



## Lithium-7 NMR Study of Several Li<sup>+</sup>-Crown Ether Complexes in Binary Acetone-Nitrobenzene Mixtures

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### Abstract

<sup>7</sup>Li NMR measurements were employed to monitor the stoichiometry and stability of Li<sup>+</sup> ion complexes with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in binary acetone-nitrobenzene mixtures of varying composition. In all cases studied, the variation of <sup>7</sup>Li chemical shift with the crown/Li<sup>+</sup> mole ratio indicated the formation of 1:1 complexes. The formation constants of the resulting complexes were evaluated from computer fitting of the mole ratio data to an equation that relates the observed chemical shifts to the formation constant. In all solvent mixtures used, the stabilities of the resulting 1:1 complexes varied in the order 15C5 > B15C5 > DC18C6 > 18C6 > 12C4 > DB18C6. It was found that, in the case of all complexes, an increase in the percentage of acetone in the solvent mixtures significantly decreased the stability of the complexes.

### Introduction

Following the discovery that alkali ions form stable complexes with macrocyclic crown ethers [1] the studies of these ligands and their interactions with a wide variety of cations, anions and neutral guests have become a major field of research that is still expanding [2–6]. It is well known that the process of ion-macrocycle association depends on several factors including the relative cation and ligand cavity sizes, the number and arrangement of the ligand binding sites the substitution on the macrocyclic ring and, especially, the nature of the solvent. Since both the metal ion and the macrocyclic ligand must be at least partially desolvated before their complex can be formed, the two solvation processes are expected to markedly influence the overall stability of the resulting complex in solution.

Due to the preferential solvation of the solutes by one of the mixed solvent components and its fundamental role in determining the thermodynamic behavior of complexation processes [4, 7, 8], there has recently been an increasing interest in the study of complexation reactions in binary mixed solvent systems.

In recent years, we have employed magnetic resonance spectrometry as a very sensitive technique [9] to study the exchange kinetics [10–13] and thermodynamics [14–17] of a number of metal ion-macrocycle complexes in non-aqueous and mixed solvents. In this paper we report the use

of lithium-7 NMR for the study of the stoichiometry and stability of Li<sup>+</sup> ion complexes with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in binary acetone-nitrobenzene mixtures at 25.0 ± 0.1 °C.

### Experimental

Crown ethers 18C6, DC18C6, DB18C6 and B15C5 (all from Merck) were purified and dried as described [18, 19]; 12C4 and 15C5 (both from Merck) were used as received. Reagent grade lithium perchlorate (Merck) was purified and dried using a previously reported method [20]. Reagent grade acetone (AC, Fluka) and nitrobenzene (NB, Merck) were used to prepare the solvent mixtures by weight.

All nuclear magnetic resonance measurements were made on a JEOL FX90Q FT-NMR spectrometer with a field of 21.13 kG. At this field, lithium-7 resonates at 33.74 MHz. A 4.0 M aqueous LiCl solution was used as external reference and the reported lithium-7 chemical shifts refer to this solution. The paramagnetic (downfield) shift from the reference is designated as being positive. The concentration of all LiClO<sub>4</sub> solutions used was 0.01 M. All chemical shift measurements were carried out at a probe temperature of 25.0 ± 0.1 °C.

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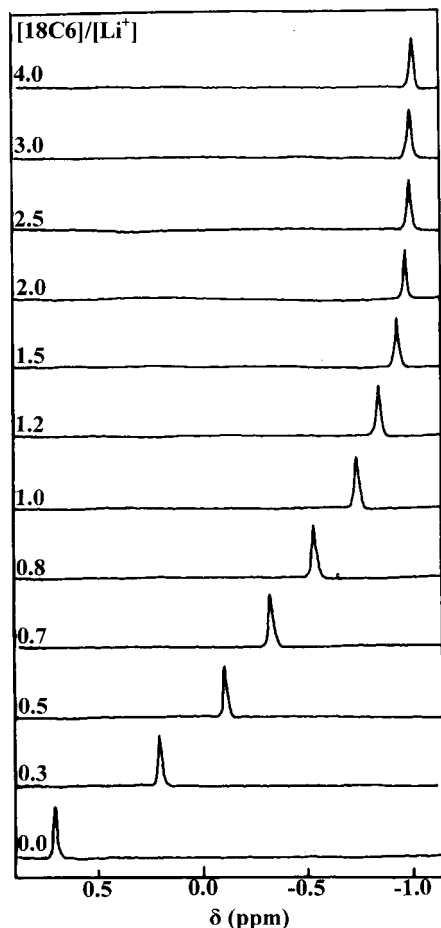


