A Comparison of Local Structures in Crystalline $P(EO)_3LiCF_3SO_3$ and Glyme-$LiCF_3SO_3$ Systems

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Summary: The newly discovered crystal structures of $CH_3(OCH_2CH_2)OCH_3(LiCF_3SO_3)_2$, monoglyme:$(LiTf)_2$, and $CH_3(OCH_2CH_2)_3OCH_3(LiCF_3SO_3)_2$, triglyme:$(LiTf)_2$, are briefly described. The coordination of lithium cations and the $CF_3SO_3^-$ anions in these structures is compared with the cation and anion coordination in the crystalline phase of high molecular weight $P(EO)_3LiCF_3SO_3$. Comparison is also made with the previously reported crystalline phase of $CH_3(OCH_2CH_2)_2OCH_3LiCF_3SO_3$, diglyme:LiTf. A tendency to form trans-gauche-trans conformations for the bond order -O-C-C-O- is noted in adjacent ethylene oxide sequences interacting with a five-coordinate lithium ion.

Introduction

In 1973 Fenton et al. [1] noted that polyethers such as poly(ethylene oxide), PEO, could dissolve significant amounts of salts resulting in ion-conducting polymeric systems. This discovery almost immediately attracted worldwide attention because of the potential application of these materials as electrolytes in high energy density, rechargeable lithium batteries. In addition to their practical applications, PEO-salt systems are also of fundamental interest because a number of PEO-salt systems form crystalline compounds, some of whose crystal structures have been solved.[2-5] From these solved crystal structures it is easy to precisely determine the local structures present in the compounds. In this paper local structures are defined as: (1) the coordination of anions and cations, and (2) the local conformation of the polyether backbone accompanying cation-ether oxygen interactions. Local structures as defined here are important because they persist in the amorphous phases of polymer-salt systems [6, 7] where a significant contribution to ionic conductivity is thought to occur.[8, 9] More importantly these structures play

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a significant role in the mechanism of ionic transport. The interaction of the cation with the anion and the ether oxygen atoms defines the local potential energy environment of the cation, which, in turn, affects the dynamics of the cation. In systems where the anion contributes to the conductivity, the interaction of the anion with the cation also significantly affects the anion transport. In polymer electrolytes with flexible backbones, the segmental motion of the polymer appears to be coupled to the dynamics of ion transport. In such systems, the cation coordination to the polyether oxygen atoms has a profound effect on the polymer segmental motion as deduced from the increase in the glass transition temperature with increasing salt concentration.

Ethylene glycol dimethyl ethers (informally called "glymes") with the general formula $CH_3O(CH_2CH_2O)_nCH_3$ (usually $n \leq 6$) can be viewed as very short chain length, structural analogs of high molecular weight PEO, $-(CH_2CH_2O)_n-$. We adopt the common practice of designating the various glyme compounds $CH_3O(CH_2CH_2O)_nCH_3$ using the prefix "mono" for the n=1 compound (monoglyme), "di" for the n=2 compound (diglyme), etc. Solutions of salts dissolved in glymes have been used to experimentally and computationally model high molecular weight PEO-salt systems [10-12]. These modeling efforts have often focused on local structures as defined above, because such local structures also play an important role in the mechanism of ionic transport in glyme-salt systems.

We recently reported the crystal structure of the 1:1 compound of diethylene glycol dimethyl ether, $CH_3(OCH_2CH_2)_2OCH_3$, (diglyme) and lithium trifluoromethane sulfonate, $LiCF_3SO_3$, (referred to here as lithium triflate and abbreviated LiTf). [13] We noted striking similarities in the local structures of the 1:1 compound and the crystalline phase of high molecular weight $P(EO)_3LiTf$. Further studies led to useful insight into local structures in diglyme-LiTf solutions and the amorphous phase of high molecular weight PEO-LiTf systems. We have now succeeded in obtaining crystal structures of several other glyme-LiTf compounds using single crystal x-ray diffraction methods. Here preliminary data from that work are reported. We expect that these data will provide the background for a deeper understanding of local structures in high molecular weight, PEO-based, polymer-salt systems.

