

## Lithium ion – crown ether complexes in a molten salt

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**Abstract** - Lithium ion forms complexes with crown ethers in a basic, room temperature molten salt. The stability constants of several of these complexes have been determined by lithium-7 NMR measurements. The binary molten salt mixture was 55/45 mole % in 1-methyl-3-ethylimidazolium chloride to aluminum(III) chloride. Stability constants for 1:1 complexes with lithium ion were found to increase in the order 18-crown-6 < 12-crown-4 < benzo-15-crown-5 < 15-crown-5 in this molten salt at 22 °C. This is the same sequence for lithium ion - crown ether complex stability as was found previously in a 55/45 mole % N-butylpyridinium chloride to aluminum(III) chloride molten salt.

### INTRODUCTION

Aluminum chloride combined with certain quaternary ammonium chloride salts yields ionic liquids at room temperature (ref. 1). These room temperature chloroaluminate molten salts have high electrical conductivity, a wide liquid range, and a broad electrochemical window that make them interesting candidates for electrolytes in batteries (ref. 2). Lewis basic melts result from combining aluminum chloride with a molar excess of the organic chloride salt. The anionic species present in basic melts are tetrachloroaluminate(1-) and "free" chloride ions. Hussey (ref. 3) has reviewed the use of the room temperature haloaluminate molten salts as aprotic solvents in electrochemical and spectroscopic studies of transition metal halide complexes. For instance, electrochemical and spectroelectrochemical properties of polynuclear rhenium(III) chloride cluster complexes were recently examined in a basic aluminum chloride/1-methyl-3-ethylimidazolium chloride [ImCl] molten salt (ref. 4). The same basic melt was the solvent in a recent EPR and electrochemical investigation of polyaniline films (ref. 5).

Rhinebarger, Rovang and Popov (ref. 6) used lithium-7 NMR chemical shift data to determine stability constants for crown ether complexes of lithium ion in a 55/45 mole % N-butylpyridinium chloride [BpCl] to aluminum(III) chloride molten salt. The objective of the present study was to determine whether a change in the organic cation from Bp<sup>+</sup> to Im<sup>+</sup> in the chloroaluminate salt would alter the stability constants of the lithium ion-crown ether complexes. Advantages of the use of ImCl over BpCl in chloroaluminate salts are a larger liquid range that includes room temperature and a broader electrochemical window. A major disadvantage of all chloroaluminate molten salts is their extreme sensitivity to moisture.

## EXPERIMENTAL

15-crown-5 [15C5] (Aldrich) and 12-crown-4 [12C4] (Sigma) were distilled under reduced pressure and dried under vacuum. 18-crown-6 [18C6] (Aldrich) was recrystallized from acetonitrile and dried under vacuum. Benzo-15-crown-5 [B15C5] (Parish) was used as received. Lithium chloride (E M Science) was dried at 100 °C for two days. ImCl was prepared by a standard method (ref. 7), repeatedly recrystallized and vacuum dried for two days. Anhydrous aluminum(III) chloride (Fluka) was purified by sublimation in a bomb tube under vacuum from an aluminum(III) chloride-sodium chloride melt a minimum of three times. ImCl/aluminum(III) chloride melts of the desired composition were prepared by slow mixing of the ingredients under dry nitrogen in a Vacuum Atmospheres Corp. glove box. Melts were vacuum filtered in the glove box through a medium porosity glass frit (Buchner funnel). Samples of molten salt containing lithium chloride and different amounts of crown ethers were prepared by weight and transferred in the glove box to NMR tubes (Wilmad 528-TR-7, 5 mm OD) with septum sealed screw caps. All lithium-7 NMR spectra were recorded on a Varian XL-300 spectrometer at 116.6 MHz, and all chemical shifts are reported in ppm relative to external lithium chloride/deuterium oxide at 0.0 ppm. NMR measurements were made unlocked with virtually no field drift. Temperature control was calibrated with appropriate Varian authentic samples of methanol and ethylene glycol.

## RESULTS AND DISCUSSION

At room temperature there is only one peak in the lithium-7 NMR spectra. Due to the fast exchange of the lithium ion between two or more different environments the observed lithium-7 NMR chemical shift is the time average of the corresponding chemical shifts weighted by the population of the species (ref. 8).

