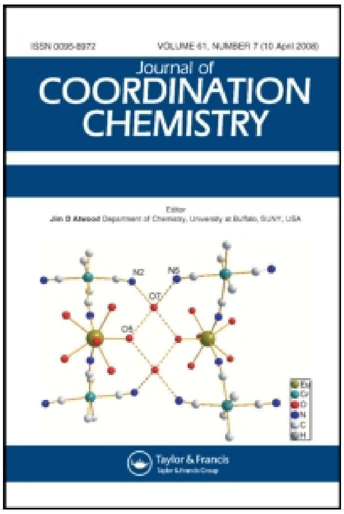

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# NUCLEAR MAGNETIC RESONANCE STUDY OF LITHIUM ION COMPLEXES WITH SEVERAL CROWN ETHERS IN BINARY ACETONITRILE-NITROMETHANE MIXTURES

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# NUCLEAR MAGNETIC RESONANCE STUDY OF LITHIUM ION COMPLEXES WITH SEVERAL CROWN ETHERS IN BINARY ACETONITRILE-NITROMETHANE MIXTURES

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Lithium-7 NMR measurements were used to determine the stoichiometry and stability of $Li^+$ complexes with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in various acetonitrile-nitromethane mixtures at 27°C. In all cases studied, the variation in the $^7Li$ chemical shift with the crown/$Li^+$ mol ratio indicated the formation of 1:1 complexes in solution. The formation constants of the resulting complexes were evaluated from computer fitting of the mol ratio data to an equation which relates the observed chemical shifts to the formation constant. It was found that, in all solvent mixtures used, the stabilities of the resulting complexes vary in the order 15C5>B15C5>DC18C6>12C4>18C6> DB18C6. There is an inverse relationships between log $K_f$ of the complexes and the mol fraction of acetonitrile in the solvent mixtures.

*Keywords:* $^7Li$ NMR; $Li^+$-crown; acetonitrile-nitromethane mixtures; stability constants.

## INTRODUCTION

It is well known that several factors influence the formation of crown ether complexes of metal ions in solution.[1–3] The most emphasized factor

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is the cavity size-cation diameter ratio although its importance has been questioned in the case of large crown ether complexates.[4–6] Other important factors are the number and the nature of heteroatoms participating in cation binding, the nature of substitutent groups on the macrocycle, the conformations of the free and complexed crown ethers and, especially, properties of the solvent such as solvating ability, dipole moment and dielectric constant. Among these parameters, the ability of solvent molecules to solvate ions and thus to compete with the crown binding sites for the coordination positions around a cation is of fundamental importance. Equally important, but often given much less attention, is the considerable interaction of some solvents with certain macrocyclic ligands.[7] There is an increasing interest in the study of complexation in binary mixed solvent systems and their interpretation in terms of solute preferential solvation by one of the mixed solvent components.[8–11]

Among a variety of methods used for the study of metal ion-crown ether complexes,[1,2] it has been found that nuclear magnetic resonance spectrometry offers a very sensitive technique for studies of changes in the immediate chemical environment of metal ions in solution.[12,13] In the past two decades, we have employed the NMR technique to investigate the thermodynamics[4,12,14–17] and the exchange kinetics of a number of metal ion-macrocycle complexes in different non-aqueous and mixed solvents.[11,16,18–22] In this paper we report the use of lithium-7 NMR for the study of $Li^+$ ion complexes with six crown ethers (*i.e.*, 12C4, 15C5, B15C5, 18C6, DC18C6 and DB18C6) in binary acetonitrile-nitromethane mixtures at 27.0 ± 0.1 °C.

## EXPERIMENTAL

Crown ethers B15C5, 18C6, DC18C6 and DB18C6 (all from Merck) were purified and dried as described,[23,24] 12C4 and 15C5 (both from Merck) were used as received. Lithium perchlorate (Merck) was purified and dried using a previously reported method.[15] Spectroscopic grade nitromethane (NM, Reidel) and acetonitrile (AN, Merck) were used to prepare the solvent mixtures by weight.

