

Ab Initio Structure Solution of the Polymer Electrolyte Poly(ethylene oxide)₃:LiAsF₆

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The crystal structure of the polymer electrolyte complex PEO₃:LiAsF₆ has been determined ab initio from X-ray and neutron powder diffraction data using a simulated annealing approach in direct crystallographic space. The structure consists of rows of Li⁺ cations encapsulated within PEO helices and coordinated by three ether oxygens and two fluorines from two anions. This is the first polymer electrolyte structure in which fluorines coordinate directly to the cations. Although the conformation of each individual polymer chain and the arrangement of the cations and anions are similar to previously determined 3:1 complexes containing Li salts, the stacking and separation of neighboring chains are markedly different. This prevents elucidation of the structure using conventional refinement by the Rietveld method.

Introduction

Many salts may be dissolved in solid coordinating polymers such as poly(ethylene oxide) [(CH₂CH₂O)_n] (PEO), resulting in the preparation of thousands of polymer electrolytes. Such materials may be considered as coordination compounds lying somewhere between classical coordination chemistry and solid state chemistry. Where lithium salts are employed, the resulting materials uniquely combine solid yet flexible mechanical properties with ionic conductivity. This combination holds the key to the development of all-solid-state electrochemical devices such as rechargeable lithium batteries, in which a film of the material is used as the electrolyte.

Despite the preparation of many polymer electrolytes and the intensive study of their physical properties, especially ionic conductivity, over the last 25 years, our knowledge of their structures remains severely limited. At certain compositions corresponding to discrete ratios of the ether oxygens to the salt, polymer electrolytes may be prepared in the form of crystalline complexes. In principle, modern methods of single-crystal diffraction could be used to provide much detailed information concerning polymer electrolyte structure. However, in practice, the poor quality of the diffraction data that is obtained from such materials negates the use of this approach in the vast majority of cases. Careful preparation can, however, provide powdered samples of polymer electrolytes that yield high-quality powder diffraction data. Unfortunately, lack of knowledge concerning the structure of polymer electrolytes, in general, precludes the use of established powder diffraction methods such as the Rietveld approach which relies on starting from a partial knowledge of the structure and refining the details using gradient least-squares fitting to the observed diffraction profile. Instead, the structures must be solved ab initio from powder diffraction data. Such structure solution represents a significant challenge. We

have developed a method of structure solution which involves generating entirely random structural models, calculating their powder diffraction patterns, and locating the global minimum in the best fit to the observed data using simulated annealing (SA).^{1,2} Critically, the chemical integrity of the molecular moieties within the structural models is maintained, thus substantially reducing the number of structural models that would otherwise be generated and rendering the approach tractable. Interest in such methods for the solution of molecular structures from powders in general has expanded rapidly in the past few years.^{3–8} We have, in particular, applied the method to solve the structures of polymer electrolytes. Recently, the power of the methodology has been demonstrated by the first structure solution of a 6:1 complex, PEO₆:LiAsF₆.⁹ This is the most complex molecular solid of any type to be solved ab initio from powder diffraction data and involves no less than 79 simultaneously varying structural parameters including 15 torsion angles.

Although the structures of several 3:1 polymer electrolyte complexes have been solved previously, differences in their structures, especially the way in which the polymer chains pack in the solid state, often renders ineffective the use of such known structures as models

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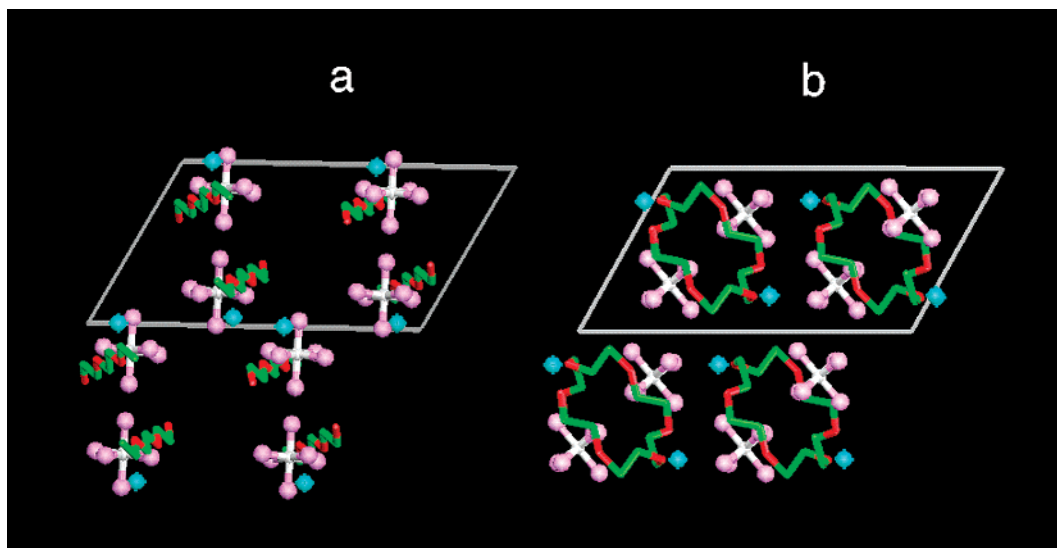


