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SYNTHESIS OF CYCLIC AZA-ETHER COMPOUNDS AND STUDIES OF THEIR USE AS ANION RECEPTORS IN NON-AQUEOUS LITHIUM HALIDE SALT SOLUTIONS

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ABSTRACT

A series of new anion receptors, based on cyclic aza-ether compounds, have been synthesized. In all of these cyclic aza-ether compounds, the electron-withdrawing group CF_3SO_2 was attached to each of the nitrogen atoms. When used as additives, all of them can significantly increase the ionic conductivity of lithium halide salts in THF solutions. This is due to the complexation between these compounds and halide anions. Ionic conductivity studies show that the complexation behavior is related to both the ring structure of the cyclic compounds and the characteristics of the halide anions. X-ray diffraction data show that the diffraction patterns of the complex crystals are different from the pure cyclic aza-ether compounds. New Bragg peaks representing a large *d*-spacing (~15 Å) are observed for the complex crystals which provides a clear evidence for complexation.

INTRODUCTION

Increasing the ionic conductivity and cation transference number of the electrolyte for lithium battery is an important goal in battery research. Several strategies have been used to enhance the ion pair dissociation to increase the ionic conductivity, such as lithium salts with anions of novel super acid salts, solvents with high dielectric constant or the addition of a neutral ligand to coordinate with either cation or anion. Some work has been reported on using crown ether as a cation complexing ligand in non-aqueous electrolyte (1-4). However, anion coordination is more preferable than cation coordination in lithium battery electrolyte, since it can increase both the conductivity and the lithium transference number. Previously, anion receptors were usually designed to complex anions through the positively charged sites, the Lewis acid metal centers or hydrogen bonding (5-7). These anion receptors cannot be used in non-aqueous electrolyte system for lithium batteries.

In our previous work, a new family of anion receptors were synthesized, based on substituted linear aza-ether compounds (8). Due to the electron-withdrawing effect from CF_3SO_2 groups at nitrogen site, the compounds can act as an anion-binding ligand.

Significant increases of ionic conductivity of LiCl in tetrahydrofuran (THF) solution were observed after adding these compounds. This increase of conductivity is due to the increase of free ion concentration resulting from the ion-pair dissociation effect of the aza-ether compounds. The complexation effect has been studied by near-edge X-ray absorption fine structure (NEXAFS) (8). Changes on coordination symmetry of Cl^- and I^- were found on addition of linear aza-ether ligands in NEXAFS studies. This gives the direct evidence that these aza compounds act as anion complexing ligand. Recently, we reported a new family of cyclic aza-ether compounds (9). Various types of cyclic compounds have been studied as hosts with potential to selectively complex guest ions. Selective complexation is important in molecular recognition and mimicking of biological processes. Also the cyclic compounds should have superior chemical stability. The effect of different ring structures of these compounds on conductivity of lithium halide salts in THF solution was studied in this paper.

EXPERIMENTAL

Four new cyclic aza-ethers anion receptors were synthesized according to the method described in our previous paper (9). All of them are new compounds. Their chemical structures are shown in Figure 1.

Conductivity Measurements

Conductivity measurements were taken using a Hewlett Packard 4129A impedance analyzer at 25°C in the frequency range from 5 Hz to 100 MHz. Cells with Pt electrodes were used for the measurements. The cell constants were calibrated by a standard 0.05 N KCl aqueous solution. All conductivities were measured in anhydrous THF solution.

Preparation of Crystals of Complex.

The complex crystals were obtained by slowly evaporating of the solvent in the co-solutions of LiX (X= Cl, Br and I) and the cyclic compound in dimethoxyethane (DME).

X-Ray Powder Diffraction Measurements

X-ray powder diffraction patterns were obtained using a Phillips PW 1729 X-ray diffractphotometer with Cu Kα radiation. The spectra were collected in the 2θ range of 4 to 40 °.