Experimental

Ethylene glycol dimethyl ether (99.9%, monoglyme), diethylene glycol dimethyl ether (99.5%, diglyme) and tri(ethylene glycol) dimethyl ether (99%, triglyme) were obtained from Aldrich and used as received. Lithium trifluoromethanesulfonate, $LiCF_3SO_3$, (99.995%) was obtained from Aldrich and heated under vacuum at 120ºC for 48 h prior to use. The reagents were stored and manipulated in a dry nitrogen glovebox (VAC, ≤ 1ppm H_2O). Solutions of monoglyme-LiTf, diglyme-LiTf, and triglyme-LiTf were prepared by dissolving LiTf directly in the liquids and stirring the solutions for 48 h at room temperature. The concentrations of the solutions, described by the ether oxygen:lithium cation ratios, were 2.5, 3:1, and 4:1 for the monoglyme-LiTf, diglyme-LiTf, and triglyme-LiTf respectively. After several weeks, an intermediate gel-like phase appeared which then produced a crystalline phase after a number of months. Single crystals specimens were isolated from the concentrated solutions.

X-ray diffraction data were collected at 173(2) K on a Siemens P4 diffractometer, using MoK (λ=0.71073 A) radiation. The data were corrected for Lorentz and polarization effects; an absorption correction was not applied since it was judged to be insignificant. The structure was solved by the direct method using the SHELXTL system, and refined by full-matrix least-squares on F using all reflections. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in the refinement with idealized parameters.

DSC thermograms were collected on a Mettler DSC 820 calorimeter under nitrogen purge in sealed aluminum crucibles. Samples were first cooled from 25°C to –100°C and then heated from -100°C to 50°C with a heating/cooling rate of 10 ^{o}C/min.

Results and Discussion

In this paper we focus on the cation and anion coordination in the monoglyme:$(LiTf)_2$, diglyme:LiTf and the triglyme:$(LiTf)_2$ crystals. These local structures are compared to the

coordination in high molecular weight $P(EO)_3LiTf$ compound as deduced from the crystal structure solution published by Lightfoot et al. [2] In all of these systems the lithium ions are coordinated by oxygen atoms from the ether backbone and the triflate anions, whereas the triflate anion is coordinated by the lithium cations. However there are some very interesting differences and similarities in the details of this coordination that are summarized in Table 1 and discussed in more detail below.

Table 1. Ionic coordination in the compounds of monoglyme, diglyme, and triglyme with $LiCF_3SO_3$ (LiTf). EO designates an ether oxygen atom and AO a triflate anion oxygen atom.

Compound	Space Gr.	Cation Coordination			Anion Coordination	
			EO	AO	Li(1)	Li(2)
Monoglyme)$(LiTf)_2$	$P\bar{1}$		1	3	3	
(Diglyme)(LiTf)	$P2_1/c$		3	2	2	
(Triglyme)$(LiTf)_2$	$P\bar{1}$	Li(1)	0	4	1	2
		Li(2)	3	2		
$P(EO)_3LiTf$	$P2_1/c$		3		2	

Monoglyme:$(LiTf)_2$. There appear to be at least two crystalline phases in the monoglyme-LiTf system, an α phase stable below -3°C and a β phase stable from -3 to at least 50°C. Details of the structures will be presented in a further publication in progress. Here we discuss the α phase, which crystallizes in the triclinic $P\bar{1}$ space group with the formula $[CH_3(OCH_2CH_2)OCH_3][LiCF_3SO_3]_2$ or monoglyme:$(LiTf)_2$. As illustrated in Figure 1 and summarized in Table 1, each lithium ion is four-fold coordinated to three oxygen atoms from three different triflate anions and one ether oxygen atom from a monoglyme molecule. The two ether oxygen atoms in a monoglyme molecule each interact with a different lithium ion. Each oxygen atom of a triflate ion is monodentate coordinated to a different lithium ion.

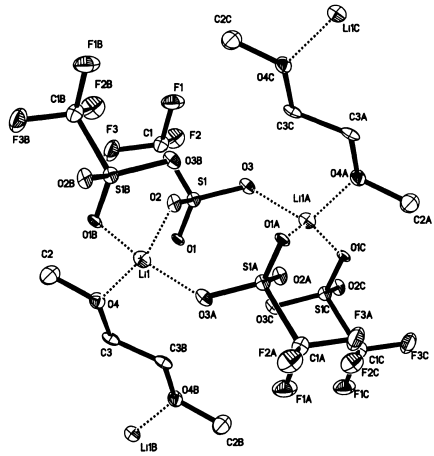

Figure 1. Diagram of the partial crystal structure of (monoglyme)$(LiTf)_2$ showing the coordinative interactions of the cations with both the anions and the ether oxygen atoms of the monoglyme molecule. Although each triflate anion interacts with three lithium ions in a monodentate fashion, most of these interactions have been suppressed for sake of clarity.

