

Crystal Structures of Poly(Ethylene Oxide)₃:LiBF₄ and (Diglyme)_n:LiBF₄ (*n* = 1,2)

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The crystal structures of PEO₃:LiBF₄, (diglyme)₂:LiBF₄, and (diglyme):LiBF₄ have been determined and are compared. The helical conformation of each polymer chain and the stacking of neighboring chains in the structure of the PEO complex is similar to that found in the complexes with Li imide and Li triflate salts of the same PEO:salt ratio. Both PEO₃:LiBF₄ and (diglyme):LiBF₄ have similar coordination around Li⁺, i.e., 3 ether oxygens and 2 fluorines from two BF₄[−] anions. However, in the former each anion bridges two neighboring Li⁺ cations located along the PEO chain axis forming a continuous chain −BF₄[−]−Li⁺−BF₄[−]−Li⁺− whereas in (diglyme):LiBF₄ two BF₄[−] anions bridge between pairs of Li⁺ forming discrete diglyme−Li⁺−(BF₄[−])₂−Li⁺−diglyme units that are linked to their neighbors predominantly by van der Waals bonding. The (diglyme)₂:LiBF₄ structure is compared with those of PEO₆:LiSbF₆ (no PEO₆:LiBF₄ exists) and (diglyme)₂:LiSbF₆. In both cases the Li⁺ cations are 6-coordinated by three ether oxygens from two different diglymes and there is no anion coordination.

Introduction

Polymer electrolytes [salts, e.g., LiI, dissolved in coordinating polymers, e.g., poly(ethylene oxide) or PEO, (CH₂CH₂O)_{*n*}] have been studied widely since their discovery some 30 years ago;^{1–3} especially those containing Li⁺ following recognition of their important properties as ionically conducting solid electrolytes for lithium batteries.⁴ Polymer electrolytes may be prepared as crystalline or amorphous solids, the former only at certain discrete compositions. Until recently it was assumed that ionic conductivity occurred only in the amorphous phase above the glass transition temperature, *T*_g, however this is not always the case and ionic conductivity can occur in crystalline polymer electrolytes.^{5,6} This discovery has heightened interest in the structures of crystalline polymer electrolytes. We have also shown that the crystal structures can provide us with models with which to interpret spectroscopic data collected on amorphous phases, thus enabling a deeper understanding of the structure of amorphous polymer electrolytes.^{7–10}

Unfortunately, determining the crystal structures of polymer electrolytes is not a routine task. In the past it has proved difficult to prepare crystalline polymer electrolytes in a form (e.g., stretched fibers) suitable for study using the established techniques of single-crystal diffraction. By developing a powerful method of *ab initio* structure solution from powders^{11–13} it has been possible to access the crystal structures of a number of important polymer electrolytes including PEO₃:LiN(SO₂CF₃)₂, PEO:NaCF₃SO₃, PEO₆:LiAsF₆, and PEO₃:LiAsF₆.^{11,14–16}

Recently, by lowering the molar mass to 500 we have succeeded in growing single crystals of a polymer electrolyte PEO₈:NaBPh₄ using an oligo(ethylene oxide) end-capped with CH₃ groups. Although we obtained single crystals, the level of disorder in this polydispersed material precluded a definitive structure solution using single crystals method alone. However, the structural model was sufficient to permit refinement of the structure using powder diffraction and high molar mass (100 000) PEO.¹⁷ The intriguing question arises

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as to the influence on the structure of further lowering the molecular weight to a point where each Li^+ ion is coordinated by discrete molecules. At such low molecular weights, ordered crystals free from polydispersity should form. As part of this study we have investigated the structures of three complexes: one of high molar mass, $\text{PEO}_3\text{:LiBF}_4$, and the other two including the diglyme molecule(s) and the same salt $[\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3]_n\text{:LiBF}_4$ ($n = 1, 2$). The structure of $\text{PEO}_3\text{:LiBF}_4$ was determined from powder X-ray and powder neutron diffraction data and the structures of $(\text{diglyme})_n\text{:LiBF}_4$ ($n = 1, 2$) were determined by single crystal X-ray diffraction. LiBF_4 is used as a salt in lithium batteries electrolytes because of its superior stability compared to LiPF_6 . Because a compromise is often required to achieve a reasonably high conductivity, the two salts are often used together.

