# Li$^+$−(Diglyme)$_2$ and LiClO$_4$−Diglyme Complexes: Barriers to Lithium Ion Migration

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**Abstract:** The lithium ion migration mechanism in Li$^+$−(diglyme)$_2$ and LiClO$_4$−diglyme complexes with coordination of Li$^+$ by 3 to 6 oxygens has been investigated using ab initio molecular orbital theory. Local minima corresponding to different coordination sites of the Li$^+$ cation and transition states between them have been located. The Li$^+$ binding energies of the Li$^+$−(diglyme)$_2$ and LiClO$_4$−diglyme complexes range from 94 to 122 and 167 to 188 kcal/mol, respectively. The binding energies increase with increasing coordination of Li$^+$ by oxygen, although the binding per Li−O bond decreases, and structures with higher coordination of Li$^+$ by oxygen exhibit longer Li−O bond lengths than the ones with lower coordination number. The barrier heights for $n + 1 \rightarrow n$ coordination of the cation by oxygen decrease with increasing coordination number $n$, with the smallest Li$^+$ migration barriers (7−11 kcal/mol) occurring for complexes with the highest coordination numbers. The reaction coordinate for lithium ion migration between coordination sites is the torsional motion of the diglyme backbone. The implications of these results for Li$^+$ migration in lithium poly(ethylene oxide) melts are discussed.

## 1. Introduction

There has been much interest in lithium polymer electrolyte studies for their potential applications in secondary battery systems, fuel cells, and other electrochemical devices. Polymer electrolytes[1,2] are generally composites of a poly(ethylene oxide) or another modified polyether and a salt such as LiCF$_3$SO$_3$, Li(CF$_3$SO$_2$)$_2$N, Li(CF$_3$SO$_2$)$_2$CH, LiClO$_4$, LiPF$_6$, and LiAsF$_6$. The ion−polymer and ion−ion interactions in these materials play an important role in their ionic conductivity. However, little is known about the role of these interactions, the nature of the charge carriers, and the ionic association process in the ionic conductivity of the electrolytes.

Recently, there have been a number of theoretical studies[3−16] aimed at characterizing the ion−polymer and ion−ion interactions in poly(ethylene oxide) (PEO) based polymer electrolytes. Sutjianto and Curtiss[3] have studied the migration barriers for the lithium cation along a single PEO chain modeled by diglyme [CH$_3$(OCH$_2$CH$_2$)$_2$OCH$_3$]. They fully optimized equilibrium structures and transition states at the HF/6-31G(d) level of theory followed by single-point calculations at the MP2/6-31G(d) level. They found significant barriers (20−27 kcal/mol) for lithium migration between monodentate, bidentate, and tridentate coordination. Lindgren et al.[4] reported calculations on lithium ion migration barriers using tetraglyme and triglyme as models for PEO at the HF/6-31G(d,p) level with single-point calculations at the MP2/6-311+G(d,p) level of theory. They reported transition states for tridentate-to-bidentate coordination and tetradentate-to-tridentate coordination and found barriers of 23 and 20 kcal/mol, respectively. Palma et al.[5] used ab initio molecular dynamics with Perdew−Wang generalized approximation density functional theory to study migration of Li$^+$ along a single PEO chain model by (CH$_2$−CH$_2$−O)$_n$, for $n = 6$, 8, 10, and 20. They found energy barrier heights of 8.5 and 9.7 kcal/mol, but did not report the coordination numbers. Halley and co-workers[6] studied the lithium ion transport in amorphous polyethylene by molecular dynamics simulations.

Numerous experiments have been carried out to understand the transport mechanisms in polymer and gel electrolytes.[17] Every et al.[18] studied the lithium ion mobility in polymer electrolytes by $^7$Li NMR spectroscopy. They concluded that a possible mechanism for lithium ion motion could be hopping of the lithium cation. They added that the ionic motion might be assisted by a secondary polymer relaxation as an alternative

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mechanism. Reiche and co-workers[19] studied the cationic transport in gel electrolyte films by photoinitiated polymerization of oligo(ethylene glycol) dimethacrylate. They found that the charge carrier transport could be enhanced by the ability of the plasticizer to compete with the polymer to coordinate with the cation. They concluded that the reducing ability of the polymer to coordinate with the cation enhances the charge carrier transport if the plasticizer has a better ability to coordinate the cation.

Spectroscopic investigations have been reported of the conformations of PEO oligomers (glymes),[20−22] $CH_3(OCH_2$-$CH_2)_nOCH_3$ for $n = 1, 2, 3$, and 6, and of PEO oligomers complexed with metal salts.[23,24] Lightfoot, Mehta, and Bruce[25] have reported a crystal structure of $(PEO)_3$:$LiCF_3SO_3$ that indicates no links between PEO chains. They added that the coordination of $Li^+$ cation is with both anion and PEO oxygens. The structure of the amorphous phase is not known.

In this paper we report an ab initio molecular orbital study of the potential energy surface for the interaction of a single $Li^+$ cation with two diglymes as a model for two PEO chains. We are not aware of any theoretical investigations of migration barriers for two chains, which is probably more realistic than one chain since in the amorphous phase it is most likely that the cation is coordinated by two or more chains. The second part of this paper is devoted to a study of the potential energy surfaces of interactions of the $LiClO_4$ ion-pair with PEO modeled by diglyme. We are not aware of any ab inito investigations on this subject. Ion-pairing in polymer electrolytes is a significant factor in the conducting properties of polymer electrolytes.[1] Thus, it is of interest to learn how ion-pair formation affects the interaction of the cation with the polymer and the cation migration barrier. In both parts of this study, local minima and transition states between them have been located. We are particularly interested in the dependence of the barrier heights for lithium migration on the coordination of the cation.

