Chem. Mater. **2003,** *15,* 4685−4690

Tetraglyme−Li$^+$ Cation Solvate Structures: Models for Amorphous Concentrated Liquid and Polymer Electrolytes (II)

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Received May 13, 2003

Three crystal structures of tetraglyme coordination complexes with lithium salts are reported—(tetraglyme)$_1$:LiAsF$_6$, (tetraglyme)$_{1/2}$:LiBF$_4$, and (tetraglyme)$_{2/5}$:LiCF$_3$CO$_2$. A novel form of six-coordinate Li$^+$ cation coordination by the ether oxygens is found resembling double-helix dimers. Structural characterization of these materials provides insight into the molecular interactions which occur among the cations, anions, and ether oxygens. Such interactions are of interest for aiding in the understanding of the many factors which contribute to ionic conductivity mechanisms in amorphous concentrated liquid and solid poly(ethylene oxide) electrolytes.

Introduction

No crystal structures of tetraglyme−Li$^+$ cation complexes have yet been reported in the scientific literature and Cambridge Crystallographic Database.[1] Such structures, however, are of considerable interest for modeling the interaction of poly(ethylene oxide) (PEO) and Li$^+$ cations in amorphous phases[2,3] where ionic conduction predominates in PEO and related polymer electrolytes.[4,5] Glymes, CH$_3$O−(CH$_2$CH$_2$O)$_n$−CH$_3$, have been extensively used to solvate Li$^+$ cations. This utility derives from the ability of the flexible glyme polyether chains to adopt numerous conformations, permitting multidentate cation coordination through the ether oxygen (EO) electron lone pairs.

Crystalline structures formed between the glymes and lithium salts are-low energy, idealized models of solvates. As such, they enable one to gain insight into the preferential coordination behavior between the cations and EO chains which exists in amorphous solid polymer electrolytes. In a previous paper, crystal structures for a number of triglyme(G3)−Li$^+$ cation solvates were reported.[6] Here, we report the crystal structures of three tetraglyme(G4)−Li$^+$ cation solvates. Tetraglyme (n = 4) is denoted as G4 after the notation used by other authors.[7,8]

Experimental Section

Materials. Preparation and storage of the reagents and single crystals were performed in a dry room (<1% relative humidity, 22 °C). G4 (tetraglyme or tetra(ethylene glycol) dimethyl ether) (Aldrich) was dried over 4-Å molecular sieves and used without further purification. LiCF$_3$CO$_2$ and LiAsF$_6$ (Aldrich) were dried under high vacuum at 110 and 70 °C, respectively, for 24 h. LiBF$_4$ (Aldrich) was purchased as anhydrous and used as-received.

Synthesis of (G4)$_1$:LiAsF$_6$. G4 (0.962 g, 4.33 mmol) was added to LiAsF$_6$ (0.604 g, 3.08 mmol). The mixture was heated while stirring to dissolve the salt. Anhydrous toluene (~5 mL) was added. Block crystals of (G4)$_1$:LiAsF$_6$ (T_m = 97 °C) grew on storage in the dry room at 22 °C for several days.

Synthesis of (G4)$_{1/2}$:LiBF$_4$. G4 (0.810 g, 3.64 mmol) was added to LiBF$_4$ (0.336 g, 3.58 mmol). The mixture was heated while stirring to dissolve the salt. Anhydrous toluene (~5 mL) was added. Block crystals of (G4)$_{1/2}$:LiBF$_4$ (T_m = 58 °C) grew slowly on storage in the dry room at 22 °C for several days to weeks. Note that although the stoichiometry of the G4:LiBF$_4$ mixture was 1:1, crystals of (G4)$_{1/2}$:LiBF$_4$ formed at 22 °C rather than a (G4)$_1$:LiBF$_4$ phase (T_m = 35 °C) (see below).

Synthesis of (G4)$_{2/5}$:LiCF$_3$CO$_2$. LiCF$_3$CO$_2$ (0.414 g, 3.45 mmol) was dissolved in anhydrous acetonitrile (~5 mL). G4 (0.724 g, 3.26 mmol) was added and the acetonitrile was removed by heating under vacuum at 60 °C for 12 h. Block crystals of (G4)$_{2/5}$:LiCF$_3$CO$_2$ (T_m > 190 °C) grew slowly on storage in the dry room at 22 °C for several days to weeks.