Figure 1. Structural model of $\text{PEO}_3\text{:LiAsF}_6$ at the beginning (a) and at the end (b) of the ab initio structure solution by simulated annealing. Blue spheres, lithium; white spheres, arsenic; magenta, fluorine; green, carbon; red, oxygen.

for the Rietveld refinement of an unknown 3:1 structure. This proved to be the case for the $\text{PEO}_3\text{:LiAsF}_6$ structure. In this paper we describe the ab initio structure solution of the crystalline $\text{PEO}_3\text{:LiAsF}_6$ complex using the SA approach. This represents the first 3:1 structure to be solved with octahedral anions as well as the first in which fluorines coordinate directly to the cations. It also permits a direct comparison of the 6:1 and 3:1 structures within the same PEO:salt system.

Experimental Section

$\text{PEO}_3\text{:LiAsF}_6$ was prepared by the solvent-casting technique. The polymer methoxy end-capped, PEO (Fluka, $M_w = 1000$, purum), and the salt, LiAsF_6 (Aldrich, 99%), were dried under vacuum respectively at 25 °C for 3 days and at 120 °C for 24 h. Stoichiometric amounts of the dried compounds were dissolved separately in anhydrous acetonitrile (Aldrich, 99.8%). The solutions were mixed and stirred overnight before being casted onto Teflon plates and the solvent was allowed to evaporate slowly at room temperature. All these manipulations were carried out in an argon-filled glovebox. The resulting compound was dried at room temperature for 1 day under vacuum to remove any residual solvent. IR spectroscopy confirmed the absence of residual acetonitrile (no $-\text{C}\equiv\text{N}$ stretch). The low molecular weight polymer was selected to maximize the crystallinity of the sample for diffraction studies. The diffraction pattern for M_w 100000 PEO possesses the same peaks but the pattern is of inferior quality with broad peaks and lower peak-to-background ratios.

For X-ray studies the powdered sample was placed under argon in a 0.7-mm glass capillary which was then sealed. Diffraction data were collected over the range 5–60° in 2θ in 0.02° steps on a Stoe STADI/P diffractometer operating in transmission mode with an incident beam Ge monochromator providing Cu $K\alpha_1$ radiation.

Ab Initio Structure Solution of $\text{PEO}_3\text{:LiAsF}_6$

The pattern was indexed on the basis of a monoclinic cell with $a = 16.690(1)$ Å, $b = 8.5912(5)$ Å, $c = 9.3945(6)$ Å, and $\beta = 119.175(5)^\circ$ using the TREOR program.¹⁰ The observed systematic absences were consistent with the space group $P2_1/a$. Four formula units in the unit cell, and hence one formula unit in the asymmetric unit

of $P2_1/a$, was assumed. This was based on an expected density in the range 1.5–1.9 g/cm³. All Li-containing polymer electrolytes studied previously exhibit densities in this range.