## 2. Theoretical Methods

The geometries of $Li^-$-(diglyme)$_2$ and $LiClO_4$−diglyme have been fully optimized at the HF/6-31G(d) level using redundant internal coordinates.[26] Various configurations having different coordination of the $Li^+$ with the diglyme oxygens were investigated. There may be many local minima due to the large numbers of diglyme conformers;[15] we have considered a limited number of possibilities. The transition states between different coordination sites were also optimized at this same level of theory. Vibrational frequencies using analytical second derivatives[27] were calculated for all local minima and transition states at the HF/6-31G(d) level of theory. The transition state structures had one imaginary frequency and the equilibrium structures had all positive frequencies. The binding energies are defined relative to the all-trans diglyme conformer. In addition, single-point calculations were done at the MP2/6-31+G(d)//HF/6-31G(d) level for the $LiClO_4$−diglyme structures and transition states.


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**Table 1.** Coordination Numbers, Li−O Bond Distances (Å), and Binding Energies (kcal/mol) in $Li^+$−Diglyme and $Li^+$−(Diglyme)$_2$ Complexes[a]

| chain | coord no. | host structure | | Li−O′ | $\Delta E_e$ |
|---|---|---|---|---|---|
| 1 | 1[b] | | $t^3g^-g^+t$ | 1.839 | 44.0 |
| | 2[b] | | $tg^+tg^-g^+t$ | 1.875, 1.866 | 68.8 |
| | 3[b] | | $tg^-t^2g^+t$ | 1.917, 1.938 | 87.1 |
| | | | | 1.933 | |
| | 4[b,c] | | $tg^+t^2g^-t^2g^+t$ | 2.006, 2.015 | 103.0 |
| | | | | 2.014, 2.007 | |
| | 5[d] | | $tg^+g^+g^-g^-t^2g^+t^2g^-t$ | 2.064, 2.084 | 110.2 |
| | | | | 2.055, 2.079 | |
| | | | | 2.020 | |
| 2 | 3[e] | Min-**1** | $t^6$ | 1.911 | 94.1 |
| | | | $tg^+g^-tg^+t$ | 1.915, 1.922 | |
| | 4[e] | Min-**2** | $tgt^4$ | 1.969, 1.999 | 110.1 |
| | | | $tg^+g^-tg^+t$ | 1.967, 1.968 | |
| | | Min-**3** | $tgt^4$ | 1.968, 1.995 | 107.6 |
| | | | $tgt^4$ | 1.981, 1.968 | |
| | 5[e] | Min-**4** | $tgt^4$ | 2.033, 2.094 | 115.3 |
| | | | $tg^+g^+tg^+t$ | 2.160, 2.084 | |
| | | | | 2.151 | |
| | | Min-**5** | $tgt^4$ | 2.005, 2.115 | 114.4 |
| | | | $tg^+t^2g^-t$ | 2.137, 2.102 | |
| | | | | 2.111 | |
| | 6[e] | Min-**6** | $tg^-t^2g^+t$ | 2.232, 2.114 | 121.5 |
| | | | $tg^-t^2g^+t$ | 2.228, 2.231 | |
| | | | | 2.113, 2.228 | |

[a] HF/6-31G(d) binding energies relative to $Li^+$ and one or two diglymes in the $t^6$ configuration. [b] From ref 3. In each case the results for the most stable structure that was located are listed. [c] From $Li^+$−triglyme complex (ref 3). Binding energy is relative to $Li^+$ and triglyme in the $t^6$ configuration. [d] This work. From $Li^+$−tetraglyme complex. Binding energy is relative to $Li^+$ and tetraglyme in the $t^6$ configuration. [e] Structures shown in Figure 1.

The conformers of diglyme in the complexes are denoted by combinations of *t* and *g*, where *t* refers to a trans arrangement of a four-atom segment with a backbone dihedral angle between 160° and 180°, while *g* refers to a gauche arrangement with dihedral angle between 50° and 90°. All calculations were performed with the GAUSSIAN 94[28] series of programs.

## 3. Results and Discussion

**A. Equilibrim Structures for $Li^+$−(Diglyme)$_2$.** Six different local minima were located for $Li^+$ interacting with two diglymes at the HF/6-31G(d) level. These minima corresponded to structures having coordination of the cation by three to six oxygens from the two diglymes. The binding energies and Li−O bond distances of these structures are listed in Table 1. The binding energies and Li−O distances of the most stable structures for interaction of $Li^+$ cation with a single diglyme from ref 3 are also included in the table for comparison. The structures of the $Li^+$−(diglyme)$_2$ complexes are illustrated in Figure 1.

**(a) Three-Coordination.** The Min-**1** ($t^6$, $tg^+g^-tg^+t$) structure has the lithium cation coordinated by three oxygens from the two diglyme chains. The lithium cation is two-coordinated to one chain and one-coordinated to the other. The total dissociation energy [$Li^+$−(diglyme)$_2 \rightarrow Li^+ + 2$(diglyme)] is 94.1 kcal/mol and the Li−O bond distances are in the range of 1.91−1.92 Å.


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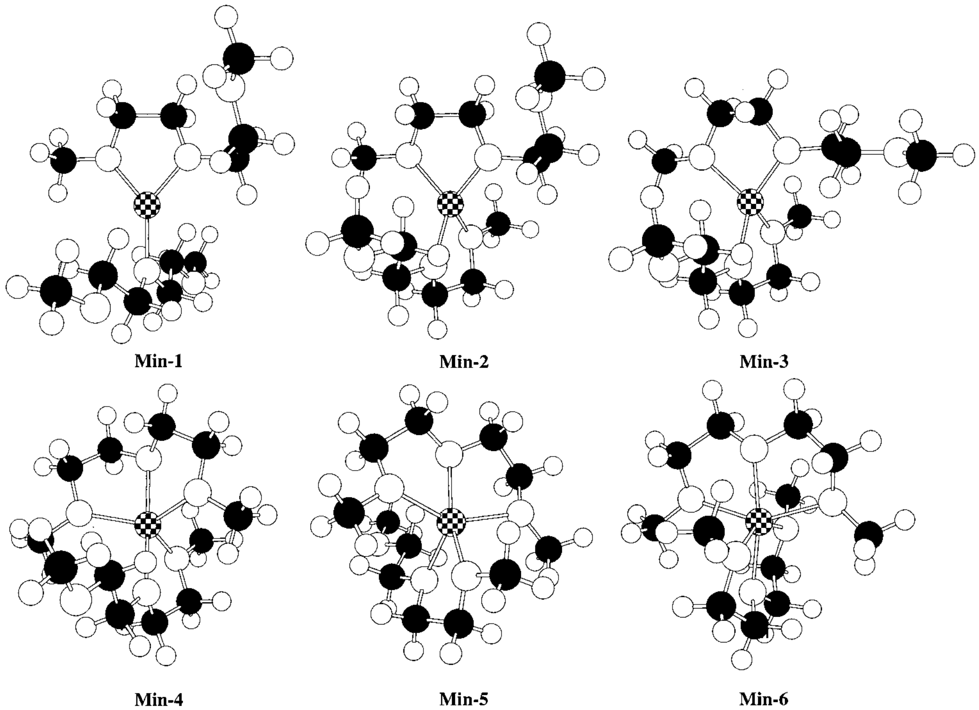