Experimental Section

All air-sensitive operations were carried out in a high-integrity glovebox. Methoxy end-capped poly(ethylene oxide) of average molecular weight 1000 (Fluka, purum) was dried under vacuum at 25 °C for 3 days. The polymer was then dissolved along with lithium tetrafluoroborate, LiBF_4 , (Aldrich, 99.999%) in acetonitrile (Aldrich, 99.8%) which had itself been dried over activated molecular sieves. LiBF_4 was heated at 110 °C in a vacuum oven for 48 h prior to use to remove any water present. The $\text{PEO}\text{:LiBF}_4$ ratio was 3:1. The resulting solution was stirred for 24 h under argon to ensure complete dissolution, and it was then cast into Teflon molds with the acetonitrile being allowed to evaporate slowly. The resulting white powder was removed from the molds and inserted into a glass capillary (0.7 mm) which was sealed with silicon grease, removed from the glovebox, and placed on the powder X-ray diffractometer.

Powder X-ray data were collected on a Stoe STADI/P diffractometer operating in transmission mode with $\text{Cu K}\alpha_1$ (1.54056 Å) radiation and a small-angle (high resolution) position-sensitive detector. To collect neutron diffraction data, deuterated samples were required. The complex for neutron diffraction study was prepared in the same way as the hydrogenated sample using methoxy-end-capped deuterated PEO (Polymer Source Inc., MW = 2000). Neutron diffraction data were collected in the d -spacing range from 1 to 10 Å on the OSIRIS powder diffractometer at the ISIS pulsed spallation source, Rutherford Appleton Laboratory.

Single crystals of $(\text{diglyme})\text{:LiBF}_4$ were prepared from dry LiBF_4 (Aldrich). The diglyme (Aldrich, anhydrous) was used as received. All preparations were carried out in a dry room (<0.1% RH, 20 °C). The LiBF_4 was measured into small vials and diglyme was added. The mixtures were stirred while heating on a hot plate to completely dissolve the LiBF_4 , and formed clear, colorless solutions. Solutions were prepared with $(\text{diglyme})\text{:LiBF}_4$ molar ratios ranging from 1.8 to 1.4 and were stored at 20 °C for several days. Single crystals of $(\text{diglyme})\text{:LiBF}_4$ grew in all of these solutions; however, the formation of single crystals of $(\text{diglyme})_2\text{:LiBF}_4$ was not observed at these compositions.

Single crystals of $(\text{diglyme})_2\text{:LiBF}_4$ were prepared using diethylene glycol dimethyl ether or diglyme (Aldrich, 99.5%) and dry LiBF_4 (Aldrich, 99.999%). A series of diglyme: LiBF_4 solutions was prepared with different ether oxygen-to-cation ratios (EO:Li). Desired amounts of diglyme and LiBF_4 were measured into glass vials, stirred for at least 24 h at room temperature, and left in the

drybox for a few weeks to allow crystals to grow. After 3–4 weeks a gellike substance was observed in the 8:1 solution, from which small single crystals grew slowly. This composition corresponds to a $(\text{diglyme})\text{:LiBF}_4$ molar ratio of 2.67.

A single crystal ($0.48 \times 0.42 \times 0.28 \text{ mm}^3$) of $(\text{diglyme})_2\text{:LiBF}_4$ was isolated and single-crystal X-ray data were collected at 173-(2) K. Similarly, a single crystal of $(\text{diglyme})\text{:LiBF}_4$ ($0.56 \times 0.42 \times 0.32 \text{ mm}^3$) was isolated and data were collected at 120(2) K. A Bruker P4 diffractometer¹⁶ using $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ Å}$) radiation was used for both crystals. The data were corrected for Lorentz and polarization effects; an absorption correction was not applied because it was judged to be insignificant. The structures were solved by the direct method using SHELXTL system¹⁷ and refined by full-matrix least squares on F^2 using all reflections. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were included with idealized parameters. For $(\text{diglyme})_2\text{:LiBF}_4$, the final $R1 = 0.058$ is based on 1199 “observed reflections” [$I > 2\sigma(I)$], and $wR^2 = 0.169$ is based on all reflections (1906 unique data). For $(\text{diglyme})\text{:LiBF}_4$, the final $R1 = 0.028$ is based on 2378 “observed reflections” [$I > 2\sigma(I)$], and $wR^2 = 0.074$ is based on all reflections (2473 unique data). Details of the crystal structural data are given in Tables 2 and 3.

Results and Discussion

Crystal Structure Determination from Powder Data.