Figure 1.  $^7\text{Li}$  NMR spectra of a 0.01 M solution of lithium perchlorate in 20% AC at various 18C6/ $\text{Li}^+$  mole ratios.

## Results and discussion

The  $^7\text{Li}$  chemical shifts of 0.01 M lithium perchlorate solutions in different AC-NB mixtures were monitored as a function of crown/ $\text{Li}^+$  ratio up to a molar ratio of 4. Typical spectra are illustrated in Figure 1 and the resulting chemical shift-mole ratio plots for different  $\text{Li}^+$ -crown ether systems in various AC-NB mixtures are shown in Figures 2–6. In all cases studied only one population-average resonance of the metal ion was observed, indicating that the exchange of  $\text{Li}^+$  ion between the two sites (i.e., the solvated cation and the complex) is faster than the NMR time scale.

In general, the behavior of the  $^7\text{Li}$  chemical shift as a function of crown ether/ $\text{Li}^+$  mole ratio shown in Figures 2–6 can be approximately divided into two groups:

1. The diamagnetic shift varies linearly with the crown/ $\text{Li}^+$  mole ratio until a mole ratio of about one is reached; further increase of the crown does not change the resonance frequency. Such behavior, which is clearly observed for  $\text{Li}^+$ -15C5 and  $\text{Li}^+$ -B15C5 in all solvent systems (Figures 2–6) and for  $\text{Li}^+$ -DC18C6 in 20% AC (Figure 6), is indicative of the formation of a quite stable 1:1 complex in solution.

2. A gradual upfield shift the  $^7\text{Li}$  resonance with increasing crown ether concentration, that does not show any tendency to level off even at a mole ratio of 4. Such beha-

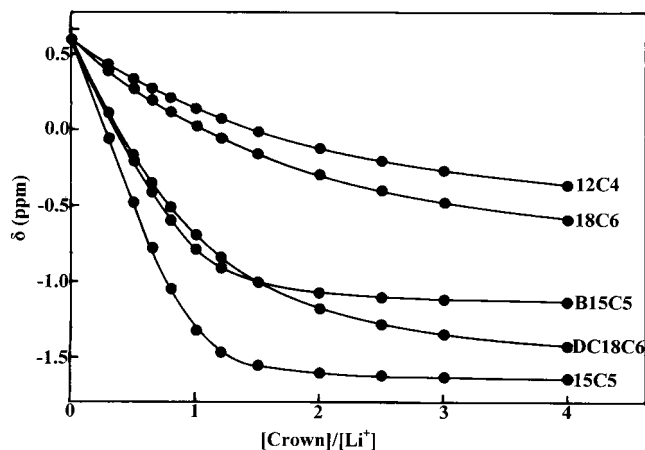


Figure 2.  $^7\text{Li}$  chemical shift as a function of crown/ $\text{Li}^+$  mole ratio in pure acetone.