**Figure 1.** Illustration of the structures of $Li^+$−(diglyme)$_2$ complexes optimized at the HF/6-31G(d) level.

**(b) Four-Coordination.** The Min-**2** ($tgt^4$, $tg^+g^-tg^+t$) and Min-**3** ($tgt^4$, $tgt^4$) structures have the lithium cation coordinated by four oxygens from the two diglyme chains. In both structures the lithium cation is two-coordinated to one chain and two-coordinated to the other in a spirane-type structure. The total dissociation energies for these two local minima are 110.1 and 107.6 kcal/mol, respectively, and the Li−O bond distances are in the range of 1.97−2.00 Å.

**(c) Five-Coordination.** The Min-**4** ($tgt^4$, $tg^+g^+tg^+t$) and Min-**5** ($tgt^4$, $tg^+t^2g^-t$) structures have the lithium cation coordinated by five oxygens from the two diglyme chains. In both structures the lithium cation is three-coordinated to one chain and two-coordinated to the other. The total dissociation energies for these two local minima are 115.3 and 114.4 kcal/mol, respectively, and the Li−O distances are in the range of 2.01−2.16 Å. There are only small differences in the Li−O bond distances between both structures.

**(d) Six-Coordination.** Min-**6** is the most stable of all of the $Li^+$−(diglyme)$_2$ structures considered in this study. It has six-coordination around the lithium cation with three-coordination from each diglyme chain. Both chains have a ($tg^-t^2g^+t$) configuration. The Min-**6** structure has the two diglymes perpendicular to each other and connected through the lithium cation (see Figure 1). The total dissociation energy of Min-**6** is 121.5 kcal/mol and the Li−O bond distances are in the range of 2.11−2.23 Å. They are longer than the Li−O bond distance in the single-coordinated $Li^+$−diglyme structure by 0.3−0.4 Å. (see Table 1).

The binding energies for the most stable $Li^+$−diglyme[3] and $Li^+$−(diglyme)$_2$ structures that we have located are plotted in Figure 2 as a function of coordination number. The binding energies tend to level off as the coordination number approaches six, i.e., the increase in binding decreases as the coordination number increases. The binding energies are in the range of 94.1−121.5 kcal/mol for two chain complexes with three to six-coordination around the lithium atom and from 44.0 to 110.0 kcal/mol for one- to five-coordination for the one-chain complexes. The binding energies per single Li−O bond are given in Table 2. The results indicate that the decrease in binding per Li−O bond in the complexes having two chains is similar to that in the complexes having one chain. In the one-diglyme

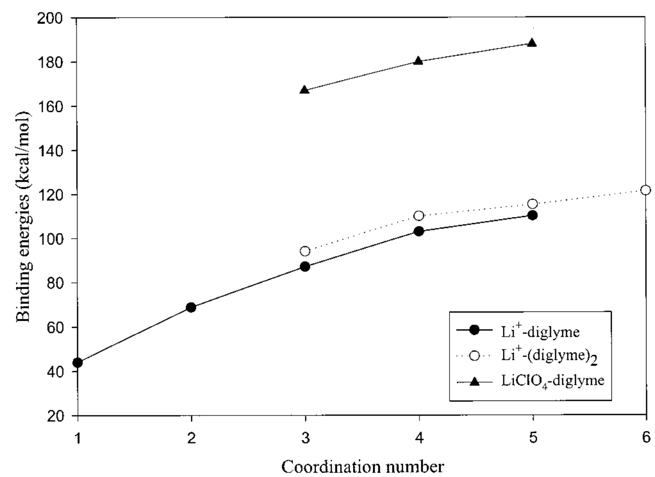


**Figure 2.** Binding energy vs coordination number for $Li^+$−diglyme, $Li^+$−(diglyme)$_2$, and $LiClO_4$−diglyme complexes (the binding energy is the energy required to remove $Li^+$ from the complex, see Tables 2 and 3).

**Table 2.** The Binding Energies (in kcal/mol) per Li−O Bond in the $Li^+$−Diglyme, $Li^+$−(Diglyme)$_2$, and $LiClO_4$−Diglyme Complexes[a]

| coord no. | $Li^+$−diglyme | $Li^+$−(diglyme)$_2$ | $LiClO_4$−diglyme[b] |
|---|---|---|---|
| 1 | 44.0[c] | | |
| 2 | 34.3[c] | | |
| 3 | 29.0[c] | 31.4 | 55.7 |
| 4 | 25.8[d] | 27.5 | 45.1 |
| 5 | 22.0[e] | 23.1 | 37.6 |
| 6 | | 20.3 | |

[a] HF/6-31G(d) binding energies relative to $Li^+$ and one or two diglymes in the $t^6$ configuration. In each case the results for the most stable structure that was located is listed. [b] In all of these structures the lithium is doubly coordinated to the $ClO_4^-$ anion. [c] From ref 3. [d] From $Li^+$−triglyme complex (ref 3). [e] From $Li^+$−tetraglyme complex.