For the purpose of solution the content of the asymmetric unit was split into three separate moieties, Li^+ cation, AsF_6^- anion, and a fragment of the polymer chain comprising three EO (ethylene oxide) units. The shape of the anion was assumed to be a perfect octahedron with the As–F distances taken from the previously established structure of $\text{PEO}_6\text{:LiAsF}_6$. No assumption was made about the specific conformation of the chain fragment with all torsion angles set initially to equal π . Each moiety was randomly inserted into the asymmetric unit (Figure 1a) and allowed to move freely within its boundaries. 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 whole range of $-\pi, \pi$, the bond lengths and the bond angles were allowed to depart from the typical values by ± 0.15 Å and $\pm 5^\circ$, respectively. In total 37 parameters were varied simultaneously during the global optimization by SA. Over 1 million trial structural models were tested against the whole powder pattern in a single SA run which converged in less than 6 h (PC Pentium III 650 MHz), giving a reasonably good fit to the experimental data ($\chi^2 = 14$, $R_{wp} = 13\%$) and corresponding to the structural model shown in Figure 1b. Further details concerning our SA algorithm may be found elsewhere.²

The SA run produced a model in which all the $(\text{CH}_2-\text{CH}_2-\text{O})_3$ units merged at the junctions of neighboring asymmetric units forming a continuous helical PEO chain and providing a useful independent test of the validity of the structure solution. The conformation of the PEO chain in the SA model, *ttgtgggtg*, is somewhat different from the conformation *ttgttgttg* found in all other 3:1 complexes. The above conformational sequences have been derived assuming that torsion angles in the range $180 \pm 45^\circ$ are trans (*t*) and $90 \pm 45^\circ$ are either gauche (*g*) or gauche-minus (*ḡ*). Li^+ is a weak scatterer of X-rays; as a result, it is difficult to locate this ion by powder X-ray diffraction. This is especially

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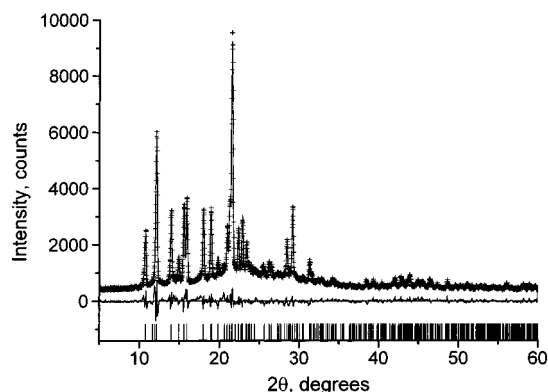


Figure 2. Observed (crosses), calculated (solid line), and difference X-ray powder diffraction patterns for $\text{PEO}_3\text{:LiAsF}_6$.

so in the case of ab initio structure solution since the trial structural models allow the Li^+ ion to be located anywhere within the unit cell. Therefore, it was not surprising that the Li^+ cation was located in a physically unreasonable position outside the PEO helices and without coordination by the ether oxygens or the anions.

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.¹¹ As in the case of the SA run, the X-ray diffraction pattern contained 2749 data points and 351 Bragg reflections. The refinement involved 64 variables and 41 soft constraints. At the start of refinement the Li^+ cation was moved inside the PEO helix. The refined structural model not only produced a much better fit to the experimental data (Figure 2) with $R_{\text{wp}} = 8.6\%$, $R_p = 6.1\%$, and $\chi^2 = 6$ but also ensured a chemically sensible coordination of the cations and exactly the same conformational pattern of the PEO chain as in all other known 3:1 complexes. Refinement based on the neutron diffraction data collected on the OSIRIS diffractometer at ISIS, Rutherford Appleton Laboratory, using a deuterated sample, simply served to confirm the X-ray structure including the position of the Li^+ ion. Bond lengths and bond angles refined from both X-ray and

Table 1. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) in $\text{PEO}_3\text{:LiAsF}_6$ ($R_{\text{wp}} = 8.6\%$, $R_p = 6.1\%$, $\chi^2 = 6$, Space Group $P2_1/a$, $a = 16.690(1)$ Å, $b = 8.5912(5)$ Å, $c = 9.3945(6)$ Å, $\beta = 119.175(5)^\circ$)