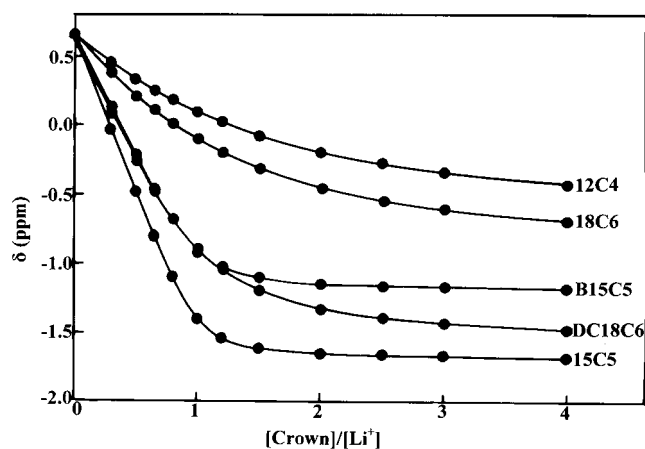


Figure 3.  $^7\text{Li}$  chemical shift as a function of crown/ $\text{Li}^+$  mole ratio in 80% AC.

avior, which is observed for  $\text{Li}^+$ -12C4 and  $\text{Li}^+$ -DB18C6 in all solvent mixtures (Figures 2–6) and for  $\text{Li}^+$ -DB18C6 in solvent mixtures of  $\geq 60\%$  AC (Figures 2–4), emphasizes the formation of a weak 1:1 complex between  $\text{Li}^+$  ion and the crown ether.

The formation constants of the resulting 1:1 complexes were calculated from the variation of  $^7\text{Li}$  chemical shift with

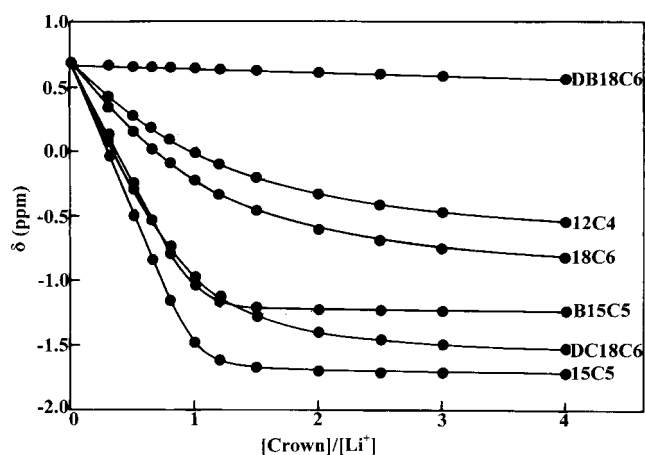


Figure 4.  $^7\text{Li}$  chemical shift as a function of crown/ $\text{Li}^+$  mole ratio in 60% AC.

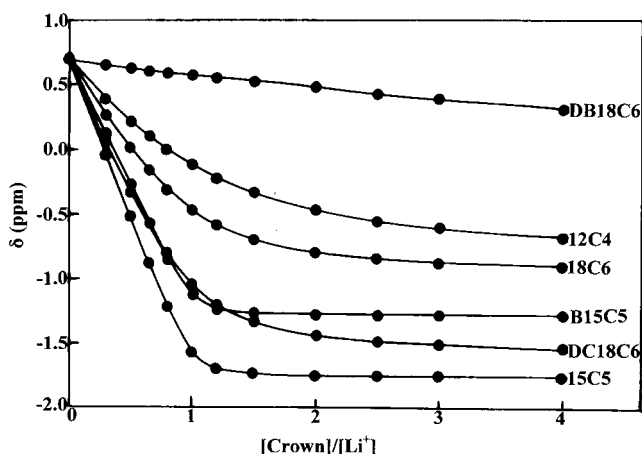


Figure 5.  $^7\text{Li}$  chemical shift as a function of crown/ $\text{Li}^+$  mole ratio in 40% AC.

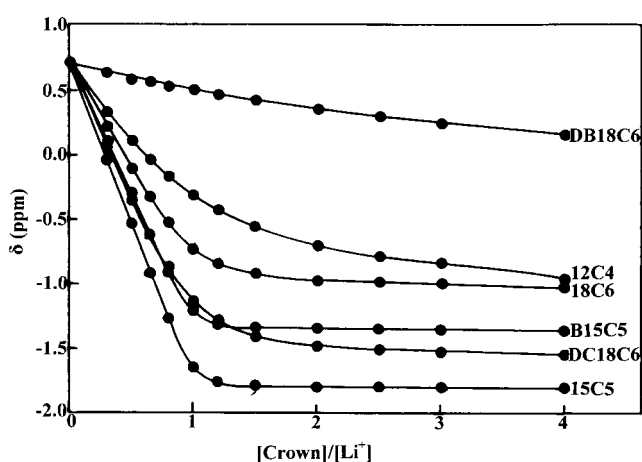


Figure 6.  $^7\text{Li}$  chemical shift as a function of crown/ $\text{Li}^+$  mole ratio in 20% AC.