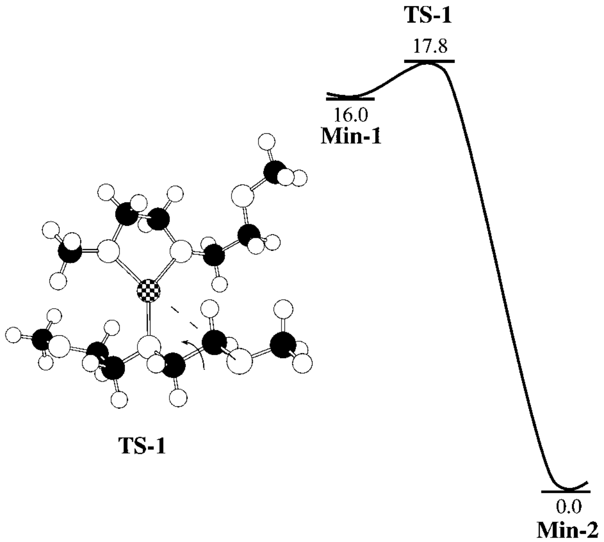


**Figure 3.** Pathway I for migration of $Li^+$ cation between three- and four-coordination sites of the $Li^+$−(diglyme)$_2$ complex. The values represent the HF/6-31G(d) relative energies (kcal/mol) and the structures of the local minima are given in Figure 1.

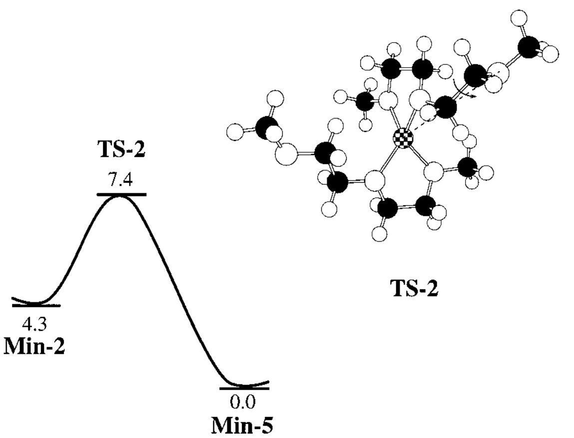


**Figure 4.** Pathway II for migration of $Li^+$ cation between four- and five-coordination sites of the $Li^+$−(diglyme)$_2$ complex. The values represent the HF/6-31G(d) relative energies (kcal/mol) and the structures of the local minimum are given in Figure 1.

structures the bond distances range from 1.84 to 2.08 Å while in the two-diglyme structures the distances range from 1.91 to 2.23 Å. Correlation effects were investigated for the binding energies in ref 3 at the MP2/6-31+G(d)//HF/6-31G(d) level and found to have little effect on the binding for the one-diglyme structures. Inclusion of correlation effects on the two-diglyme structures should have similarly small effects.

**B. Transition State Structures for $Li^+$−(Diglyme)$_2$.** We have investigated the potential energy surface of the $Li^+$−(diglyme)$_2$ complex to find the transition states between three- and four-coordination sites (pathway I) and between four- and five-coordination sites (pathway II). These pathways are models for $Li^+$ migration involving two PEO chains. Schematics of the potential energy surfaces for pathways I and II are shown in Figures 3 and 4, respectively.

**(a) Pathway I.** Pathway I contains a three-coordination local minimum (Min-**1**), a four-coordination local minimum (Min-**2**), and the transition state (TS-**1**) between them. The structures for the minima are shown in Figure 1 and the structure for the transition state is shown in Figure 3. The reaction coordinate corresponds to rotation about an OCCO dihedral angle that *makes* a fourth Li−O bond or *breaks* the fourth Li−O bond. At the barrier the dihedral angle OCCO is 132.8°. The barrier for three-coordination → four-coordination is 1.8 kcal/mol, while the barrier for four-coordination → three-coordination is 17.8 kcal/mol.

**(b) Pathway II**. Pathway II contains a four-coordination local minimum (Min-**2**), a five-coordination local minimum (Min-**5**), and the transition state (TS-**2**) between them. The structures for the minima are shown in Figure 1 and the structure for the transition state is shown in Figure 4. The reaction coordinate corresponds to rotation about an OCCO dihedral angle that *makes* a fifth Li−O bond or *breaks* the fifth Li−O bond. At the barrier the dihedral angle OCCO is 66.2°. The barrier for four-coordination → three-coordination is 3.1 kcal/mol, while the barrier for five-coordination → four-coordination is 7.4 kcal/mol. Hence, the forward barrier increases and the reverse barrier decreases compared to pathway I.

**C. Equilibrium Structures for $LiClO_4$−Diglyme.** Six different local minima were located for diglyme interacting with $LiClO_4$ at the HF/6-31G(d) level. The structures of the $LiClO_4$−diglyme complexes are illustrated in Figure 5. In each case the $LiClO_4$ was considered with a bidentate structure, i.e., the lithium cation is bound to two oxygens of $ClO_4^-$ anion as this is its most favorable bonding configuration. Some key bond distances such as the Li−O and Cl−O bonds, together with the binding energies, are given in Table 3. The O′ indicates the oxygen atom in the diglyme. The O″ and O‴ indicate the two distinct oxygen atoms in the $LiClO_4$, where the O″ is the one interacting with the lithium atom. The oxygen coordination numbers of the $Li^+$ in the $LiClO_4$−diglyme complexes are included in Table 3. The six local minima can be classified in terms of three different types of structures: single, double, and triple coordination of $LiClO_4$ to the diglyme. If the oxygens from $LiClO_4$ are included in the coordination, these minima correspond to three-, four-, and five-coordination, respectively.

**(a) Three-Coordination (One-Coordination to Diglyme).** Three different local minima were studied for three-coordination: Min-**7** ($t^6$-$LiClO_4$), Min-**8** ($t^3g^-g^+t$-$LiClO_4$), and Min-**9** ($tg^-g^+t^3$-$LiClO_4$). In all of these structures the $Li^+$ cation is coordinated to three oxygens since the $LiClO_4$ remains coordinated to two oxygens from the perchlorate anion. The total dissociation energies ($LiClO_4$−diglyme → $Li^+$ + $ClO_4^-$ + diglyme) of these structures are all close to 167 kcal/mol. In two of these structures, the $LiClO_4$ is attached to the one end of the diglyme and in a third it is attached to the center. The Li−O′ bond distances range from 1.89 to 1.90 Å in these structures (see Table 3).