X-ray powder diffraction data of excellent quality were obtained from $\text{PEO}_3\text{:LiBF}_4$, Figure 1. Although complexes such as $\text{PEO}_3\text{:LiCF}_3\text{SO}_3$, $\text{PEO}_3\text{:NaClO}_4$, and $\text{PEO}_3\text{:LiAsF}_6$ were already known, these structures did not prove adequate models for $\text{PEO}_3\text{:LiBF}_4$ to permit refinement by the Rietveld method. Structure determination by simulated annealing (SA), as described by us previously,^{11,12} was employed to determine the $\text{PEO}_3\text{:LiBF}_4$ crystal structure.

The pattern was indexed using the TREOR program²⁰ on the basis of a monoclinic cell with refined values of the lattice constants $a = 14.706(1) \text{ Å}$, $b = 8.2361(5) \text{ Å}$, $c = 8.6837(9) \text{ Å}$, $\beta = 94.985(6)^\circ$. The observed systematic absences were consistent with the space group $P21/n$. Four formula units in the unit cell, and hence one formula unit in the asymmetric unit of $P21/n$ was assumed, based on the expected density. All previously studied polymer electrolytes exhibit densities that are similar to each other.

For the purpose of solution, the content of the asymmetric unit was split into three separate moieties: a Li^+ cation, a BF_4^- anion, and a fragment of the polymer chain comprising 3 EO units. The shape of the anion was assumed to be a perfect tetrahedron with the B–F distances taken from previously established structures that contained tetrafluoroborate anions. The initial position, orientation, and conformation of the chain fragment was adopted from the previously established structure of $\text{PEO}_3\text{:NaClO}_4$.²¹ The cation and anion were randomly inserted into the asymmetric unit and all three fragments were allowed to move freely within its boundaries, however the random moves which violated continuity of the polymer chain at the junction of

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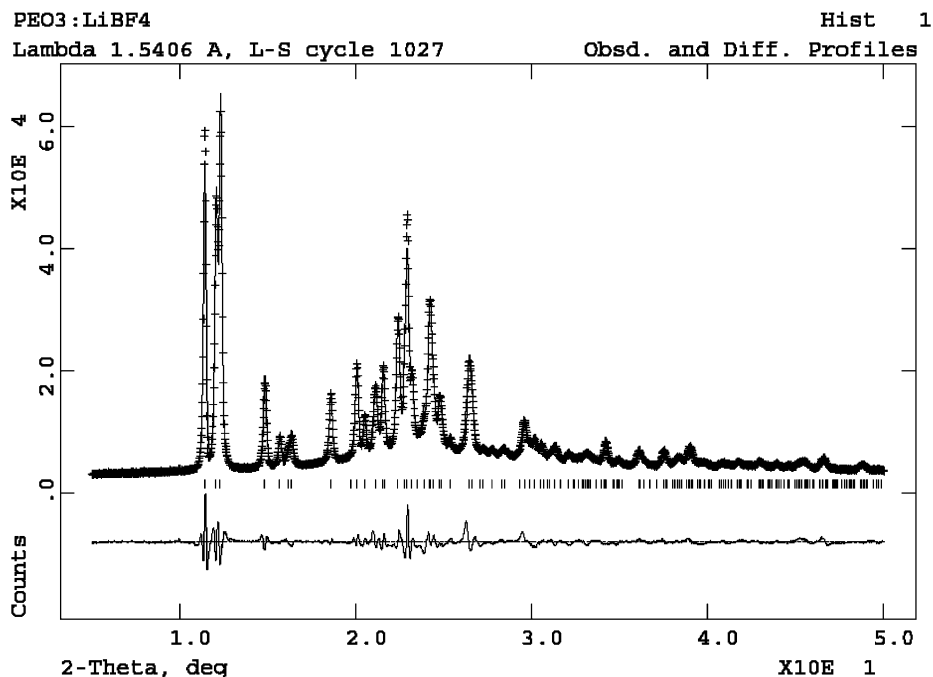


Figure 1. Observed (crosses), calculated (solid line), and difference X-ray powder diffraction patterns for PEO₃:LiBF₄.