the crown ether/ $\text{Li}^+$  mole ratio. It has been found that, in the cases where there is a fast exchange between free and complexed metal ions, the observed chemical shift of the resulting single NMR signal is given by [21].

$$\delta_{\text{obs}} = \left\{ \left[ K_f C_{\text{Li}} - K_f C_{\text{crown}} - 1 \right] + \left( K_f^2 C_{\text{crown}}^2 - K_f^2 C_{\text{Li}}^2 - 2K_f^2 C_{\text{crown}} C_{\text{Li}} + 2K_f C_{\text{crown}} + 2K_f C_{\text{Li}} + 1 \right)^{1/2} \right\} (\delta_{\text{Li}} - \delta_{\text{Li crown}}) / 2K_f C_{\text{Li}} + \delta_{\text{Li crown}} \quad (1)$$

where  $K_f$  is the formation constant for the 1:1 complex.  $C_{\text{crown}}$  and  $C_{\text{Li}}$  are the analytical concentrations of crown ether and  $\text{Li}^+$ , respectively, and  $\delta_{\text{Li}}$  and  $\delta_{\text{Li crown}}$  are the respective chemical shifts of the free and complexed lithium ion. A non-linear least-squares curve fitting program KIN FIT [22] was used to evaluate the  $K_f$  and  $\delta_{\text{Li crown}}$  values for the 1:1 complexes. A sample computer fit of the  $^7\text{Li}$  chemical shift-mole ratio data is shown in Figure 7 and all the calculated  $\log K_f$  values are summarized in Table 1. As seen from Figure 7, there is a satisfactory agreement between the calculated and observed chemical shifts, supporting the formation of a 1:1 complex in solution.

From the data given in Table 1, it is immediately obvious that for a given crown ether the stability of the resulting

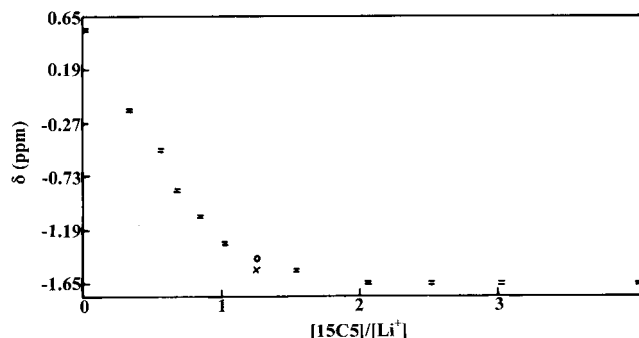


Figure 7. Computer fit of  $^7\text{Li}$  chemical shift vs  $15\text{C}5/\text{Li}^+$  mole ratio in pure acetone: (x) experimental points; (o) calculated points; (=) experimental and calculated points are the same within the resolution of the plot.

complex is very much dependent on the solvent mixture composition. In all cases the stability increases significantly with increasing amount of NB in the solvent mixture. It has been well documented that the solvating ability of the solvent, as expressed by the Gutmann donor number [23], plays a key role in different complexation reactions [4, 6, 8, 10–21]. Acetone is a solvent of relatively high solvating ability ( $\text{DN} = 17.0$ ) which can compete with the crown ether for lithium ion. Thus, it is not unexpected that addition of nitrobenzene as a low donicity solvent ( $\text{DN} = 4.4$ ) to acetone will increase the stability of the complex considerably.