RESULTS AND DISCUSSION

The ionic conductivity data of lithium halide salts, LiCl, LiBr and LiI, with and without cyclic aza-ether compounds as additives in anhydrous THF are listed in Table 1. Because the molecular weights of compounds **1**, **2**, **3** and **4** are rather large (770, 903,1078, and 1253 respectively) and vary over a wide range, dilute solutions, 0.1 M, were used in conductivity measurement to minimize the viscosity effect on conductivity.

As shown in Table I, the ionic conductivities of lithium halide salts in THF solutions were very low and increased in the order of LiI >LiBr >LiCl. The large difference in ionic conductivity for different lithium halide salts can be attributed to two major factors: solubility of the salts and the concentration of ion pairs. With addition of cyclic aza-ether compounds, both the solubility and the ionic conductivity of lithium salts in THF solutions were significantly increased. Using 0.1 M of cyclic aza-ether compounds **1**, **2**, **3** and **4** as additive in THF solution of 0.1 M LiCl, the respective conductivities are significantly increased from 7.50×10^{-6} S/cm for pure salt to 2.99×10^{-4}, 5.90×10^{-4}, 1.57×10^{-3} and 1.54×10^{-3} S/cm. Based on the results of our early published work on the linear aza-ether compounds, this enhancement in solubility and conductivity is due to the anion complexation effect of the CF_3SO_2 substituted aza compounds, which dissociate the ion-pair and increase the solubility of the salts and the population of free Li^+ Ions (8). However, comparison of compound **3** and **5** provides more supporting evidence for the anion complexing effect of these aza compounds. Conductivity of 0.1 M lithium chloride solution in THF only slightly increase to 1.62×10^{-5} S/cm when compound **5** was used as additive. The only difference between compound **5** and **3** is that the substituted group is tolysulfonyl in compound **5** but CF_3SO_2 in compound **3**. The stronger effect on conductivity enhancement of CF_3SO_2 substituted aza-ether compared to tolysulfonyl substituted one indicates this anion complexation effect are originated from the electron-withdrawing effect of substituted group at nitrogen sites (the electron-withdrawing effect of CF_3SO_2 group is much stronger than that of tolysulfonyl group). The oxygen in tolysulfonyl group has higher negative charge density than that of CF_3SO_2 group. If these aza compounds enhanced the conductivity through cation complexation at oxygen site, the compound **5** would have had stronger effect than compound **3**. Although anion complexation effect is clearly related to substituted CF_3SO_2 group at N atom in aza-ether compound, the anion-binding site for anion within sulfonamide group (N or S) in aza-ether ligand need to be further studied. The conductivity values for LiCl, together with those for LiBr and LiI salts, are plotted in Figure 4 versus the number of N atom in the CF_3SO_2 substituted cyclic aza compounds. As the number of N atoms increases from 4 in compound **1** to 6 in compound **4**, the ionic conductivity of LiCl, LiBr and LiI increases accordingly. This indicates that the degree of complexation increases with the increasing number of binding site (sulfonamide group). This is the same as that observed with linear aza-ether compounds (8). However, there is an interesting phenomena in Figure 4, which is different from the linear compounds. Although the binding site in compound **4** (7 sulfonamide groups) is larger than that in compound **3** (6 sulfonamide groups), compound **4** show similar effect on conductivity enhancement as compound **3**. This implies the possibility of a maximum in complexation effect in compound **3** due to its ring structure containing six-nitrogen units. This strong complexation effect of compound **3** also caused a rapid crystal precipitation in 0.1 M LiI solution, which prevented conductivity measurements in this solution.

The effect of the molar ratio between cyclic aza-ether compounds and lithium halide salts on conductivity was also studied in dilute solutions. The results are given in Table II. When compound **1** or **2** was used as an additive, the conductivity of 0.025 M LiCl in THF solution increases with increasing of additive-to-salt ratio from 1:1 to 3:1. However, when compounds **3** and **4** were used as additives, the increase of additive-to-salt ratio did not increase the conductivity. This indicates all the LiCl ion pair in solution has been completely dissociated when compound **3** or **4** are used as ligand in 1:1 additive-to-salt ratio. Compound **1** and **2** are relatively weak ligand for Cl^-, the high additive-to-salt ratio helps to further increase the degree of complexation. Nevertheless, even the compound **1** and **2** are used in 3:1 additive-to-salt ratio, the conductivities of LiCl solutions are still lower than those using compounds **3** and **4** in a 1:1 additive-to-salt ratio. This implies that the ring structure play more important role on complextaion stability than concentration effect for cyclic aza ligand.