All nuclear magnetic resonance measurements were made on a JEOL FX90 Q FT-NMR Spectrometer with a field strength 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 $LiClO_4$ solutions used was 0.01 M. All chemical shift measurements were carried out at a probe temperature of 27.0 ± 0.1 °C.

The formation constants of 1:1 complexes were calculated from the variation of $^7Li$ chemical shift with the crown/$Li^+$ mol ratio. It has been shown that, in the cases where there is fast exchange between free and complexed metal ions, the observed chemical shift of the resulting single NMR signal is given by[25]

$$\begin{aligned}\delta_{obs} = \{[(&K_fC_M - K_fC_L - 1)\\ &+ (K_f^2C_L^2 + K_f^2C_M^2 - 2K_f^2C_LC_M + 2K_fC_L + 2K_fC_M + 1)^{1/2}\}\\ &(\delta_M - \delta_{ML})/2K_fC_M\} + \delta_{ML}\end{aligned} \tag{1}$$

where $K_f$ is the concentration formation constant for the 1:1 complex, $C_L$ and $C_M$ are the analytical concentration of the crown ether and $Li^+$ ion, respectively, and $\delta_M$ and $\delta_{ML}$ are the respective chemical shifts of the free and complexed lithium ion. A non-linear least-squares curve fitting program, KINFIT,[26] was used to evaluate $K_f$ and $\delta_{ML}$ values for the 1:1 complexes.

## RESULTS AND DISCUSSION

Lithium-7 chemical shifts were determined as a function of crown/$Li^+$ ion mol ratios in different AN-NM mixtures and sample mol ratio plots are shown in Figures 1–3. In all cases studied, only one resonance for the $Li^+$ ion was observed irrespective of the crown/metal ion mol ratio. In general, if the mean lifetime for the exchange of the metal ion between the two sites (*i.e.*, free ion in the bulk solution and the complex) is smaller than $\sqrt{2}/\pi\ \Delta\nu$ ($\Delta\nu$ is the difference between the characteristic resonance frequencies of the two sites in hertz), only one population-average resonance is observed.

As can be seen, in general, the behaviour of the chemical shift as a function of the crown/$Li^+$ mole ratio can be approximately divided into two groups, as follows.

1. The chemical shift (upfield or downfield) varies linearly with the crown concentration until a crown/$Li^{\bullet}$ mol ratio of 1:1 is reached. Further addition of the crown ether does not change the $^7Li$ resonance frequency. Such behaviour which is observed for almost all crown ethers in pure nitromethane (Figure 3) and in the case of 15C5 and