L-O1	2.22(2)	C1-O1-C6	114(2)	
Li-O2	2.22(2)	O1-C1-C2	110(2)	
Li-O3	2.10(2)	C1-C2-O2	105(2)	
Li-F3	2.13(2)	C2-O2-C3	110(2)	
Li-F4	2.20(2)	O2-C3-C4	104(2)	
		C3-C4-O3	106(2)	
As-F1	1.70(2)	C4-O3-C5	108(2)	
As-F2	1.64(2)	O3-C5-C6	110(2)	
As-F3	1.67(2)	O1-C6-C5	106(2)	
As-F4	1.67(2)			
As-F5	1.67(2)			
As-F6	1.64(2)			
		C1-C2-O2-C3	-153	t
C1-C2	1.56(2)	C2-O2-C3-C4	160	t
C3-C4	1.57(2)	O2-C3-C4-O3	81	g
C5-C6	1.53(2)	C3-C4-O3-C5	-149	t
O1-C1	1.42(2)	C4-O3-C5-C6	150	t
C2-O2	1.44(2)	O3-C5-C6-O1	-108	\bar{g}
O2-C3	1.42(2)	C5-C6-O1-C1	-173	t
C4-O3	1.42(2)	C6-O1-C1-C2	175	t
O3-C5	1.41(2)	O1-C1-C2-O2	-66	\bar{g}
O1-C6	1.41(2)			

neutron data are well within experimental errors. The refined structural parameters of $\text{PEO}_3\text{:LiAsF}_6$ are listed in Table 1.

Discussion

The basic structural features of the $\text{PEO}_3\text{:LiAsF}_6$ complex are similar to the other 3:1 structures (Figure 3).^{1,12-15} Each PEO chain adopts the conformation of a 6(1) helix. Li^+ ions are located within each coil of the helix with each Li^+ ion being coordinated by three ether oxygens and one fluorine from each of two AsF_6^- ions. The anions are located near the edge of the PEO chains with each bridging between two Li^+ ions along the chain by donating one F to each of two neighboring Li^+ ions (Figure 3b). The anions do not coordinate cations on neighboring chains; hence, there is no ionic cross-linking. Each PEO chain is associated with a dedicated set of Li^+ and AsF_6^- ions. This is the first structure

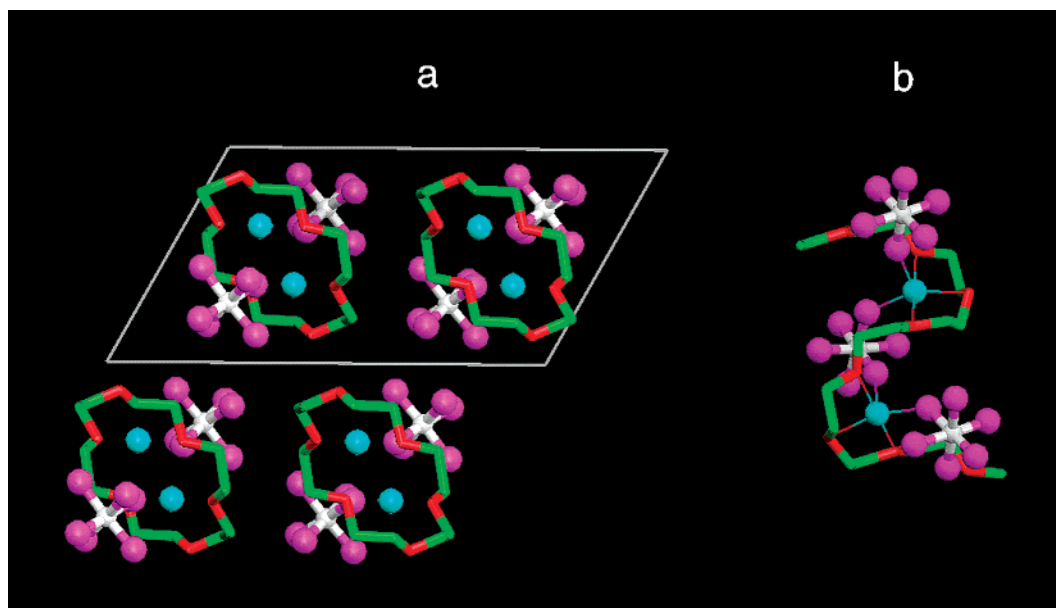


Figure 3. Structure of $\text{PEO}_3\text{:LiAsF}_6$. (a) View of the structure along the b axis. (b) Single PEO chain with associated ions (hydrogens not shown). Thin lines indicate coordination around the Li^+ cation and the color code is given in the caption to Figure 1.