The relative lithium-7 NMR chemical shift as a function of the total (analytical) lithium/crown ether mole ratio is shown in Fig. 1 at room temperature for various ligands. Approximating each curve with two linear portions the projections of the intersections are in the vicinity of a

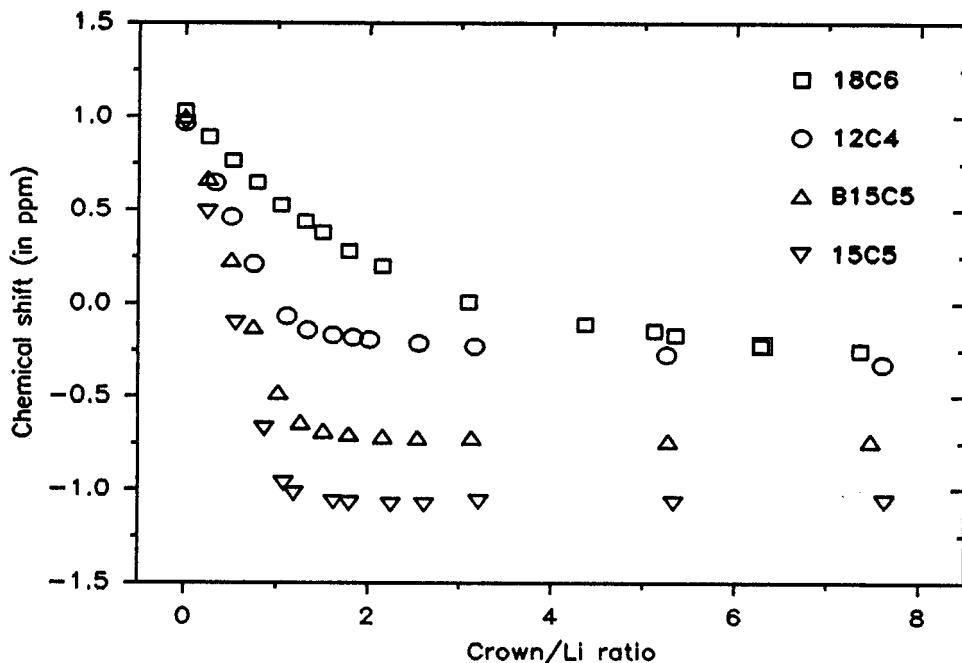


Fig. 1. Relative chemical shift vs analytical crown ether/Li ratio in 55/45 mole % ImCl/AlCl<sub>3</sub> molten salt at 22 °C (B15C5 at 30 °C).

crown ether/lithium ion mole ratio of 1. Therefore the dominating species is the 1:1 lithium ion-crown ether complex (ref. 9). The sharper the break the more stable the complex.

Considering the "free" and the complexed lithium ions, the chemical shift is given by

$$\delta_{obs} = \delta_M + \frac{\delta_{ML} - \delta_M}{2C_M K_{11}} \{ (K_{11}(C_M + C_L) + 1) + [(K_{11}(C_M + C_L) + 1)^2 - 4K_{11}C_M C_L]^{1/2} \} \quad (1)$$

where  $\delta$  is the relative chemical shift of the species, and  $C_M$  and  $C_L$  are the total concentrations of the lithium ion and the crown ether, respectively.  $K_{11}$  is the stability (formation) constant of the ML species. The three parameters  $\delta_M$ ,  $\delta_{ML}$  and  $K_{11}$  were fitted to the observed chemical shift and sample composition data using the non-linear Levenberg-Marquardt method (ref. 10). The results are summarized in Table 1.

TABLE 1. Stability constants, relative lithium-7 NMR chemical shifts and their standard deviations of various lithium - crown ether complexes in a 55/45 mole % ImCl/AlCl<sub>3</sub> molten salt at 22 °C (B15C5 at 30 °C).

Ligand	K <sub>11</sub>		δ <sub>M</sub>		δ <sub>ML</sub>	
	value	s	value (ppm)	s (ppm)	value (ppm)	s (ppm)
12C4	1225	208	1.011	0.025	-0.264	0.015
15C5	11418	2838	1.040	0.017	-1.047	0.009
B15C5	3213	799	1.026	0.026	-0.755	0.019
18C6	67.8	3.8	1.049	0.011	-0.586	0.024

The concentrations and stability constants are expressed on the mole fraction scale.

The fitted and measured relative chemical shifts of the uncomplexed lithium ion are in excellent agreement.

The observed order of the stability constants for these four crown ethers with lithium ion in 55/45 mole % 1-methyl-3-ethylimidazolium chloride to aluminum(III) chloride is the same as that reported previously (ref. 6) in 55/45 mole % N-butylpyridinium chloride.

The small stability constants are consistent with the formation of generally weak lithium - crown ether complexes in other solvents (ref. 11). The order found can be explained considering the sizes of the lithium ion, 0.74 Å (ref. 12), and the crown ether cavities (see Table 2).

TABLE 2. Crown ether cavity sizes

crown ether	cavity radius (Å)
12C4	0.60
15C5	0.85
B15C5	0.85
18C6	1.30

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