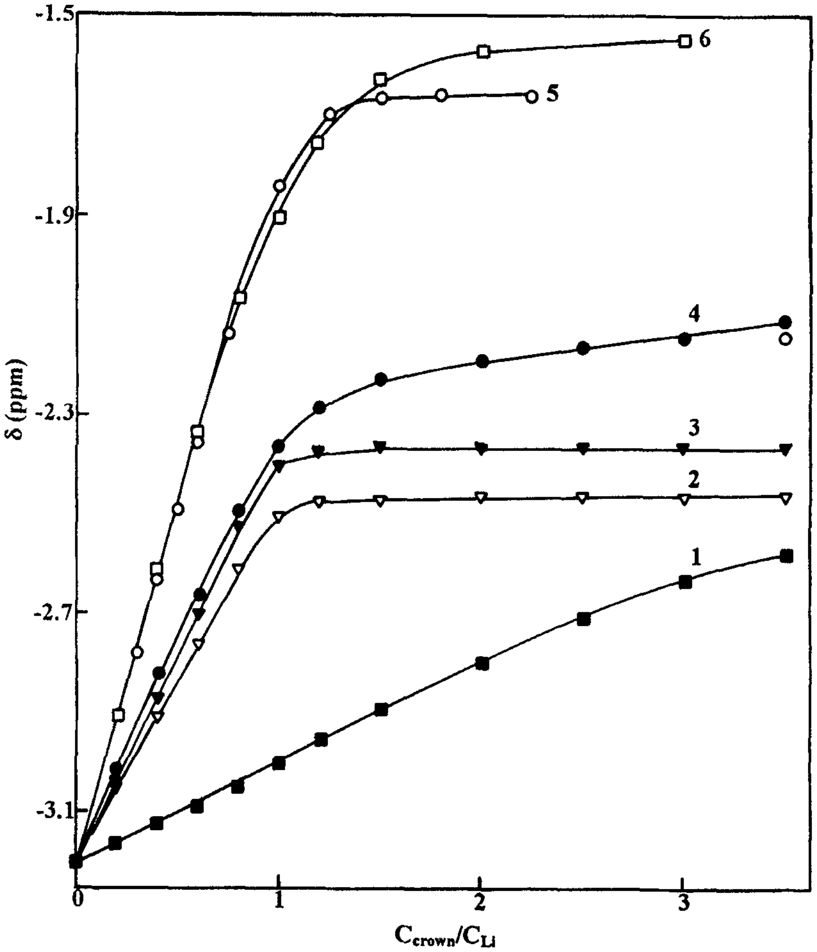

FIGURE 1 Lithium-7 chemical shift as a function of crown/$Li^+$ mol ratio for different crown ethers in pure acetonitrile: (1) DB18C6; (2) B15C5; (3) 15C5; (4) 18C6; (5) DC18C6; (6) 12C4.

B15C5 in other solvents (Figures 1 and 2) is indicative of the formation of a stable 1:1 ($Li^+$-crown) complex in solution. It usually occurs in solvents of medium and low donicity.[4,15]

2. An increase in the crown ether concentration gradually shifts the $^7Li$ resonance downfield and the chemical shift does not seem to reach a limiting value even at mol ratios of about 3.5. Typical examples are the behaviour of $Li^+$-12C4 and, especially, $Li^+$-DB18C6 in pure acetonitrile (Figure 1) and in 40% acetonitrile (Figure 2) and it is