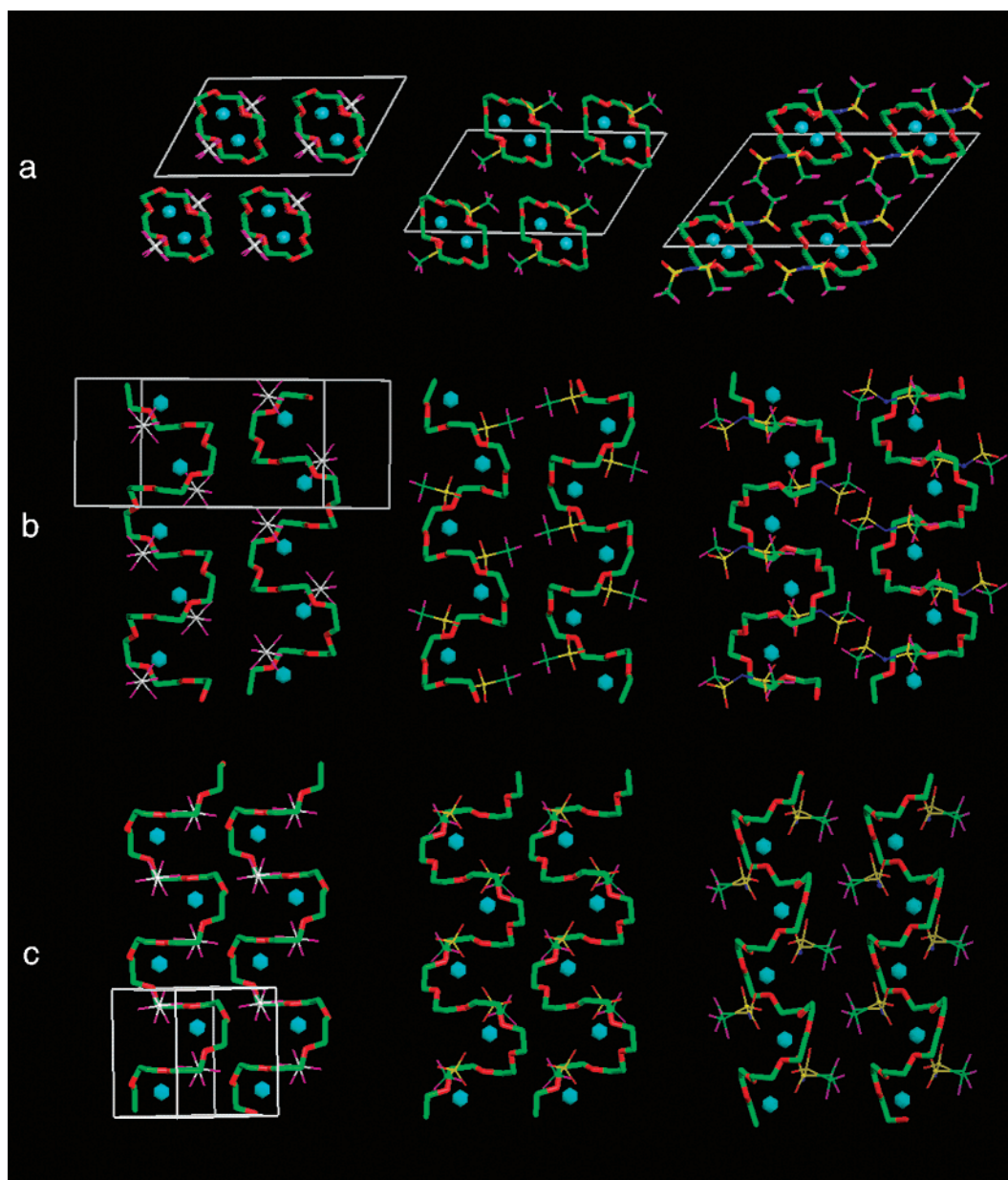


Figure 4. The structures of (left to right) $\text{PEO}_3\text{:LiAsF}_6$, $\text{PEO}_3\text{:LiCF}_3\text{SO}_3$, and $\text{PEO}_3\text{:LiN}(\text{SO}_2\text{CF}_3)_2$. The color code is given in the caption to Figure 1. (a) View along the axes of the helices. (b) View of two neighboring helices along a direction perpendicular to the a axes. (c) View of two neighboring helices along a direction perpendicular to the c axes.