An important description of local structure is the conformation of the ethylene oxide backbone. This is summarized in Table 2 for all of the compounds discussed in this paper. The conformation is described by the dihedral angles for the bond sequence -O-C-C-O-, e.g. in the monoglyme:$(LiTf)_2$ compound the conformation is trans-trans-trans, or ttt. In the table, gauche (g) designates an angle between 30° and 90 °, gauche minus ($\bar{g}$) is an angle between -30° and -90°, and trans (t) describes an angle between 150° and 210°. Table 2 also gives pairs of lithium ion-ether oxygen bond distances for two oxygen atoms separated by a CH_2CH_2 spacer, and values of the O-C-C-O angle between the two oxygen atoms. In all other glyme-LiTf crystals studied to date and in the $P(EO)_3LiTf$ compound, the conformation about the C-C bond is gauche, in contrast to the trans angle measured in monoglyme:$([LiTf)_2$. This unusual conformation may result from the particular nature of the lithium ion coordination. A lithium ion interacts with three oxygen atoms from three different triflate ions. Therefore steric hindrance allows only one additional oxygen atom from a monoglyme molecule to interact with the lithium ion, resulting in a four-fold cation coordination. In order for the second oxygen atom of a

monoglyme molecule to participate in a similar coordination with another lithium ion, the monoglyme molecule adopts a ttt configuration.

Table 2. Lithium-oxygen distances and local backbone conformation.

Compound	n	Li-O_n	Li-O_{n+1}	-O_n-C-C-O_{n+1}-	Conf.
$P(EO)_3LiCF_3SO_3$	1	2.38	1.72	70.3	tgt
	2	1.72	2.01	-44.1	tg't
	3	2.01	2.38 [a]	64.3	tgt
Monoglyme-$LiCF_3SO_3$	1	1.866	1.866 [b]	180	ttt
Diglyme(I)-$LiCF_3SO_3$	1	2.166	2.044	56.2	tgt
	2	2.044	2.113	-55.3	tg't
	3	2.113			
Diglyme(II)-$LiCF_3SO_3$	1	2.105	2.075	50.1	tgt
	2	2.075	2.105	-54.3	tg't
	3	2.105			
Triglyme$(LiCF_3SO_3)_2$	1		2.019	-74.4	tg'g
	2	2.019	2.087	52.5	tgt
	3	2.087	2.049	-55.9	tg't

a) O_4 is symmetrically equivalent to O_1.
b) Symmetrically equivalent but different lithium ions.

Diglyme:LiTf. As reported previously, [13] the 1:1 compound of diglyme-LiTf crystallizes in the monoclinic $P2_1/c$ space group with a unit cell containing four dimers, two of which are identical and slightly different in structure from the other identical pair. Each dimer contains two triflate ions, two lithium ions, and two diglyme molecules with the positions of each chemically equivalent pair related by a crystallographically imposed center of symmetry. Each lithium ion is five-fold coordinate to three oxygen atoms of a diglyme molecule and two triflate oxygen atoms, one from each of the two triflate ions in the dimer. The two triflate anions then link the two lithium ions together to form the dimeric structural unit. These coordination data are shown in Figure 2 and summarized in Table 1.

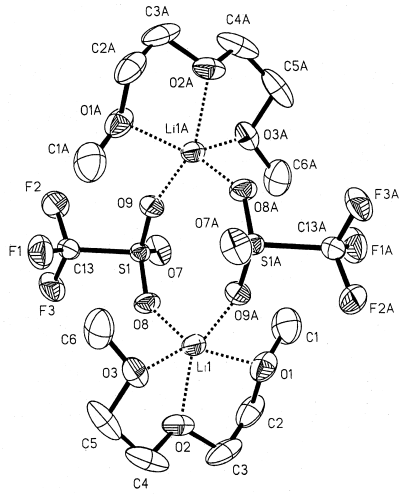

Figure 2. Diagram of a dimeric unit in the (diglyme)(LiTf) crystal structure showing the coordinative interactions of the cations with both the anions and the ether oxygen atoms of the diglyme molecule. A version of this diagram has been previously published and is included here for sake of completeness.