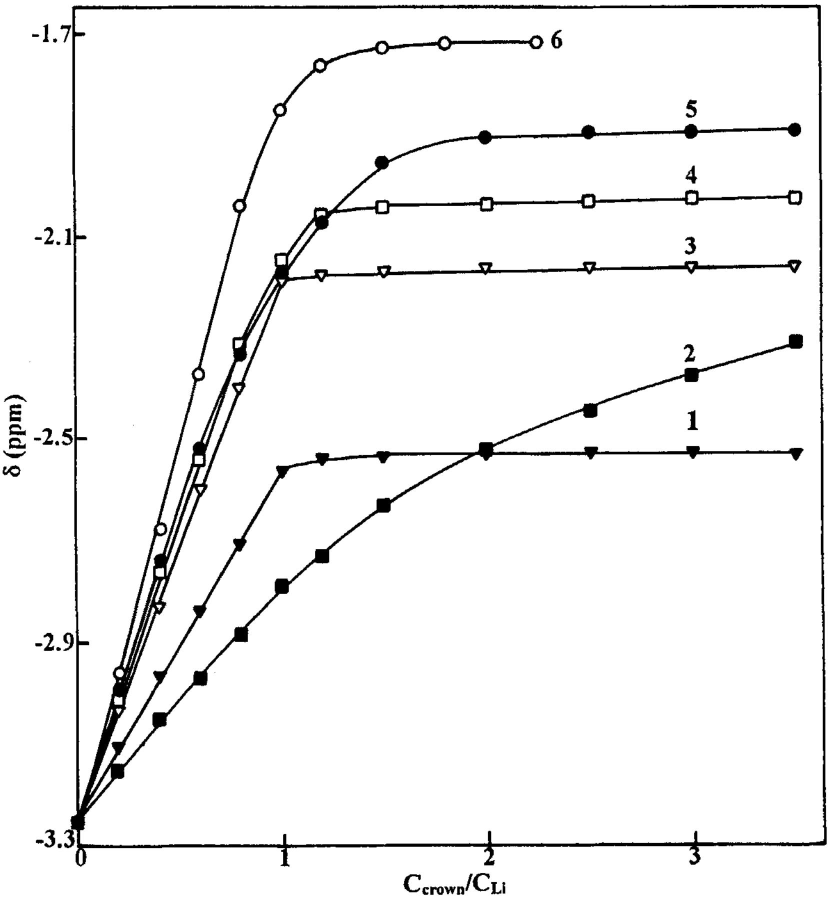

FIGURE 2 Lithium-7 chemical shift as a function of crown/Li$^+$ mol ratio for different crown ethers in 40% acetonitrile solution: (1) 15C5; (2) DB18C6; (3) B15C5; (4) 12C4; (5) 18C6; (6) DC18C6.

indicative of the formation of a weak complex. As a rule of thumb, it could be concluded that the more curvature exists around mol ratio 1 in the chemical shift-mol ratio plots, the weaker the resulting 1:1 complex.

Formation constants of the resulting 1:1 complexes were evaluated from the variation of the observed chemical shift with the crown/Li$^+$ mol ratio. The procedure has been described in previous publications.[17,25] A sample computer fit of the $^7$Li chemical shift-mol ratio data is shown in

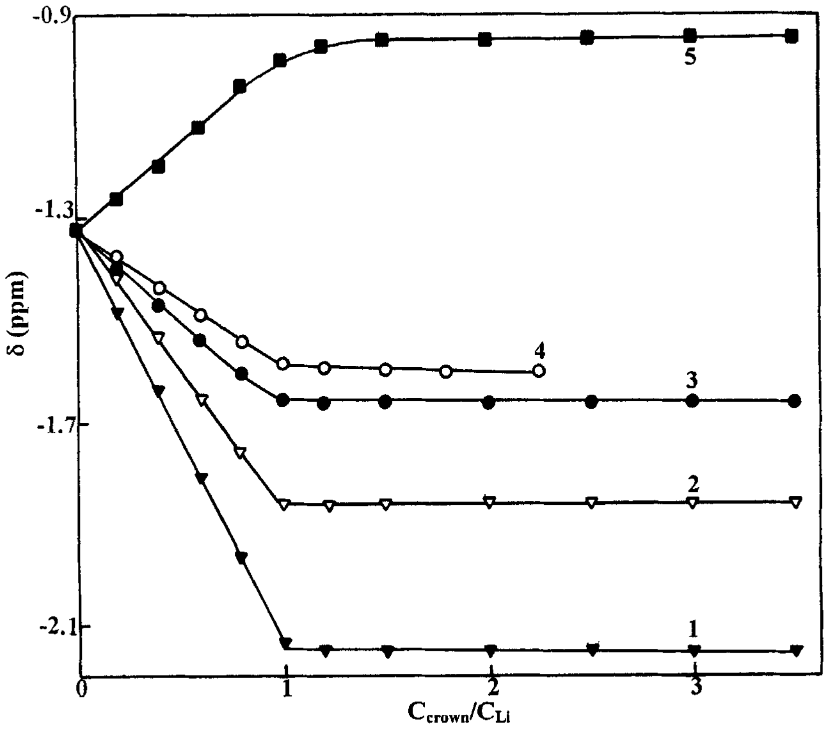

FIGURE 3 Lithium-7 chemical shift as a function of crown/$Li^+$ mol ratio for different crown ethers in pure nitromethane: (1) 15C5; (2) B15C5; (3) 18C6; (4) DC18C6; (5) DB18C6.

