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COMPLEXATION OF ALKYLAMMONIUM SALTS BY CROWN ETHERS UNDER ANHYDROUS CONDITIONS

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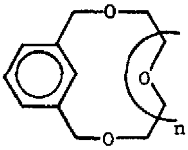
The ability of crown ethers to form complexes with a large number of salts in a wide variety of solvents is well established[1] and for many such complexes the association constants (K_a) in methanol and water have been reported[1]. Since the most useful property of crown ethers is their capacity to solubilize salts in apolar solvents, the K_a values in these media are of practical utility.

As we found[2] that the presence of small amounts of water has a large effect on the relative complexing capacities of crown ethers 1a-1f[3], we have measured the



1a , n = 2
1b , n = 3
1c , n = 4
1d , n = 5
1e , n = 6
1f , n = 7

relative association constants of their tert-butylammonium hexafluorophosphate complexes under strictly anhydrous conditions. The method used is illustrated by the following experiment. A 0.4 M solution of t-BuNH$_3$.PF$_6$ in water[4] (2.0 ml) was equilibrated with a 0.5 M solution of crown ether in CDCl$_3$ (1.0 ml), after which the chloroform layer was dried over molecular sieves (4Å)[5]. The relative concentrations of salt and crown ether (R_a = [ammonium salt]/[crown ether]) and the chemical shift of the tert-butyl group (δ_{Bu}) were determined by 90-MHz PMR spectroscopy.

As is apparent from Table I, the chemical shifts of the complexes are dependent on the presence of water. In agreement with our results from a more detailed study of the role of water[2], we find that the chemical shifts of the complexes formed by crown ethers containing large rings (1d-1f) are most sensitive. For instance, removal of water from the complex of 1d results in a downfield shift of 0.186 ppm, whereas the δ_{Bu} value of the complex of 1b shows hardly any change.

TABLE I

Complexation of crown ethers with t-BuNH$_3$.PF$_6$ in CDCl$_3$

Crown ether	R_a (a)	δ_{Bu} (b)	
		before drying	after drying
1a	0.008	1.095	1.043
1b	0.93	0.830	0.825
1c	0.45	0.974	0.997
1d	0.65	0.968	1.154
1e	0.49	1.154	1.258
1f	0.48	1.203	1.304

Estimated accuracies: (a) 10 %; (b) ± 0.003 ppm.

The observed differences in chemical shift (Table I) between the various complexes allow us to use the δ_{Bu} values as a sensitive tool to determine the relative complexing capaciti of the various crown ethers. For this purpose, small portions of a 0.5 M solution of crown ether **1b** in CDCl$_3$ were added to the solutions containing complexed **1a** and **1c**-**1f**.

The competitive complexation between two crown ethers **1b** and **1x** can be described by equations (1)-(3):

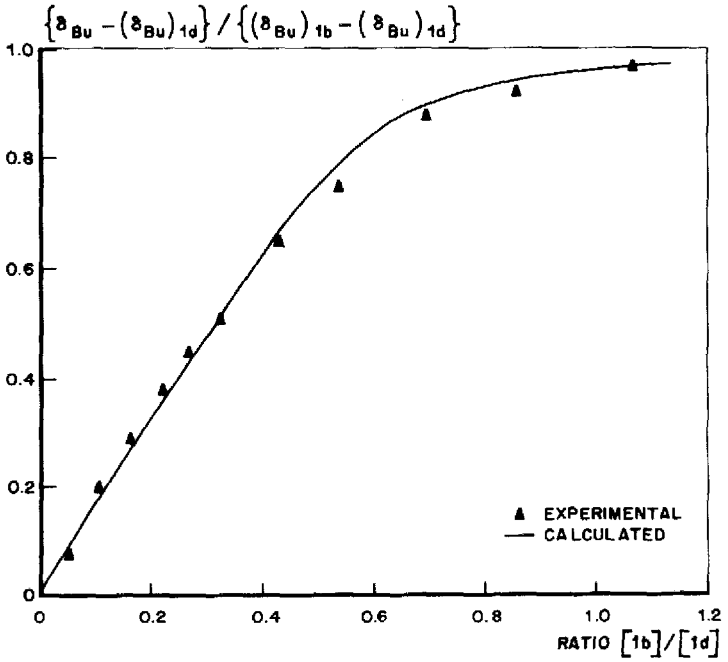
$$\mathbf{1x} + \underline{t}\text{-BuNH}_3^{\oplus}.\text{PF}_6^{\ominus} \overset{K_{1x}}{\rightleftharpoons} \underline{t}\text{-BuNH}_3^{\oplus}.\mathbf{1x}.\text{PF}_6^{\ominus} \tag{1}$$