**(b) Four-Coordination (Two-Coordination to Diglyme).** Two minima were studied for four-coordination: Min-**10** ($tg^-tg^+g^-t$-$LiClO_4$) and Min-**11** ($tg^+t^4$-$LiClO_4$). The Min-**10** structure is more stable than Min-**11** by less than 1 kcal/mol. In both structures, the $Li^+$ cation is in the center of a tetrahedral-type coordination. The total dissociation energies ($LiClO_4$−diglyme → $Li^+$ + $ClO_4^-$ + diglyme) of these structures are close to 180 kcal/mol. The $LiClO_4$ binding energies to the diglyme in Min-**10** and Min-**11** are 37.7 and 37.2 kcal/mol, respectively. Both binding energies are larger than for the three-coordination structures.

**(c) Five-Coordination (Three-Coordination to Diglyme).** The five-coordination structure Min-**12** ($tg^-t^2g^+t$-$LiClO_4$) is the most stable structure of the six $LiClO_4$−diglyme structures considered in this study. The total dissociation energy of this complex is 188.0 kcal/mol. The dissociation energy for $LiClO_4$−diglyme → $Li^+$−diglyme + $ClO_4^-$ is 100.8 kcal/mol, the

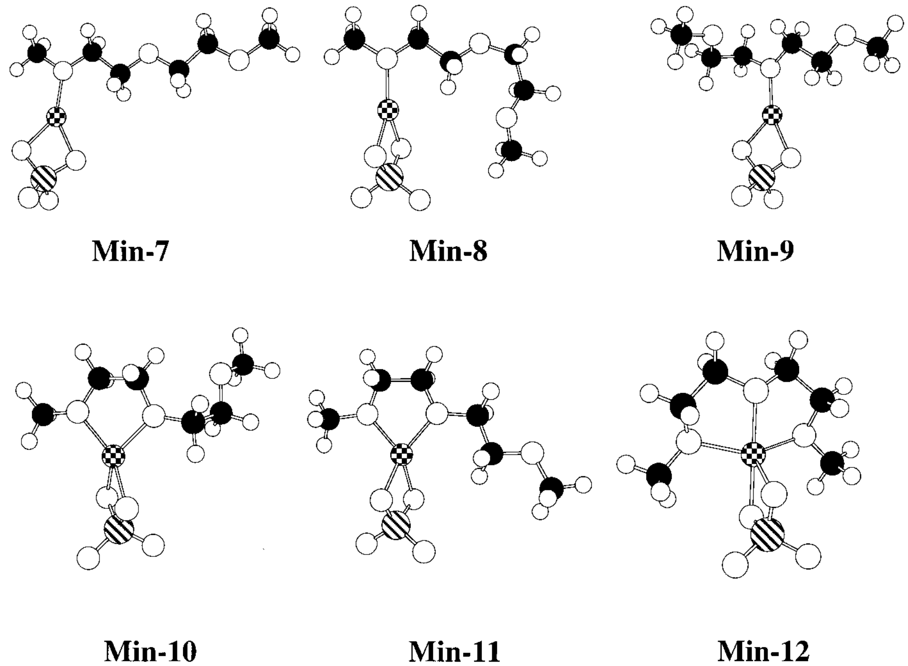


**Figure 5.** Illustration of the structures of $LiClO_4$−diglyme structures optimized at the HF/6-31G(d) level.

**Table 3.** Key Bond Distances (Å) and Binding Energies $\Delta E$ (kcal/mol) in the $LiClO_4$−Diglyme Structures[a]

| structure | oxygen coord | | bond distances[b] | | | | binding energies | | |
|---|---|---|---|---|---|---|---|---|---|
| | with diglyme | total | Li−O′ | Li−O″ | Cl−O″ | Cl−O‴ | $\Delta E_e$[c] | $\Delta E_e$[d] | $\Delta E_e$[e] |
| Min-**7** | 1 | 3 | 1.890 | 1.927 | 1.482 | 1.424 | 24.2 | 127.5 | 166.9 |
| $t^6$-$LiClO_4$ | | | | 1.927 | 1.482 | 1.424 | | | |
| Min-**8** | 1 | 3 | 1.902 | 1.935 | 1.480 | 1.425 | 24.2 | 122.8 | 166.9 |
| $t^3g^-g^+t$ -$LiClO_4$ | | | | 1.944 | 1.480 | 1.427 | | | |
| Min-**9** | 1 | 3 | 1.886 | 1.933 | 1.481 | 1.425 | 24.3 | 125.2 | 167.0 |
| $tg^-g^+t^3$-$LiClO_4$ | | | | 1.930 | 1.481 | 1.424 | | | |
| Min-**10** | 2 | 4 | 1.981 | 1.980 | 1.476 | 1.427 | 37.7 | 111.7 | 180.4 |
| $tg^-tg^+g^-$ -$LiClO_4$ | | | 1.955 | 1.983 | 1.476 | 1.429 | | | |
| Min-**11** | 2 | 4 | 1.962 | 1.982 | 1.476 | 1.427 | 37.2 | 113.9 | 179.9 |
| $tg^+t^4$-$LiClO_4$ | | | 1.982 | 1.975 | 1.477 | 1.429 | | | |
| Min-**12** | 3 | 5 | 2.079 | 2.065 | 1.472 | 1.431 | 45.3 | 100.8 | 188.0 |
| $tg^-t^2g^+t$ -$LiClO_4$ | | | 2.056 | 2.038 | 1.471 | 1.431 | | | |
| | | | 2.079 | | | | | | |