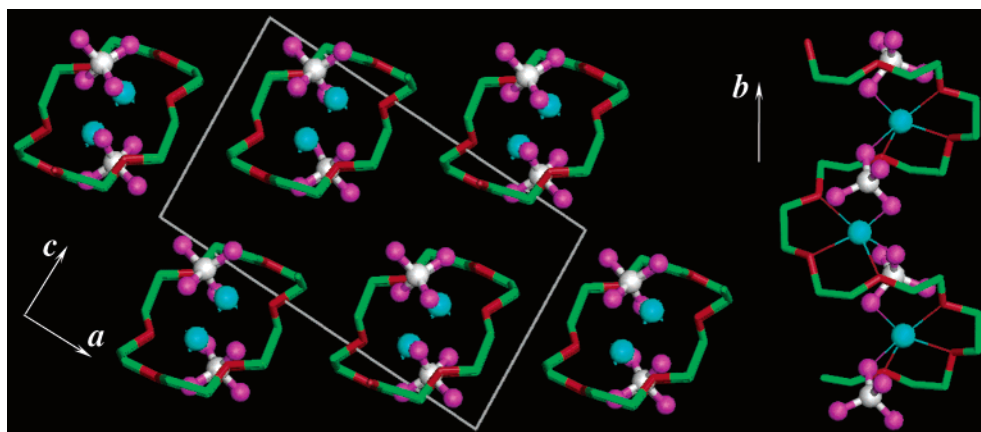


Figure 2. Structure of PEO₃:LiBF₄. Left: View of the structure along *b* axis. Right: Single PEO chain with associated ions (hydrogens not shown). Blue spheres, lithium; white spheres, boron; magenta, fluorine; green, carbon; red, oxygen. Thin lines indicate coordination around the Li⁺ cation.

neighboring asymmetric units were prohibited. In addition, the bond lengths, bond angles, and torsion angles of the chain served as variables during the solution. Unlike the torsion angles, which were varied within the range of 50°, the bond lengths and the bond angles were allowed to depart from the typical values by only ± 0.15 Å and $\pm 5^\circ$ respectively. In total 37 parameters were varied simultaneously during the global optimization by SA. Over 800 000 trial structural models were tested against the whole powder pattern in a single SA run which converged in 1 h (PC Pentium III 650 MHz) giving a reasonable fit to the experimental data ($R_{wp} = 13\%$).

The model obtained from the SA procedure was subjected to refinement by the Rietveld method using X-ray and neutron data within the GSAS suite of programs.²² As in the case of the SA run, the X-ray diffraction pattern contained 2253 data points and 206 Bragg reflections. The refinement involved 61 variables and 31 soft constraints. The refined structural model not only produced a much better fit to the experimental data (Figure 1) with $R_{wp} = 6.5\%$, $R_p = 4.5\%$,

but also ensured a chemically sensible coordination of the cations and the same basic helical conformation of the PEO chain as in all other known 3:1 complexes. Refinement based on the neutron diffraction data confirmed the X-ray structure and verified the position of the Li⁺ ion.

Crystal Structures. PEO₃:LiBF₄. The crystal structure of PEO₃:LiBF₄ is represented in Figure 2. The basic structure is similar to that of the other 3:1 complexes. Each PEO chain adopts a right-handed helical conformation. The Li⁺ ions are located in each loop of the helix and are coordinated by three ether oxygens from the PEO chain and one F from each of two BF₄[−] ions. Each BF₄[−] ion bridges between two neighboring Li⁺ ions thus forming a $-\text{Li}-\text{F}-\text{B}-\text{F}-\text{Li}-$ zigzag sequence along the chain axis. Two of the F atoms on each BF₄[−] ion do not coordinate to any other species. Each PEO chain with its dedicated set of Li⁺ and BF₄[−] ions is isolated from the other chains; i.e., there is no ionic cross-

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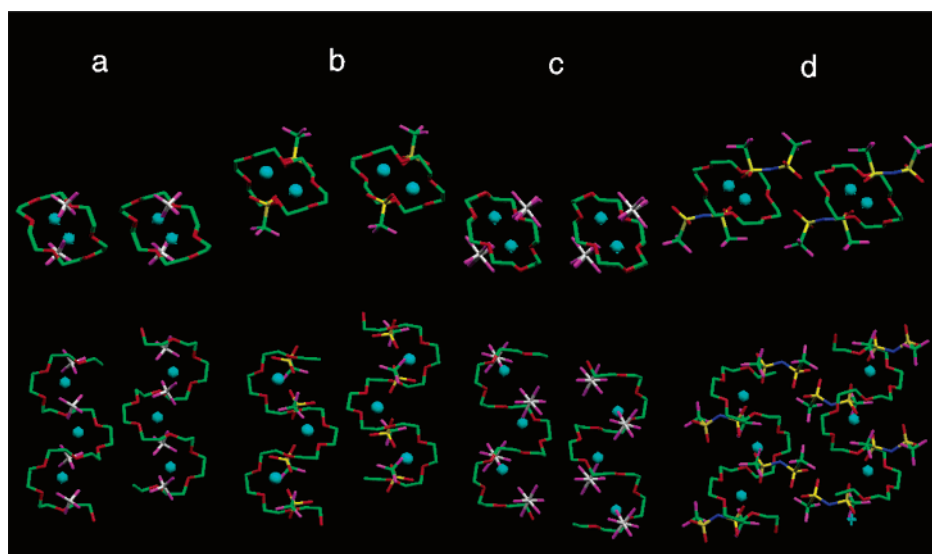