$$\mathbf{1b} + \underline{t}\text{-BuNH}_3^{\oplus}.\text{PF}_6^{\ominus} \overset{K_{1b}}{\rightleftharpoons} \underline{t}\text{-BuNH}_3^{\oplus}.\mathbf{1b}.\text{PF}_6^{\ominus} \tag{2}$$

$$\underline{t}\text{-BuNH}_3^{\oplus}.\mathbf{1x}.\text{PF}_6^{\ominus} + \mathbf{1b} \overset{K_{rel}}{\rightleftharpoons} \underline{t}\text{-BuNH}_3^{\oplus}.\mathbf{1b}.\text{PF}_6^{\ominus} + \mathbf{1x} \tag{3}$$

The relative association constants $K_{rel.} = K_{1x}/K_{1b}$ can be calculated from equation (4), in which $A = R_a\ (K_{rel.}-1)$, $C = [1b]/[1x]$, and $B = K_{rel.}+C-A$.

$$\frac{\delta_{Bu}-(\delta_{Bu})_{1x}}{(\delta_{Bu})_{1b}-(\delta_{Bu})_{1x}} = \frac{-B+\sqrt{B^2+4AC}}{2A} \tag{4}$$



CHEMICAL SHIFTS FOR THE COMPETITIVE COMPLEXATION OF CROWN ETHERS 1b AND 1d
FIGURE 1

A typical titration curve is shown in Fig. 1 for the complex of **1d**; it is clear that on addition of free crown ether **1b** the salt is almost completely transferred from **1d** to **1b**. Furthermore, the calculated curve nicely fits the experimental data, indicating that equations (1)-(3) quantitatively describe the salt transfer at the concentrations studied (0.2-0.5 M).

TABLE II

Relative complexing abilities of crown ethers with t-$BuNH_3.PF_6$ in $CDCl_3$ at 27 ± 1 °C

Crown ether	$K_{rel}^{(a)}$ x 100	Crown ether	$K_{rel}^{(a)}$ x 100
1a	0.2	**1e**	3.0
1b	100	**1f**	5.0
1c	1.2	18-crown-6	1.0×10^4
1d	1.5		

(a) Estimated accuracy: 30 %.

In contrast to the results of aqueous extraction experiments[2], we find a sharp maximum in the complexing ability as a function of the ring size of the crown ether (Table II). The association constant is almost a hundred times higher for crown ether **1b** than for any of the other crown ethers. Apparently, the cavity is either too small (**1a**) or too large (**1c**-**1f**) to accomodate the cation in a 1 : 1 type complex. The best crown ether in this series (**1b**), is still a weaker complexing agent than 18-crown-6, which is included in Table II.

It is interesting to note that the structural requirements for complexation are much more pronounced for *t*-$\mathrm{BuNH_3^{\oplus}}$ than for $\mathrm{K^{\oplus}}$, which cation shows much less specificity in the formation of complexes with the same series of crown ethers[7].

REFERENCES AND FOOTNOTES

(1) J.J. Christensen, D.J. Eatough and R.M. Izatt, *Chem. Revs.*, **74**, 351 (1974).

(2) F. de Jong, D.N. Reinhoudt and C.J. Smit, *Tetrahedron Letters*, previous paper.

(3) D.N. Reinhoudt and R.T. Gray, *Tetrahedron Letters*, 2105 (1975).

(4) Prepared from equal volumes of 0.8 M *t*-$\mathrm{BuNH_3^{\oplus}Cl^{\ominus}}$ and 0.8 M $\mathrm{LiPF_6}$ in water.

(5) Less than 5 % of the crown ether was removed when the solutions were dried for a short time only (≤20 h). Longer contact times with sieves ultimately led to complete removal of crown ether

(6) All salt-transfer reactions studied were fast on the PMR time scale.

(7) R.T. Gray and D.N. Reinhoudt, *Tetrahedron Letters*, 2109 (1975).