However, LiI has almost no change in conductivity when the ligand-to-salt ratio is increased from 1:1 to 2:1 with compounds **1**, **2**, **3** or **4** as additives. Considering that ionic conductivity of LiI increased with increase of binding site from compounds **1** to **3**, the complexation between compound **1** and **2** with I^- should have not reach their maximum. The Increase of concentration for compounds **1** and **2** cannot increase the conductivity of LiI as for LiCl can only be explained by that the Cl^- was complexed with two molecular cyclic aza compound with a sandwich structure, while I^- only could form a complex with one molecular cyclic compound. Considering the fact that compounds **3** and **4** are stronger anion receptors than compounds **1** and **2**, it is reasonable to assume that the both Cl^- and I^- anion are complexed with one molecules of compounds **3** or **4**. Therefore increase of additive-to-salt ratio for compound **3** and **4** did not increase the conductivity for both LiCl and LiI. The different complexation behavior of halide anions with the cyclic aza-ether compounds may be due to the hard-soft characteristic of anions. The value of ion radii is in the order of $I^- > Cl^-$, the binding strength of ion pair is in the order $Li^+Cl^- > Li^+I^-$ (10) High polarizability of I^- yields strong binding with aza-ether compound, I^- could form stable complexes with one molecule of compounds **1** or **2** (even though compounds **1** and **2** have less binding sites). Cl^- anion is less soft than I^-, the complexes formed between Cl^- and one molecule of compounds **1** or **2** are not stable. Therefore the second ligand molecule is needed to form a stable complex.

Although conductivity studies provide interesting indication of a complexation effect by the cyclic aza compounds, it still is not direct evidence of complexation. In our previous work, we have successfully used the NEXAFS technique to study the anion complexation effect of linear aza-ether compounds. Unfortunately, white line splitting was not observed in LiCl solutions with cyclic compounds as shown in Figure 3, since the white line edge splitting effect could only be observed with an asymmetric distribution of ligands surrounding the anion (8). Therefore, the application of this technique is limited in detecting anion complexation with a highly symmetric cyclic ligand. However, due to the strong complexation effect and the highly symmetric structure of compound **3**, the polycrystals of complexes with LiI, LiBr and LiI were obtained. Therefore, the complexation effect of compound 3 was studied by powder X-ray diffraction (XRD). Compound **3** has very strong tendency to form a complex with I^-. When the solution of 0.1 M LiI and compound **3** were mixed together, needle shaped crystals precipitated within a minute. The other two crystal samples were grown by slowly evaporating co-solutions of compound **3** and LiCl or LiBr in DME. The respective melting points for these complex polycrystals were 242 °C for LiI, 209 °C for LiBr and 207 °C for LiCl. All of these crystals have sharp melt points and show comparable high melting point as that of pure compound **3** (204 °C). This indicated that these polycrystals are not a simple physical mixture. Figure 5 shows XRD patterns for the crystalline material obtained from the solution of LiI and compound **3**, the pure compound **3**, and LiI salt. The diffraction pattern of the product obtained from the co-solution is totally different from pure compound **3** and no Bragg peak belonging to LiI salt can be identified in its spectrum. This is direct evidence for the formation of a complex. New Bragg peaks around $2\theta = 5^\circ$ were observed in the XRD pattern for the complex. These Bragg peaks represent a structure with large *d*-spacing within the crystal. These low angle Bragg peaks might be originated from the I^- to I^- *d*-spacing. As shown in Figure 6, the crystal materials obtained from co-solutions of LiCl or LiBr salt and compound **3** also have different diffraction patterns compared to pure compound **3**. There are also Bragg peaks at a low angle around ~ 5 ° in the spectra for the complexes.