[a] Structures shown in Figure 5. Results are from HF/6-31G(d) optimizations. [b] Li−O′ is the bond between oxygen in the diglyme and the $Li^+$ cation, Li−O″ is the bond between the $Li^+$ cation and the oxygen in the anion $ClO_4^-$. Cl−O″ is the bond in $ClO_4^-$ containing the oxygen facing the diglyme and Cl−O‴ is the bond in $ClO_4^-$ containing the oxygen that is away from the diglyme. [c] Binding energy for diglyme−$LiClO_4$ → $LiClO_4$ + diglyme ($t^6$). [d] Binding energy for (diglyme)Li−$ClO_4$ → (diglyme)Li + $ClO_4^-$. [e] Binding energy for diglyme−Li−$ClO_4$ → diglyme ($t^6$) + $Li^+$ + $ClO_4^-$.

smallest of all optimized local minima, and the dissociation energy for diglyme-$LiClO_4$ → diglyme + $LiClO_4$ is 45.3 kcal/mol, the largest of all the optimized structures. This binding energy is smaller than the binding energy of $Li^+$−diglyme (three-coordination) by 41.8 kcal/mol. Thus, the presence of the anion weakens the $Li^+$−diglyme binding energy. The Li−O′ and Li−O″ bond distances range from 2.04 to 2.08 Å (Table 3) and are the longest of the optimized $LiClO_4$−diglyme structures. This structure resembles its parent structure, the triply coordinated $Li^+$−diglyme.[3] The Li−O′ bond distances are longer by ca. 0.15 Å in Min-**12** than in the $Li^+$−diglyme. The $O''_1$−Li−$O''_2$ plane is perpendicular to the $O'_1$−$O'_2$−$O'_3$ plane. The $O'_2$−Li−Cl angle is 142.7°, and the $O'_2$−Li−$O''_1$ and the $O'_2$−Li−$O''_2$ angles are 177.2° and 108.4°, respectively.

In the optimized $LiClO_4$−diglyme structures including the transitions states structures, the Li−O bond distances range from 1.89 to 2.08 Å (see Table 3) compared to 1.84 to 2.23 Å (see Table 1) for the $Li^+$−diglyme and $Li^+$−$(diglyme)_2$ complexes. Neutron diffraction studies[29] indicate the existence of a peak around 2.0 Å in lithium perchlorate−PEO melts. The calculated Li−O bond distances in the optimized $LiClO_4$−diglyme structures are in good accord with the experimental results. Lightfoot, Mehta, and Bruce[25] have reported crystal structures of $(PEO)_3$:$LiCF_3SO_3$ indicating that coordination of the $Li^+$ cation is with both the anion and PEO oxygens. Our optimized $LiClO_4$−diglyme structures are in agreement with their results.

The binding energies for the most stable $LiClO_4$−diglyme structures that we have located are plotted in Figure 2 as a function of coordination number. The binding energies are in the range of 167−188 kcal/mol and the increase in binding energy decreases as the coordination number increases (see Table 3). This is similar to the trend for $Li^+$−diglyme and $Li^+$−$(diglyme)_2$. The binding energies per single Li−O bond in $LiClO_4$−diglyme are given in Table 2. The average binding per Li−O bond is 55.7, 45.1, and 37.6 kcal/mol in the most stable

(29) Baboul, A. G.; Curtiss, L. A.; Saboungi, M. L.; Ansell, S.; Mao, G.; Price, D. L. *Proceedings of the Eleventh Molten Salts Symposium*. *Electrochem. Soc.* **1998**, *98−11*, 341.

**Table 4.** The Key Bond Distances (Å) in the Lithium Perchlorate Diglyme Transition States[a]

| | oxygen coord | | bond distances[b] | | | |
|---|---|---|---|---|---|---|
| structure | with digylme | total | Li−O′ | Li−O″ | Cl−O″ | Cl−O‴ |
| TS-**3** | 1 | 3 | 1.893 | 1.930 | 1.481 | 1.425 |
| $t^3$-LiClO$_4$ | | | | 1.929 | 1.481 | 1.425 |
| TS-**4** | 1 | 3 | 1.874 | 1.931 | 1.489 | 1.423 |
| $tg^-g^+t^3$-LiClO$_4$ | | | | 1.931 | 1.480 | 1.425 |
| TS-**5** | 2 | 4 | 1.964 | 1.983 | 1.977 | 1.989 |
| $tg^-t^2g^+t$-LiClO$_4$ | | | | | | |

[a] Structures shown in Figure 5. Results are from HF/6-31G(d) optimizations. [b] Li−O′ is the bond between oxygen in the diglyme and the Li$^+$ cation, Li−O″ is the bond between the Li$^+$ cation with the oxygen in the anion ClO$_4^-$. Cl−O″ is the bond in ClO$_4^-$ containing the oxygen facing the diglyme, and Cl−O‴ is the bond in ClO$_4^-$ containing the oxygen that is away from the diglyme.

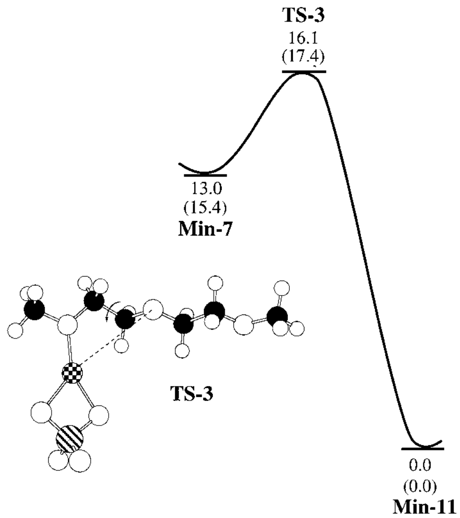


**Figure 6.** Pathway III for migration of Li$^+$ cation between three- and four-coordination sites of the LiClO$_4$−diglyme complex. The values represent the relative energies (kcal/mol) at the HF/6-31G(d) and MP2/6-31+G(d)//HF/6-31G(d) levels (the latter are in parentheses). Structures of the local minimum are given in Figure 5.

three-, four-, and five-coordination structures, respectively. Thus, with increase in the LiClO$_4$ coordination to the diglyme the total binding energy increases, and bond dissociation energy of the individual Li−O bond decreases. The binding energies of the ClO$_4^-$ anion to Li$^+$−diglyme range from 101 to 128 kcal/mol, while the binding energies of LiClO$_4$ to diglyme range from 24 to 45 kcal/mol. Thus, the latter bond is much easier to break than the former. The binding energy of Li−ClO$_4$ at the HF/6-31G(d) level of theory is 142.7 kcal/mol indicating that the Li−ClO$_4$ bond is weakened in the LiClO$_4$−diglyme complex.