Figure 3. Fragments of the structures of (a) $\text{PEO}_3\text{:LiBF}_4$, (b) $\text{PEO}_3\text{:LiCF}_3\text{SO}_3$, (c) $\text{PEO}_3\text{:LiAsF}_6$, and (d) $\text{PEO}_3\text{:LiN}(\text{SO}_2\text{CF}_3)_2$. Top: View along the axes of the helices. Bottom: View of two neighboring helices along a direction perpendicular to the a axes.

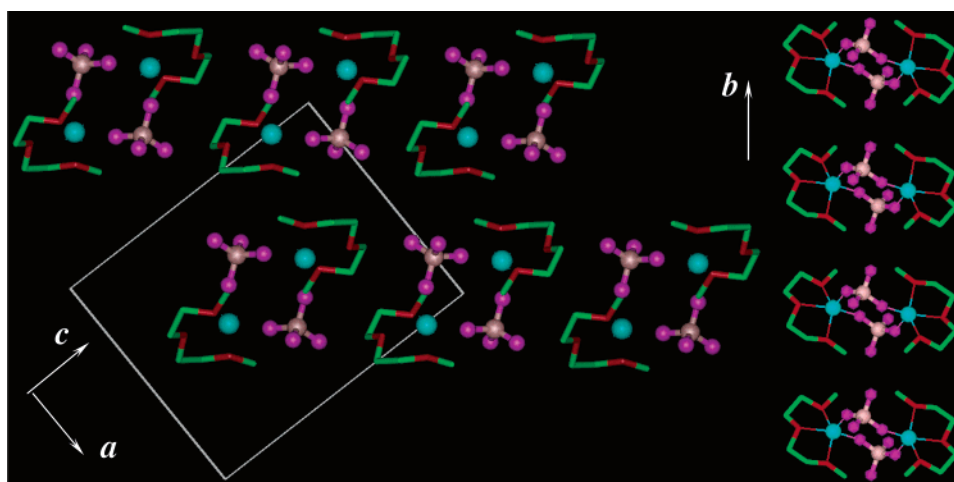


Figure 4. Structure of (diglyme): LiBF_4 . Left: View of the structure along b axis. Right: Side view of the columns of diglymes with associated ions (hydrogens not shown). Thin lines indicate coordination around the Li^+ cation.

linking between chains which are only held together in the crystal structure by weak van der Waals interactions. The packing of the chains within the structure is shown in Figures 2 and 3. Selected bond lengths and angles for this polymer electrolyte are presented in Table 1. All bond lengths and angles fall within expected limits.

The structures of various 3:1 complexes are compared in Figure 3 where the basic similarity of the different structures is evident. The chain conformation of the BF_4^- complex most closely resembles that of the triflate and imide complexes. The sequence of torsion angles for corresponding segments of the PEO chain are presented in Table 1. The repeat along the chain, commencing with the torsion angle associated with the C–O bond is $ttgtt\bar{g}tt\bar{g}$ which is identical to that for the triflate and the imide complexes, serving to emphasize the similarity of the conformations.^{11,23} It is also evident from Figure 3 that the packing of the chains is similar to that of the triflate and imide complexes. Both triflate and imide may be thought of as tetrahedral anions about the sulfur ion attached to the oxygens which coordinate directly to the lithium cations. In this sense they are similar to BF_4^- ,

Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in $\text{PEO}_3\text{:LiBF}_4$

Li–O1	2.20(1)	C1–C2–O1	107.8(1)	
Li–O2	2.20(1)	C2–O1–C3	114.1(1)	
Li–O3	2.20(1)	O1–C3–C4	107.8(1)	
Li–F1	1.9(2)	C3–C4–O2	107.8(1)	
Li–F2	2.2(2)	C4–O2–C5	114.1(1)	
		O2–C5–C6	107.8(1)	
B–F1	1.381(1)	C5–C6–O3	107.8(1)	
B–F2	1.381(1)	C6–O3–C1'	114.1(1)	
B–F3	1.380(1)	O3–C1'–C2'	107.8(1)	
B–F4	1.381(1)			
C1–C2	1.540(1)	C1–C2–O1–C3	–131	t
C3–C4	1.540(1)	C2–O1–C3–C4	154	t
C5–C6	1.540(1)	O1–C3–C4–O2	53	g
C2–O1	1.430(1)	C3–C4–O2–C5	–169	t
O1–C3	1.430(1)	C4–O2–C5–C6	170	t
C4–O2	1.430(1)	O2–C5–C6–O3	–64	g
O2–C5	1.430(1)	C5–C6–O3–C1'	–152	t
C6–O3	1.430(1)	C6–O3–C1'–C2'	161	t
O3–C1'	1.430(1)	O3–C1'–C2'–O1'	–93	g