CONCLUSION

Four cyclic aza-ether compounds were synthesized. When used as additives, they significantly increase the ionic conductivity of THF solutions containing lithium halide salts. The effect on ionic conductivity of these new cyclic compounds is due to the formation of complexes with anions, which dissociate the ion-pairs. The degree of complexation depends on both the ring structure of the cyclic compounds and soft-hard base-acid characteristic of the halide anions. The crystal samples grown from co-solutions of compound **3** and lithium halide salts have different XRD patterns from the pure cyclic compound and the pure salts. This is direct evidence for the formation of complex between the cyclic compound and the lithium salts. The unique crystal formation property of compound **3** is related to the highly symmetric structure of this compound.

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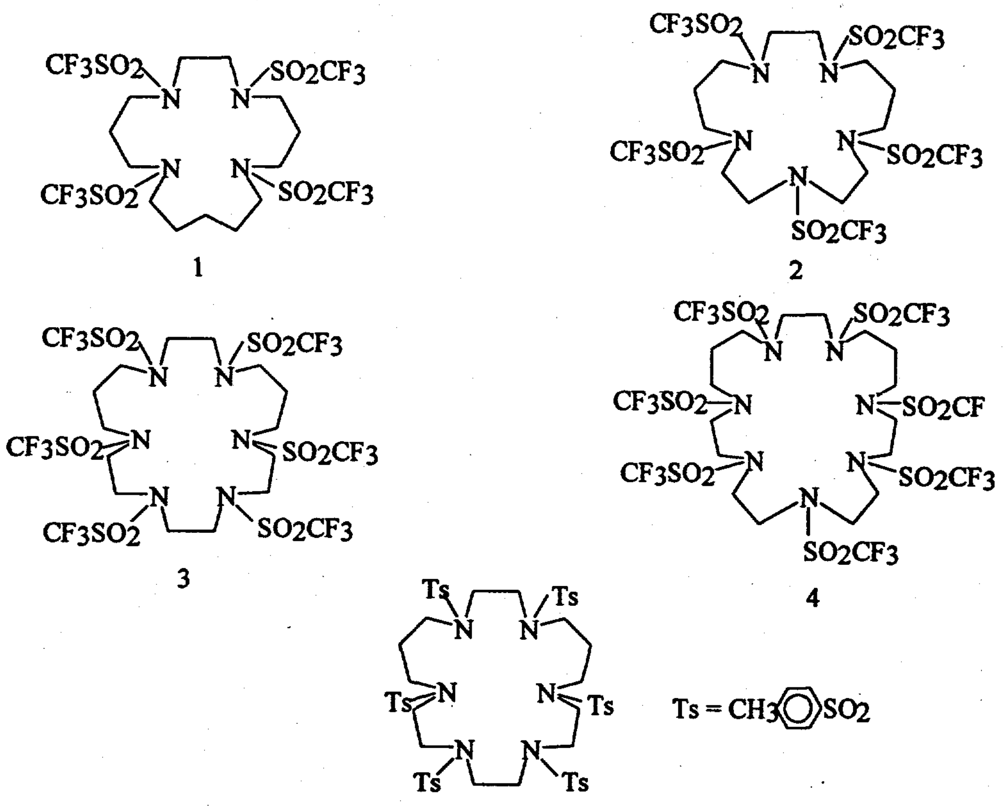
Table I. The ionic conductivity of 0.1 M lithium halide salts with cyclic aza-ether compounds as additive (molar ratio 1:1) in THF solution at 25 °C.

	Conductivity (S cm^{-1})		
Anion receptor	LiI	LiBr	LiCl
Salt only	2.45×10^{-4}	2.91×10^{-5}	7.50×10^{-6}
1	1.20×10^{-3}	6.57×10^{-4}	2.99×10^{-4}
2	1.50×10^{-3}	1.17×10^{-3}	5.90×10^{-4}
3	---[a]	1.81×10^{-3}	1.57×10^{-3}
4	1.63×10^{-3}	1.73×10^{-3}	1.54×10^{-3}
5	3.05×10^{-4}	7.75×10^{-5}	1.62×10^{-5}

[a] Crystals rapidly grow from the solution.