The data given in Table 1 clearly indicate that, in a given AC-NB mixture, the stability of  $\text{Li}^+$  complexes decreases in the order  $15\text{C}5 > \text{B}15\text{C}5 > \text{DC}18\text{C}6 > 18\text{C}6 > 12\text{C}4 > \text{DB}18\text{C}6$ . Obviously, the consonance between the ionic size of  $\text{Li}^+$  ( $1.72 \text{ \AA}$ ) [24] and the size of the macrocyclic ring is an important factor in determining the stability of the resulting complexes [2–6]. The ring sizes of crown ethers are not known precisely, but on the basis of molecular models, the ring sizes of  $12\text{C}4$ ,  $15\text{C}5$  and  $18\text{C}6$  are  $1.2\text{--}1.5 \text{ \AA}$ ,  $1.7\text{--}2.2 \text{ \AA}$  and  $2.6\text{--}3.2 \text{ \AA}$ , respectively [25]. Thus, it seems reasonable to assume that the best fitting condition of  $\text{Li}^+$  ion inside the cavity of 15-crowns results in the formation of the most stable complexes in the series.

On the other hand,  $12\text{C}4$  and the 18-crowns used have too small and too large cavities for  $\text{Li}^+$  ion, respectively. Thus, their lithium complexes are much weaker than those with 15-crowns (Table 1). It is interesting to note that, although there are some literature reports on the formation of both 1:1 and 2:1 (ligand to metal ion) complexes between  $12\text{C}4$  and  $\text{Li}^+$  ion in the literature [26], no clear cut evidence for the formation of a  $\text{Li}^+(12\text{C}4)_2$  complex was observed in this study. We also tried to fit the resulting chemical shift-mole ratio data to a model that takes into account the formation of both 1:1 and 2:1 complexes for the  $\text{Li}^+ - 12\text{C}4$  system [14], but the resulting computer fit was very poor, emphasizing again the predominance of a 1:1 complexation in solution.

Table 1 shows that among 18-crowns used, where the ring frame remains the same, the formation constants of the resulting complexes decrease in the order  $\text{DC}18\text{C}6 > 18\text{C}6 > \text{DB}18\text{C}6$ . The presence of two benzo groups in  $\text{DB}18\text{C}6$  would cause a significant decrease in the stability of the

Table 1. Formation constants of Li<sup>+</sup> complexes with different crown ethers in various acetone-nitrobenzene mixtures at 25 °C

Solvent composition (wt% AC in NB)	log K <sub>f</sub>					
	12C4	15C5	B15C5	18C6	DC18C6	DB18C6
100	1.89 ± 0.02	3.58 ± 0.01	3.22 ± 0.03	1.92 ± 0.01	2.51 ± 0.02	<0.3
80	2.07 ± 0.02	3.74 ± 0.02	3.53 ± 0.08	2.23 ± 0.04	2.87 ± 0.06	<0.3
60	2.25 ± 0.04	3.91 ± 0.10	3.87 ± 0.17	2.38 ± 0.01	2.97 ± 0.03	0.64 ± 0.19
40	2.34 ± 0.02	4.15 ± 0.03	4.08 ± 0.10	2.88 ± 0.02	3.12 ± 0.02	1.25 ± 0.06
20	2.51 ± 0.02	4.40 ± 0.06	4.28 ± 0.20	3.45 ± 0.06	3.33 ± 0.07	1.75 ± 0.03

resulting lithium complex, compared with Li<sup>+</sup>-18C6. This is due to some combination of the electron withdrawing effect of the benzo groups which weakens the electron-donor ability of the ring oxygens and the reduced flexibility of the macrocycle which prevents the molecule wrapping itself around the cation. The net result is a much weaker cation-ligand interaction. A similar argument could be made for the diminished stability of Li<sup>+</sup>-B15C5 in comparison with that of the Li<sup>+</sup>-15C5 complex. On the other hand, the existence of two cyclohexyl groups in DC18C6 can pump electrons into the ligand ring and thus increase the basicity of the oxygen atoms, while the flexibility of the macrocycle remains more or less the same as for 18C6 [19]. Thus, it is not surprising to observe the highest stability for the Li<sup>+</sup>-DC18C6 complex among the 18-crowns used.

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