although, of course BF_4^- is a symmetric tetrahedral ion whereas the triflate and especially the imide ions are not.

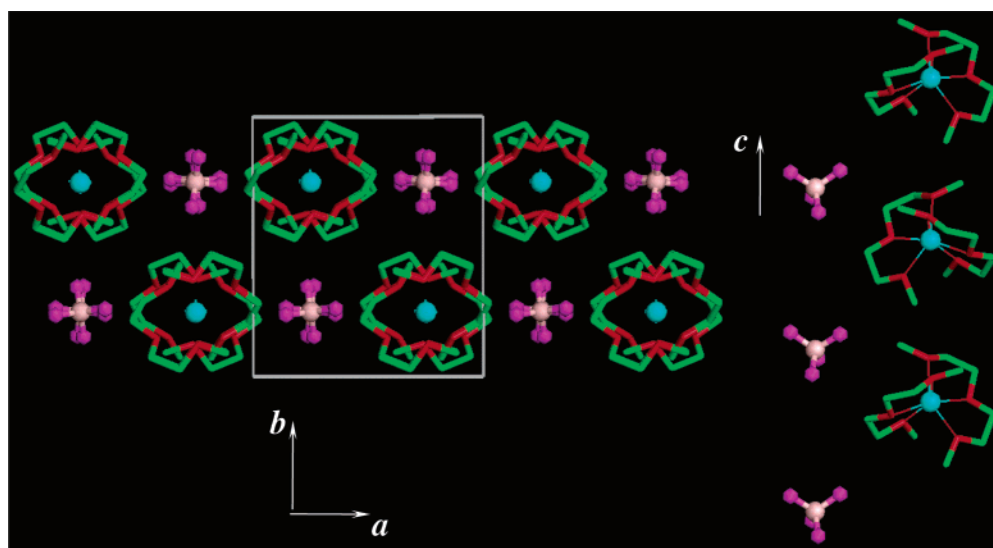


Figure 5. Structure of $(\text{diglyme})_2:\text{LiBF}_4$. Left: View of the structure along b axis. Right: Side view of the columns of diglymes with associated ions (hydrogens not shown). Thin lines indicate coordination around the Li^+ cation.

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in $(\text{Diglyme}):\text{LiBF}_4$

Li–O1	2.087(2)	C1–O1–C2	111.61(6)	
Li–O2	2.058(2)	O1–C2–C3	106.84(7)	
Li–O3	2.061(2)	C2–C3–O2	106.32(7)	
Li–F1	1.903(1)	C3–O2–C4	113.86(6)	
Li–F2	1.901(1)	O2–C4–C5	106.30(6)	
		C4–C5–O3	106.62(7)	
B–F1	1.404(1)	C5–O3–C6	112.66(7)	
B–F2	1.406(1)			
B–F3	1.376(1)			
B–F4	1.379(1)			
C1–O1	1.431(1)	C1–O1–C2–C3	176.05(7)	t
O1–C2	1.426(1)	O1–C2–C3–O2	56.19(8)	g
C2–C3	1.501(1)	C2–C3–O2–C4	–170.75(7)	t
C3–O2	1.426(1)	C3–O2–C4–C5	165.27(7)	t
O2–C4	1.429(1)	O2–C4–C5–O3	–51.71(8)	g
C4–C5	1.498(1)	C4–C5–O3–C6	–163.18(8)	t
C5–O3	1.426(1)			
O3–C6	1.419(1)			

Although the BF_4 complex is similar to triflate and imide, there is some shift of the lithium cation positions as can be seen in Figure 3.