**D. Transition State Structures for LiClO$_4$−Diglyme.** We have investigated the potential energy surface of the LiClO$_4$−diglyme complex to find the transition states between three- and four-coordination structures (pathways III and IV) and between four- and five-coordination structures (pathway V). These pathways are models for LiClO$_4$ migration along a PEO chain. Schematics of the potential energy surfaces for pathways III, IV, and V are shown in Figures 6−8, respectively. The transition states were optimized at the HF/6-31G(d) level. Each one of them was verified as having one imaginary frequency. Key bond lengths in the transition structures are summarized in Table 4.

**(a) Pathway III.** This pathway, illustrated in Figure 6, contains a three-coordination local minimum (Min-**7**), a four-coordination local minimum (Min-**11**), and the transition state (TS-**3**) between them. The structures for the minima are shown in Figure 5 and the structure for the transition state is shown in Figure 6. The reaction coordinate corresponds to rotation about an OCCO dihedral angle that *makes* a second Li−O bond to the diglyme (three-coordination → four-coordination) or *breaks* the second Li−O bond to the diglyme (four-coordination → three-coordination). At the barrier the dihedral angle OCCO is 125.9°. The barrier for three-coordination → four-coordination in this pathway is 3.1 kcal/mol, while the barrier for four-coordination → three-coordination is 16.1 kcal/mol. Single-point MP2/6-31+G(d)//HF/6-31G(d) calculations give similar barriers (see Figure 6).

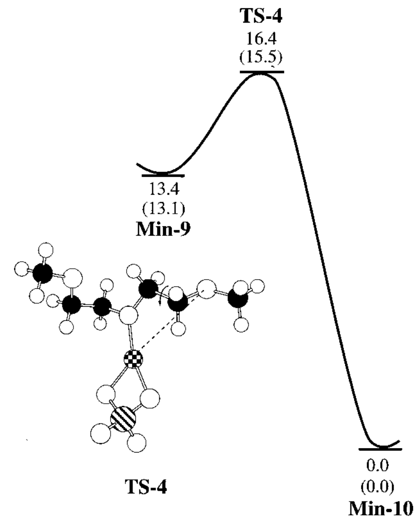


**Figure 7.** Pathway IV for migration of Li$^+$ cation between three- and four-coordination sites of the LiClO$_4$−diglyme complexes. The values represent the relative energies (kcal/mol) at the HF/6-31G(d) and MP2/6-31+G(d)//HF/6-31G(d) levels (the latter are in parentheses). Structures of the local minimum are given in Figure 5.

In our previous study[3] of Li$^+$ coordination with a *single* diglyme chain, the corresponding forward barriers (one-coordination → two-coordination) were 0.2 to 1.7 kcal/mol at the HF/6-31G(d) level. Therefore, the forward barrier is slightly larger when the anion is present. In contrast the reverse barrier is smaller when the anion is present. For Li$^+$ coordination with a single diglyme chain the reverse barriers (two-coordination → one-coordination) are 24.1 to 28.3 kcal/mol[3] compared to 16.1 kcal/mol in pathway III.

**(b) Pathway IV.** This pathway, illustrated in Figure 7, is similar to pathway III. It contains a three-coordination local minimum (Min-**9**), a four-coordination local minimum (Min-**10**), and the transition state (TS-**4**) between them. The structures for the minima are shown in Figure 5 and the structure for the transition state is shown in Figure 7. Similar to pathway III the reaction coordinate corresponds to rotation about an OCCO dihedral angle that *makes* a second Li−O bond to the diglyme or *breaks* the second Li−O bond to the dyglyme. At the barrier the dihedral angle OCCO is 50.4°. The barrier for three-coordination → four-coordination in this pathway is 3.0 kcal/mol, while the barrier for four-coordination → three-coordination is 16.4 kcal/mol. Single-point MP2/6-31+G(d)//HF/6-31G(d) calculations give similar barriers (see Figure 7).

**(c) Pathway V.** This pathway, illustrated in Figure 8, contains a four-coordination structure (Min-**11**), a five-coordination structure (Min-**12**), and the transition state (TS-**5**) between them. The barrier from the four-coordination structure (Min-**11**) to the five-coordination structure (Min-**12**) is 3.1 kcal/mol. The

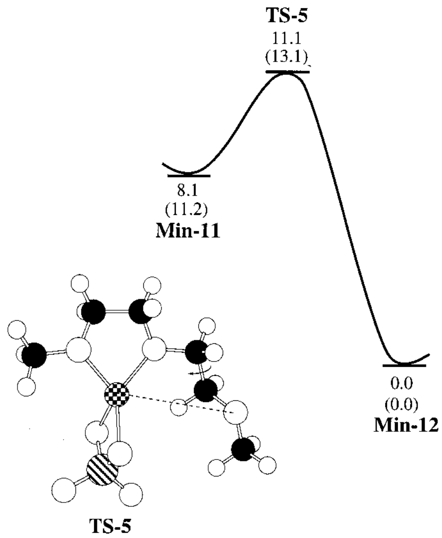


**Figure 8.** Pathway V for migration of $Li^+$ cation between four- and five-coordination sites of the $LiClO_4$−diglyme complex. The values represent the relative energies (kcal/mol) at the HF/6-31G(d) and MP2/6-31+G(d)//HF/6-31G(d) levels (the latter are in parentheses). Structures of the local minimum are given in Figure 5.

reverse barrier (five-coordination to four-coordination) is 11.1 kcal/mol. The reaction coordinate corresponds to rotation about an OCCO dihedral angle of diglyme that makes a third Li−O bond with diglyme. Single-point MP2/6-31+G(d)//HF/6-31G(d) calculations give similar barriers (see Figure 8).