solution of a 3:1 complex containing octahedral anions. The angle between two F atoms in an AsF_6^- ion coordinating neighboring Li^+ ions along the chain (F–As–F) is 90° . This contrasts with previously studied 3:1 complexes which contained tetrahedral anions such as ClO_4^- with the corresponding angle (O–Cl–O) being 109° . Evidently, the 90° angle still permits satisfactory bridging between neighboring cations along the chain. Bridging of Li^+ cations by octahedral anions containing fluorine, however, has been observed in other types of

molecular compounds.¹⁶ This is also the first 3:1 complex in which coordination of the cation by the anion occurs by donation of fluorine atoms. Other partially fluorinated anions such as triflate, CF_3SO_3 , or imide $\text{N}(\text{SO}_2\text{CF}_3)_2$ coordinate through the oxygen atoms. These oxyfluorides are also “tetrahedral” anions and therefore have an O–S–O angle which is greater than 90° . The bond lengths listed in Table 1 are all in good agreement with those observed for other PEO complexes. Since this is the first example of an anion in which the fluorines coordinate directly to the cations, we have compared the Li–F distance reported here with those for other compounds such as the salt LiAsF_6 (Li–F 2.04 Å).¹⁷ Our results are in good agreement with such structures.

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Nevertheless, the lithium coordination geometry is different. In the salt LiAsF_6 , the Li^+ ions are in an octahedral coordination whereas in $\text{PEO}_3\text{:LiAsF}_6$, as in all 3:1 complexes determined so far, it is in a distorted trigonal bipyramidal coordination.

The structures of two 3:1 complexes containing lithium salts, $\text{PEO}_3\text{:LiCF}_3\text{SO}_3$ and $\text{PEO}_3\text{:LiN}(\text{SO}_2\text{CF}_3)_2$, have been solved previously and it is interesting to compare these with the $\text{PEO}_3\text{:LiAsF}_6$. First, the PEO chains exhibit almost the same degree of elongation along the helical axes in all three compounds. The difference between the shortest helix (8.59 Å for $\text{PEO}_3\text{:LiAsF}_6$) and the longest (8.66 Å for $\text{PEO}_3\text{:LiN}(\text{SO}_2\text{CF}_3)_2$) being only 1%. To aid comparison between the structures, all three have been placed in comparable orientations defined by the positions of the cations and the cross section of the PEO chains, as shown in Figure 4a. With their relative orientations maintained while the structures were rotated, the views shown in Figure 4b,c were generated. They show the three structures as viewed along the *a* and *c* axes of their unit cells. It is evident from Figure 4b,c that the relative orientation of the chains in $\text{PEO}_3\text{:LiAsF}_6$ is similar to that in $\text{PEO}_3\text{:LiN}(\text{SO}_2\text{CF}_3)_2$ whether viewed along *a* or *c*; however, the disposition of the chains in the case of $\text{PEO}_3\text{:LiCF}_3\text{SO}_3$ is different. It is also apparent that the relative positions of the anions are quite similar between the AsF_6 and $\text{N}(\text{SO}_2\text{CF}_3)_2$ structures but distinct from CF_3SO_3 . Although the geometry of the AsF_6 and $\text{N}(\text{SO}_2\text{CF}_3)_2$ structures are similar, the larger imide ion ensures a significantly greater separation of the chains. It becomes evident, in light of the above analysis, why, despite the apparent similarity between the 3:1 structures, it has not proved possible to refine the structure of one 3:1 complex using another as the starting model. This emphasizes the

significance of ab initio structure solution from powders in the context of polymer electrolyte structures.

Solution of the $\text{PEO}_3\text{:LiAsF}_6$ complex makes it possible to compare directly the 6:1 and 3:1 structures within the same system. The structures are very different, emphasizing the major effect that changing the salt content by a factor of 2 can have on the structures adopted, even between the same polymer and salt. In the case of the 6:1 structure the PEO chains do not adopt a helical conformation but fold to form a half cylinder. Pairs of such chains interlock to form cylindrical tunnels within which the Li^+ ions reside. Each lithium is therefore coordinated by two PEO chains simultaneously, involving three ether oxygens from one chain and two from the other chain. The 6:1 structure is the only known example in which the cations are simultaneously coordinated by two PEO chains. Furthermore, the anions reside outside the tunnels formed by the PEO chains and do not coordinate directly to the Li^+ ions. A discussion of correlations between the observed structures and the conduction properties of polymer electrolytes can be found elsewhere.¹⁸

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Supporting Information Available: Table of atomic coordinates, diffraction pattern, and indexing (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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