(Diglyme): LiBF_4 . The structure of $(\text{diglyme}):\text{LiBF}_4$ in which the ether oxygens-to-cation ratio is the same as in the $\text{PEO}_3:\text{LiBF}_4$ is shown in Figure 4. The lithium ions are arranged in two columns rather than in the zigzag arrangement in the polymer complex. As in $\text{PEO}_3:\text{LiBF}_4$ each lithium cation in the $(\text{diglyme}):\text{LiBF}_4$ is 5-coordinated by three ether oxygens from a single diglyme molecule and by two fluorines from two BF_4^- anions. Each of the BF_4^- anions is simultaneously coordinated to a neighboring Li^+ cation, i.e., two BF_4^- anions bridge between pairs of Li^+ ions. As a result, the structure consists of discrete diglyme– Li^+ –(BF_4^-) $_2$ – Li^+ –diglyme units, Figure 4, that are linked only by van der Waals bonding to the neighboring units forming columns along the b axis. Selected bond lengths, bond angles, and torsion angles in the structure of $(\text{diglyme}):\text{LiBF}_4$ are presented in Table 2.

(Diglyme) $_2$: LiBF_4 . The crystal structure of this compound is shown in Figure 5. As in the $(\text{diglyme}):\text{LiBF}_4$ structure the lithium ions in $(\text{diglyme})_2:\text{LiBF}_4$ are arranged in columns. Each lithium ion is coordinated by two diglyme molecules,

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) in $(\text{Diglyme})_2:\text{LiBF}_4$

Li–O1	2.156(5)	C1–O1–C2	112.3(2)	
Li–O2	2.117(2)	O1–C2–C3	106.8(2)	
Li–O3	2.143(4)	C2–C3–O2	106.6(2)	
		C3–O2–C4	114.2(2)	
B–F1A	1.359(3)	O2–C4–C5	106.7(2)	
B–F1	1.359(3)	C4–C5–O3	107.5(2)	
B–F2	1.374(3)	C5–O3–C6	111.5(2)	
B–F2A	1.374(3)			
C1–O1	1.419(3)	C1–O1–C2–C3	–177.7(2)	t
O1–C2	1.413(3)	O1–C2–C3–O2	–56.7(3)	g
C2–C3	1.490(4)	C2–C3–O2–C4	169.3(2)	t
C3–O2	1.418(3)	C3–O2–C4–C5	–177.5(2)	t
O2–C4	1.422(3)	O2–C4–C5–O3	53.1(3)	g
C4–C5	1.485(4)	C4–C5–O3–C6	177.8(3)	t
C5–O3	1.414(3)			
O3–C6	1.422(3)			

with each molecule donating its three ether oxygens to the lithium ion thus completing a six-coordinate, distorted octahedral, arrangement around Li^+ . If we think of each diglyme molecule as being located approximately in a plane then one plane is rotated by 90 degrees with respect to the other. The Li^+ –diglyme complexes are stacked one on top of the other with the BF_4^- anions located between the diglyme stacks. There is no coordination of the BF_4^- anions to the lithium cations. The conformation of each diglyme molecule in $(\text{diglyme})_2:\text{LiBF}_4$ is similar to that in $(\text{diglyme}):\text{LiBF}_4$ (Table 3).

The $(\text{diglyme})_2:\text{LiBF}_4$ complex contains six ether oxygens per Li^+ ion whereas both $\text{PEO}_3:\text{LiBF}_4$ and $(\text{diglyme}):\text{LiBF}_4$ contain 3 and the coordination around Li^+ by the ether oxygens is respectively 6 and 3. Unfortunately a 6:1 complex between PEO and LiBF_4 does not exist. As a result, it is not possible to make a direct comparison between $(\text{diglyme})_2:\text{LiBF}_4$ and a polymer structure with LiBF_4 and the same ether oxygen-to-cation ratio. However, it is instructive to compare $(\text{diglyme})_2:\text{LiBF}_4$ with another diglyme complex in which two diglyme molecules coordinate each Li^+ along with the 6:1 PEO complexes studied previously.^{15,24,25} The crystal