Table II. The effect of ligand-to-salt ratios on the ionic conductivity of 0.025M lithium halides with cyclic aza-ether compounds as additive in THF solution at 25°C.

	Ratio	Conductivity (S cm^{-1})	
Anion receptors	ligand: Salts	LiI	LiCl
1	1:1	2.19×10^{-4}	4.94×10^{-5}
	2:1	2.65×10^{-4}	1.22×10^{-4}
	3:1	---	3.26×10^{-4}
2	1:1	3.77×10^{-4}	1.44×10^{-4}
	2:1	3.67×10^{-4}	2.55×10^{-4}
	3:1	---	3.26×10^{-4}
3	1:1	5.71×10^{-4}	4.82×10^{-4}
	2:1	5.34×10^{-4}	5.08×10^{-4}
	3:1	---	5.15×10^{-4}
4	1:1	5.36×10^{-4}	5.41×10^{-4}
	2:1	5.47×10^{-4}	4.97×10^{-4}
	3:1	---	5.15×10^{-4}



1

2

3

4

5

Figure 1 Chemical structure of cyclic aza-ether anion receptors. The number under each structure corresponds to the compound number used in text.

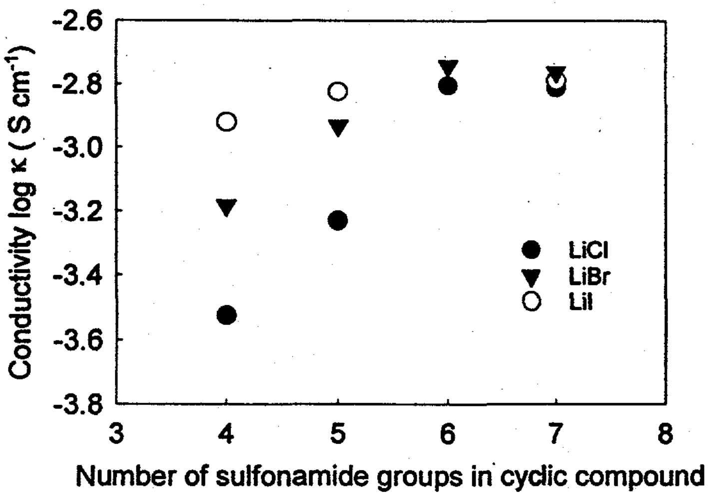


Figure 2 Relationship between number of sulfonamide group within cyclic aza-ether compounds and the ionic conductivity of THF solutions containing 0.1 M LiCl, LiBr and LiI with cyclic compounds 1 to 4 as additives

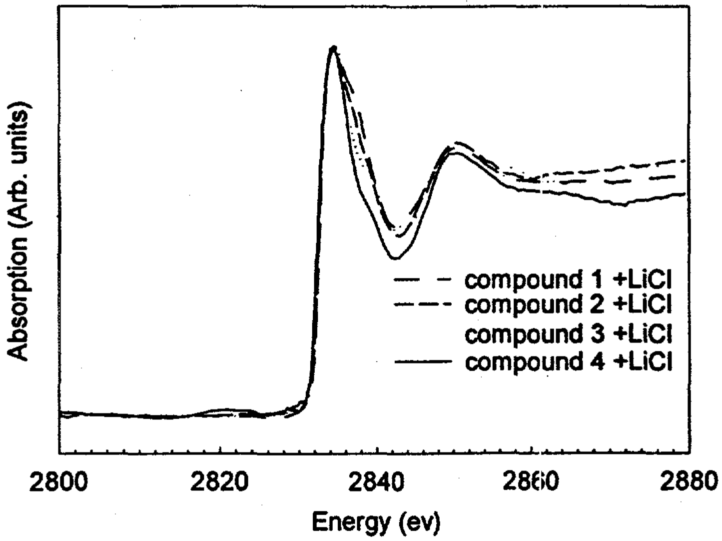


Figure 3 Near-edge x-ray absorption spectra at the K edge of chlorine for 0.2 M LiCl and 0.2 M compounds **1** to **4** in THF solutions.