We have previously commented on the striking similarities in both cation coordination and anion coordination between the diglyme-LiTf compound and the high molecular weight $P(EO)_3LiTf$ compound.[13] It is also useful here to call attention to the similarity in the backbone conformation sequence as shown in Table 2, a pattern which will be repeated in the triglyme-LiTf structure described below.

Triglyme:$(LiTf)_2$. The compound triglyme:$(LiTf)_2$ crystallizes in the $P\bar{1}$ space group forming polymeric chains along the c axis. The onset of melting occurs around 30°C with the peak of the melting transition at 43 °C. The coordination of the lithium cations is quite unusual, with both five-fold coordinate and four-fold coordinate lithium ions in the unit cell. The five-fold coordinate lithium ions interact with three ether oxygen atoms and two triflate oxygen atoms. However the four-fold coordinate lithium ions interacts only with triflate oxygen atoms, one from each of four triflate ions. The coordination of the triflate ion is also somewhat complicated. Here each triflate ion interacts with a total of three lithium ions in a monodentate fashion. Two of these are four-fold lithium ions and the third is a five-fold lithium ion. Figure 3 shows the

pattern of coordination for this structure, with additional structural data summarized in Tables 1 and 2.

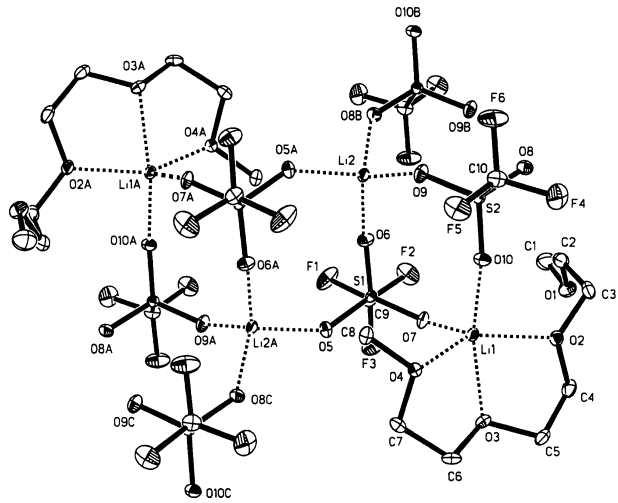

Figure 3. Diagram of the partial crystal structure of (triglyme)$(LiTf)_2$ showing the coordinative interactions of the cations with both the anions and the ether oxygen atoms of the triglyme molecule. Although each triflate anion interacts with three lithium ions in a monodentate fashion, some of these interactions have been suppressed for sake of clarity.

It is significant that although the triglyme molecule has four ether oxygen atoms available for coordination of lithium ions, only three oxygen atoms from adjacent ethylene oxide units interact with a lithium ion, leaving the fourth triglyme oxygen atom free. As noted above, this lithium ion also interacts with two triflate oxygen atoms, one from each of two triflate ions. This is the same local structure observed in the crystalline high molecular weight $P(EO)_3LiTf$ compound.

Conclusions

In the three glyme-LiTf crystal structures examined here, there are several interesting trends. Because the oxygen atoms from the triflate anions and the glyme backbone can coordinate the lithium ions, the resulting crystal structures reflect the relative strengths of these competing interactions, mediated by solid state packing effects. In all of these structures the triflate anions are monodentate coordinated by either two or three lithium cations. When all triflate anions are

two-fold coordinate as in the case of the diglyme-LiTf and $P(EO)_3LiTf$ structures, the lithium ions are five-fold coordinated. In the monoglyme-LiTf structure, all triflate anions are three-fold coordinated and the lithium ions are four-fold coordinated. Although the triflate ions are also three-fold coordinated in the triglyme:$(LiTf)_2$ structure, there are both four-fold and five-fold lithium ions. These five-fold coordinated lithium ions in triglyme:$(LiTf)_2$ are also coordinated by three ether oxygen atoms from adjacent ethylene oxide units in the triglyme molecule. This is the same pattern of backbone coordination found in the diglyme:LiTf and $P(EO)_3LiTf$ structures, which also have five-fold coordinated lithium ions. Finally we note that the coordination of a lithium ion by three ether oxygen atoms from adjacent ethylene oxide units in the systems discussed here seems to be facilitated by a triad of -O-C-C-O-units involving gauche conformations about the C-C bonds and primarily trans conformations about the C-O bonds.

Acknowledgements

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