In our previous study[3] of $Li^+$ coordination with a single diglyme chain, the corresponding forward barrier (two-coordination → three-coordination) was 1.8 kcal/mol at the HF/6-31G(d) level. Therefore, as in the case of pathways III and IV, the forward barrier is slightly larger when the anion is present. Also as in the case of pathways III and IV the reverse barrier is smaller when the anion is present. For $Li^+$ coordination with a single diglyme chain, the reverse barrier (three-coordination → two-coordination) is 22.9 kcal/mol[3] compared to 11.1 kcal/mol in pathway V.

## 4. Implication for Lithium Cation Migration

The binding energies for the most stable $Li^+$−iglyme, $Li^+$−(diglyme)$_2$, and $LiClO_4$−diglyme structures are plotted in Figure 2. The plots indicate that the binding energies tend to level off as the coordination number increases for all three types of complexes. In other words, the increase in binding $\Delta(\Delta E)$ decreases as the coordination number increases. The binding energies of the $Li^+$−diglyme and $Li^+$−(diglyme)$_2$ structures are in the range of 44.0−121.5 kcal/mol. The binding energies of the $LiClO_4$−diglyme structure are larger (166.9−188.0 kcal/mol) because of the presence of the anion, but the same trends with increasing coordination are observed.

The results for the potential energy surfaces indicate that migration of the lithium cation from one coordination site to the next occurs with the making or breaking of Li−O bonds whether or not the cation is attached to the $ClO_4^-$ anion. The reaction coordinate for this process is the torsional motion of the diglyme backbone.

The dependence of the barriers between structures on the total Li−O coordination number is summarized in Table 5 including previous results[3] from $Li^+$−diglyme. In this table and the following discussion, the coordination numbers of the $LiClO_4$−diglyme structures are taken to be the sum of the oxygens from diglyme and $ClO_4^-$ that coordinate to the $Li^+$ cation. The reverse

**Table 5.** Forward and Reverse Barriers of Different Pathways for Lithium Migration in the $Li^+$−Diglyme, $Li^+$−(Diglyme)$_2$, and $LiClO_4$−Diglyme Complexes at the HF/6-31G(d) Level of Theory

| system | no. of diglymes | Li−O coord no. | forward barriers | reverse barriers |
|---|---|---|---|---|
| $Li^+$−diglyme[a] | 1 | 1 → 2 | 0.2−1.7 | 24.1−28.3 |
| | | 2 → 3 | 1.8 | 22.9 |
| $Li^+$−(diglyme)$_2$ | 2 | 3 → 4 | 1.8 | 17.8 |
| | | 4 → 5 | 3.1 | 7.4 |
| $LiClO_4$−diglyme | 1 | 3 → 4 | 3.0−3.1 | 16.1−16.4 |
| | | 4 → 5 | 3.1 | 11.1 |

[a] Reference 3.

barriers are approximately the difference between the binding energies of the structures having ($n$ + 1) and $n$ oxygen coordination with $Li^+$. For example, the reverse barrier for five-coordination to four-coordination $Li^+$−(diglyme)$_2$ is 7.4 kcal/mol and the difference in binding energies of the two structures is 4.3 kcal/mol. The reverse barrier for four-coordination to three-coordination $Li^+$−(diglyme)$_2$ is 17.8 kcal/mol and the difference in binding energies of the two structures is 16.0 kcal/mol. The trends are similar when the anion is present. The reverse barrier for five-coordination to four-coordination $LiClO_4$−diglyme is 11.1 kcal/mol and the difference in binding energies of the two structures is 8.0 kcal/mol. The reverse barrier for four-coordination to three-coordination $LiClO_4$−diglyme is 16.1−16.4 kcal/mol and the difference in binding energies of the two structures is 13.0−13.4 kcal/mol. Thus, higher $Li^+$ coordination with oxygen reduces the migration barriers due to the smaller energy difference between the complexes with higher coordination. These conclusions are similar whether or not the cation is attached to an anion. It is noted that when the cation moves with the anion, it will not result in conductivity since the $LiClO_4$ is neutral. The potential energy surfaces of the interactions of other salts with the PEO are being investigated, and will be reported in a separate publication.

The results of this study suggest that lithium cation migration in poly(ethylene oxide) salt melts occurs because of the flexibility of the polymer backbone and that low migration barriers require high coordination of the cation by the polymer. Recent molecular dynamics simulations[6] of $Li^+$−PEO using pair potentials indicate that six is the most probable coordination number of $Li^+$. Coupled with our results, this suggests that in Li−PEO melts the barriers for $Li^+$ migration will be small because of high coordination numbers.

## 5. Conclusions

In this paper we have reported an ab initio molecular orbital study of the potential energy surface for the interaction of a single $Li^+$ cation with two diglymes as a model for two PEO chains. The second part of this paper is a study of the potential energy surfaces of interactions of $LiClO_4$ with PEO modeled by diglyme. In both parts of this study, local minima and the transition states between them have been located. The following conclusions can be drawn from this study.

(1) There are numerous local minima on the potential energy surfaces of these complexes. The binding energies increase with increasing coordination of $Li^+$ by oxygen (up to six oxygens), although the average binding per Li−O bond decreases. The Li−O bond distances in $Li^+$−diglyme, $Li^+$−(diglyme)$_2$, and $LiClO_4$−diglyme complexes are 1.84−2.23 Å, with the longer distances occurring for structures with higher coordination of the cation by oxygens. This range of distances is consistent with a recent neutron diffraction study of a lithium perchlorate−PEO melt.[29]

(2) The potential energy surfaces indicate that migration of lithium cation from one coordination site to another occurs with the making or breaking of Li−O bonds whether or not the cation is attached to the $ClO_4^-$ anion. The reaction coordinate for this process is the torsional motion of the diglyme backbone.

(3) The smallest $Li^+$ migration barriers (7−11 kcal/mol) are found between structures with the highest coordination numbers due to the small energy difference between the structures with higher coordination. Larger barriers (16−29 kcal/mol) are found for structures with lower coordination because of the larger energy difference between them. These conclusions are similar whether or not the cation is attached to an anion.

(4) The results of this study suggest high coordination of the lithium cation by the polymer will result in small barriers to migration of the cation between different coordination sites.

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