Figure 4 and all the calculated log $K_f$ values are summarized in Table I. It should be noted that the method generally becomes unreliable for very stable complexes (*i.e.*, $K_f > 10^5$). It is seen that there is a satisfactory agreement between the formation constants obtained for the $Li^+$-crown complexes in pure acetonitrile with those previously reported in the literature. As is obvious, the method used for the calculation of formation constants does not take into account possible ion association in $LiClO_4$ solutions. The literature indicates that in acetonitrile the ionic association of the salt is quite small.[27] It is reasonable to expect that similar condition will prevail in nitromethane, which has about the same dielectric constant as acetonitrile. Thus, at the low concentration of lithium perchlorate which were used, it seems unlikely that complex formation has significant competition by ion pair formation.[15]

The data given in Table I clearly indicate that, in a given AN-NM mixture, the stability of $Li^+$ complexes decreases in the order 15C5 >

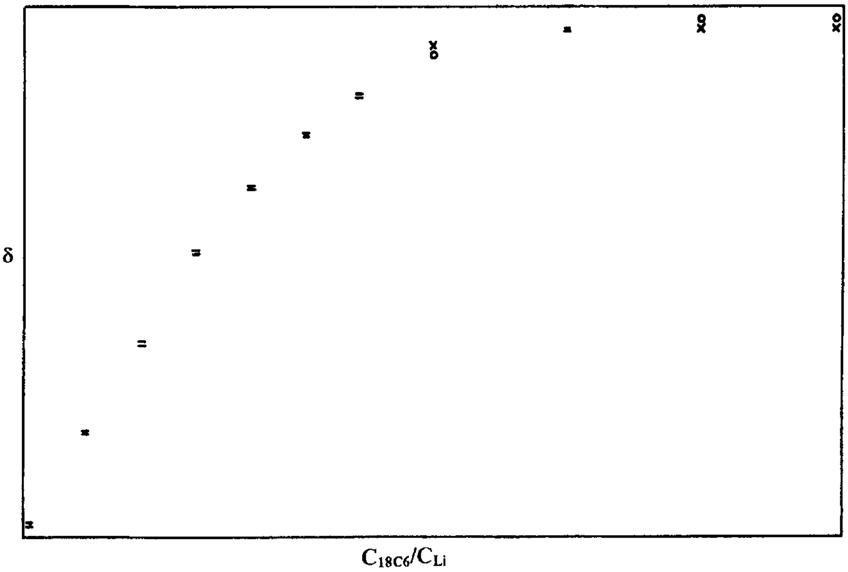

FIGURE 4 Computer fit of $^7Li$ chemical shift vs 18C6/$Li^+$ mol ratio in 40% acetonitrile solution: (x) experimental points; (o) calculated points; ( = ) experimental and calculated points are the same within the resolution of the plot.

B15C5 > DC18C6 > 12C4 > 18C6 > DB18C6. Obviously, the consonance between the ionic size of $Li^+$ ion and the size of the macrocyclic ring is an important factor in determining the stabilities of the $Li^+$-crown ether complxes. According to Pedersen and Frensdorff[28] the cavity sizes of 12 C4, 15C5 and 18C6 are 1.2–1.5 Å, 1.7–2.2 Å and 2.6–3.2 Å, respectively. They should be nearly the same for the corresponding substituted crown ethers. Lithium ion with an ionic diameter of 1.72 Å[29] seems to have the best fitting conditions for the cavities of 15C5 and B15C5; thus they form the most stable complexes in the series; 12C4 and the 18-crowns used have too small and too large cavities for $Li^+$ ion, respectively. Thus their lithium complexes are much weaker than those with 15-crowns. It is interesting to note that, although there are some literature reports on the formation of both 1:1 and 2:1 (sandwich) complexes between $Li^+$ ion and 12C4,[30] no clear cut evidence for the formation of the $Li^+(12C4)_2$ complex was observed in this study. We also tried to fit the resulting chemical shift-mol ratio data to a model which takes into account the formation of both 1:1 and 2:1 complexes for the $Li^+$-12C4 system, but the resulting computer fit was very inconvenient, emphasizing again the predominance of 1:1 complex formation in solution.