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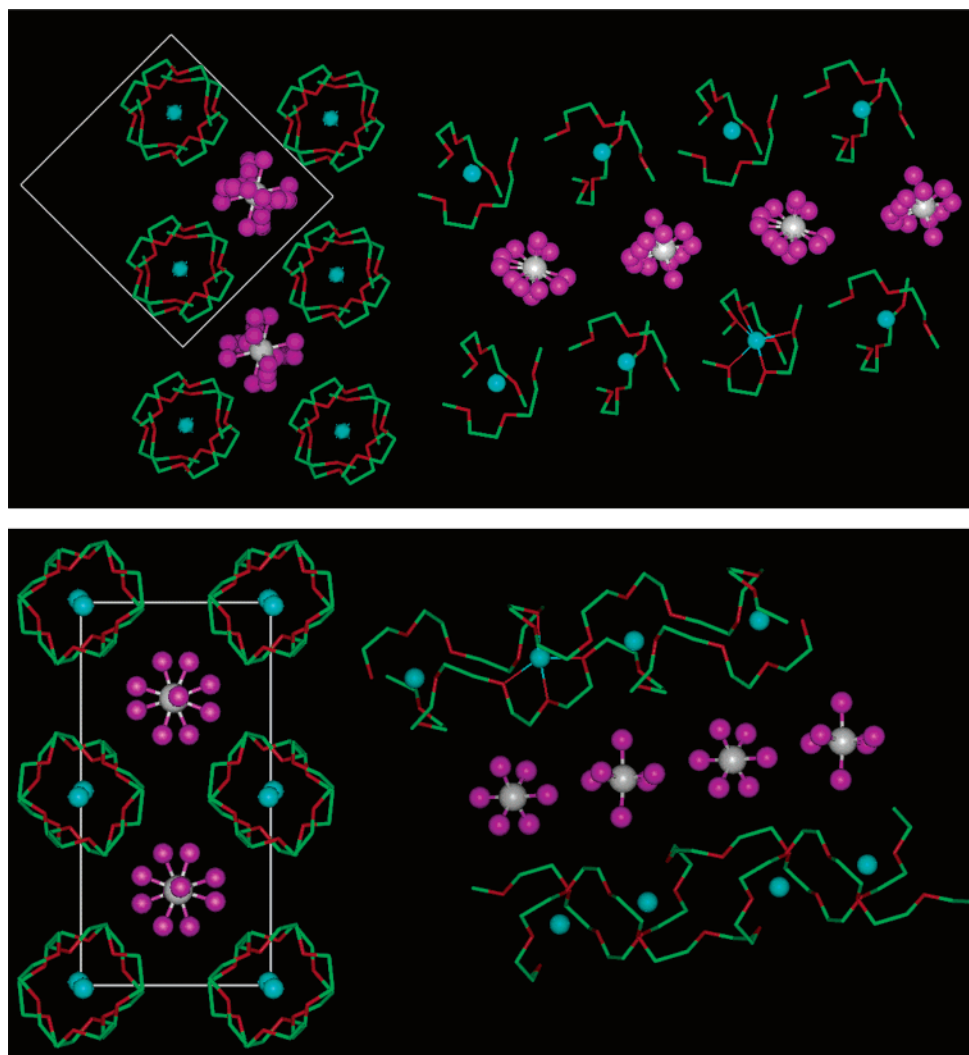


Figure 6. Structures of $(\text{diglyme})_2:\text{LiSbF}_6$ (top) and $\text{PEO}_6:\text{LiSbF}_6$ (bottom). Left: View of the structure along a showing rows of Li^+ ions perpendicular to the page. Right: View of the structure showing the relative position of the chains and their conformation (hydrogens not shown). Thin lines indicate coordination around the Li^+ cation. Note that in the diglyme complex the occupancy of fluorine sites is 0.5.

structures representing the $(\text{diglyme})_2:\text{LiSbF}_6$ and the 6:1 complex with LiSbF_6 are shown in Figure 6. The structures of the two complexes are very similar with respect to the coordination of Li^+ cations and the location of the anions between the Li^+ –(ethylene oxide) stacks. Comparing the diglyme structures with the PEO 6:1 complex reveals a number of structural similarities. One can see that if the diglyme molecules were to be linked along the stacks they would describe two interlocking chains as is observed in the PEO 6:1 complexes. Furthermore, there is a remarkable similarity between the two structures when viewed down the b -axis in Figure 6. The stacks of lithium–diglyme complexes appear as tunnels when viewed in this way with the anions between the tunnels, just as is observed for PEO 6:1 complexes. Unlike the case of the PEO 6:1 complex, the Li–diglyme complexes are too far apart along the columns for ion transport.

It is interesting that the single-crystal structure determinations of the diglyme complexes indicate many features that are similar to the PEO complexes with the same ether oxygen-to-cation ratio, emphasising the significant role of local ion–molecule interactions in determining the local structure even in a long chain polymer. It will be interesting to explore the complexes of other low molecular weight glymes formed with a variety of salts and to extend this investigation to higher molecular weight glymes to determine the point at which discrete molecular structures give way to polymeric compounds.

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Supporting Information Available: Crystallographic information files (cif) and a table of atomic coordinates (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.