	-	-	1.0 -	1.0 -	1.1 -
	W	0.9	0.9 -	1.1	1.0	1.0	0.9 -	0.9 -	1.0 -

a) Ligand signal. b) Water signal. c) Indicate the lack of the complex.

notation " - " in Table 1 indicates the lack of the complex. Virtually all the data in Table 1 are found to be consistent with those from other sources.[7)]

The observed spectral changes can roughly be explained by the following equilibria:

$$M(H_2O)_i + L = M(H_2O)_jL + (i - j)H_2O \quad (1)$$

$$M(H_2O)_jL + L = M(H_2O)_kL_2 + (j - k)H_2O \quad (2)$$

$$mH_2O + L = L(H_2O)_m \quad (3)$$

where $i > j > k$. According to Eqs. 1 and 2, the amount of water liberated increases as the titration proceeds. After the second equivalence point was reached, the water liberated begins to combine with the excess ligand to produce a hydrated ligand (Eq. 3). Taking into account that the signal of the free water appears at higher field than that of the coordinated one (spectrum (2)), the observed spectral changes on complexation are well explained. Since the ligand protons are linked to the donor site across the carbon atom, the complexation is expected to exert a minor influence for the signal of the ligand protons when the electron density of the donor site is affected by the complexation or the hydration. All the ligand curves support this view.

From the findings that the chemical shift of water was much more sensitive than the ligand signals, that the water curves were all constituted by two or more line portions, and that, fortunately, most curves were V-shaped, it can be concluded that the water signal, as compared with the ligand signal, is useful for the stoichiometry determination of the complexes, especially, those with the highly hydrated cations.

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