Table 1 shows that among 18-crowns used, where the ring frame remains the same, the formation constants of the resulting $Li^+$ complexes decrease in the order DC18C6 > 18C6 > DB18C6. The presence of two benzo groups in DB18C6 would cause a significant decrease in the stability of the resulting lithium complex, compared with $Li^+$-18C6. This behaviour could be 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-crown interaction. A similar argument could be made for the diminished stability of $Li^+$-B15C5 in comparison with that of $Li^+$-15C5 complex. On the other hand, the existence of two cyclohexyl groups in DC18C6 can inductively enhance the electron density of 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.[24] Thus it is not unexpected to observe the highest stability for $Li^+$-DC18C6 complex among the 18-crowns used.

A clear anomaly found in Table I is the stability reversal for $Li^+$-12C4 and $Li^+$-18C6 complexes; 18C6, with increased number of the ring donating oxygen atoms and much higher flexibility, is expected to form a more stable $Li^+$ complex than 12C4, such as that observed for the case of DC18C6. In all solvent mixtures used, the $Li^+$-12C4 complex is more stable than $Li^+$-18C6. Such unexpected behaviour could be most probably related to the difference in the specific solvation of the crown ethers with the solvent mixture components.[31] It is well known that the crown ether 18C6 forms relatively stable 1:1 complexes with both

TABLE I Formation constants of $Li^+$ complexes with different crown ethers in various acetonitrile-nitromethane mixtures at 27°C

| Solvent composition (wt% acetonitrile in nitromethane) | log $K_f$ | | | | | |
|---|---|---|---|---|---|---|
| | 12C4 | 15C5 | B15C5 | 18C6 | DC18C6 | DB18C6 |
| 100 | 3.12 ± 0.06<br>3.40[a] | 4.8 ± 0.2<br>>4[b] | 4.51 ± 0.09 | 2.30 ± 0.05<br>2.34[b] | 3.14 ± 0.05 | 0.86 ± 0.08 |
| 80 | 3.19 ± 0.03 | 4.9 ± 0.1 | 4.7 ± 0.2 | 2.49 ± 0.02 | 3.32 ± 0.08 | 1.18 ± 0.05 |
| 60 | 3.36 ± 0.03 | >5 | 5.2 ± 0.2 | 2.70 ± 0.02 | 3.9 ± 0.2 | 1.56 ± 0.04 |
| 40 | 3.84 ± 0.04 | >5 | >5 | 3.11 ± 0.03 | 4.2 ± 0.1 | 1.85 ± 0.02 |
| 20 | 4.5 ± 0.2 | >5 | >5 | 3.87 ± 0.09 | >5 | 2.22 ± 0.06 |
| 0 | — | >5 | >5 | >5 | >5 | 4.1 ± 0.3 |

[a] Ref. 34. [b] Ref. 30.

acetonitrile[7,32] and nitromethane molecules.[7] It is therefore reasonable to assume that there is a considerable interaction between acetonitrile and nitromethane and 18C6 which would obviously destabilize the $Li^+$-18C6 complex in the solvent mixtures used. However, more detailed information on the solvation of the crown ethers with the components of the AN-NM solvent mixtures is needed to clarify the situation.

The fundamental importance of solvent properties on the stabilities of the $Li^+$-crown ether complexes is very evident from the data given in Table I. In general, complex stability decreases with increasing amounts of acetonitrile in the solvent mixture. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number,[33] plays a key role in different complexation reactions.[3,4,6,11–24] Acetonitrile and nitromethane are solvents of similar dielectric constant (*i.e.*, $\varepsilon_{AN} = 37.5$ and $\varepsilon_{NM} = 35.6$),[33] but of quite different donor numbers (*i.e.*, $DN_{AN} = 14.1$ and $DN_{NM} = 2.7$).[31] Consequently, with complexation of $Li^+$ with crown ethers, acetonitrile more strongly competes with crown ethers for the metal ion than does nitromethane. Thus it is not surprising that addition of nitromethane to acetonitrile will increase the stability of $Li^+$-crown ether complexes considerably.

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