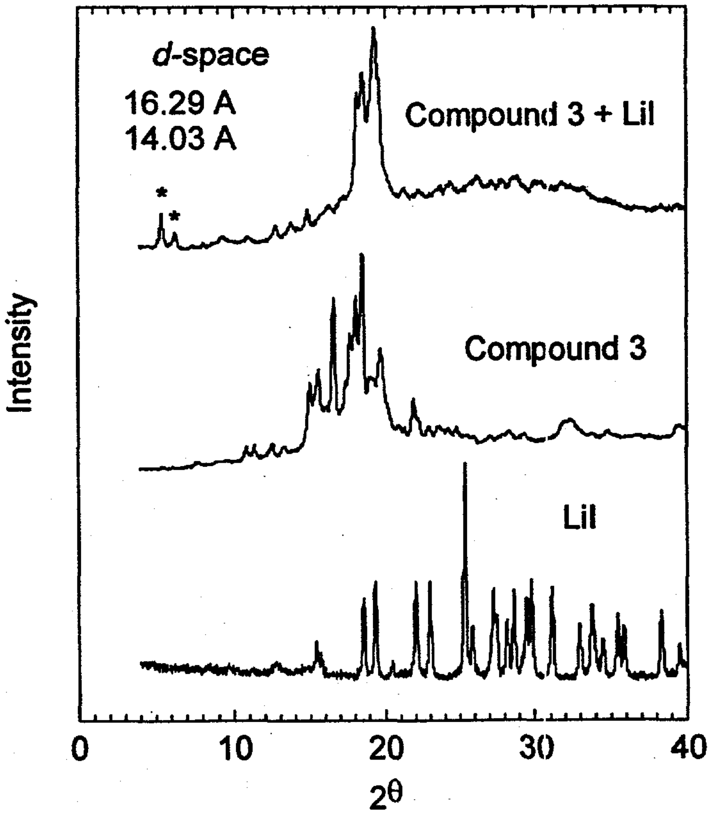


Figure 4 X-ray powder diffraction spectra of pure compound **3**, LiI and crystals obtained from the DME solution containing compound **3** and LiI.

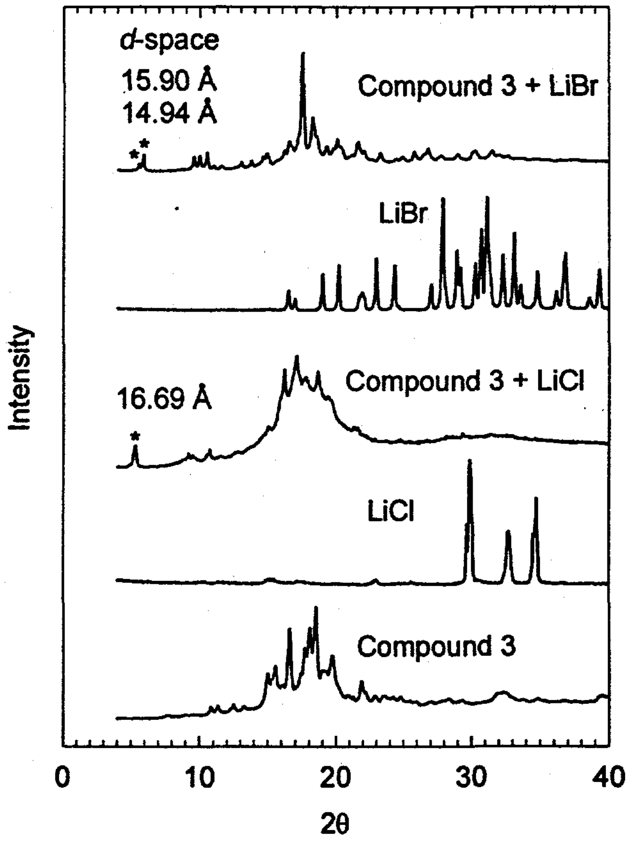


Figure 5 X-ray powder diffraction spectra of pure compound **3**, LiCl, LiBr and crystals obtained from the DME solutions containing compound **3** and LiCl or LiBr.