General Procedures. Melting temperatures were determined from the peak temperatures of heating thermograms using a Perkin-Elmer Pyris 1 differential scanning calorimeter. Samples were hermetically sealed in Al pans in the dry room. The sample pans were slowly cooled from 20 to −120 °C and then heated from −120 to 140 °C at a heating rate of 10 °C/min.

X-ray Structural Determination. Single crystals of (G4)$_1$:LiAsF$_6$, (G4)$_{1/2}$:LiBF$_4$, and (G4)$_{2/5}$:LiCF$_3$CO$_2$ were placed on the tip of a 0.1-mm-diameter glass capillary and mounted on a Bruker SMART system diffractometer for data collection at −100 °C. An inert atmosphere glovebag was used to prevent exposure of the crystals to moisture in the air. Data collection was carried out using Mo Kα radiation (graphite monochro-

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10.1021/cm034352r CCC: $25.00

Table 1. Crystal and Refinement Data

structure	$(G4)_1$:$LiAsF_6$	$(G4)_{1/2}$:$LiBF_4$	$(G4)_{2/5}$:$LiCF_3CO_2$
chemical formula	$C_{20}H_{44}Li_2O_{10}As_2F_{12}$	$C_{20}H_{44}Li_4O_{10}B_4F_{16}$	$C_{30}H_{44}Li_5O_{20}F_{15}$
fw	836.27	819.55	1044.35
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbcn*	$P2_1/c$	$P2_1/c$
a (Å)	12.3788(18)	19.720(2)	12.715(5)
b (Å)	22.512(3)	8.9762(10)	17.667(7)
c (Å)	12.3431(18)	21.360(2)	22.509(9)
β (deg)	90	102.607(2)	104.539(7)
V (Å^3)	3439.6(9)	3689.8(7)	4894(3)
Z	4	4	4
T (K)	173(2)	173(2)	173(2)
ρ_{calc} (g cm^{-3})	1.615	1.475	1.417
μ (mm^{-1})	2.052	0.156	0.148
crystal size (mm)	0.10 × 0.10 × 0.03	0.40 × 0.30 × 0.30	0.46 × 0.42 × 0.30
F(000)	1696	1680	2136
$2\theta_{max}$ (deg)	25.05	27.51	25.11
N (R_{int})	3230 (0.0380)	8445 (0.029)	8669 (0.026)
N [$I > 2\sigma(I)$]	2354	6030	3625
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0466, 0.1193	0.0420, 0.1009	0.0743, 0.1912
R1,[a] wR2[b] (all data)	0.0680, 0.1303	0.0635, 0.1145	0.0979, 0.2112
GOF[c]	1.066	1.026	1.040
$\Delta e_{min,max}$ (e Å^{-3})	−0.514, 1.166	−0.209, 0.311	−0.618, 0.773

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

mator). Intensity data were corrected for absorption and decay.[9] Final cell constants were calculated from the *xyz* centroids of the strong reflections from the actual data collection after integration.[10] Structures were solved using SHELXS-86[11] ($(G4)_1$:$LiAsF_6$), SHELXS-97[11] ($(G4)_{1/2}$:$LiBF_4$), and SIR92[12] ($(G4)_{2/5}$:$LiCF_3CO_2$) and refined using SHELXL-97.[11] Direct-methods solutions were calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The program PLATON[13] was used for checking the structures. Additional refinement information is found in the Supporting Information.

Results and Discussion

Single-Crystal Structure of $(G4)_1$:$LiAsF_6$. Crystallographic data for $(G4)_1$:$LiAsF_6$ are reported in Table 1. This structure consists of double-helix dimers in which two six-coordinate Li^+ cations are coordinated by two G4 molecules (Figure 1a and Supporting Information). Each cation is coordinated by three EOs from each G4 molecule with the central EO of each G4 molecule coordinated to both cations. The O−Li distances of the noncentral EOs are short (1.982(3)−2.065(7) Å) while the O−Li distances for the bidentate central EOs are relatively long (2.505(10)−2.527(8) Å), indicating weaker coordination bonds (Table 2). The AsF_6^- anions which lie between the $[(G4)Li]_2^{2+}$ dimers are not coordinated to the cations (Figure 1b). One of the two AsF_6^- anions in the asymmetric unit is disordered (see Supporting Information).

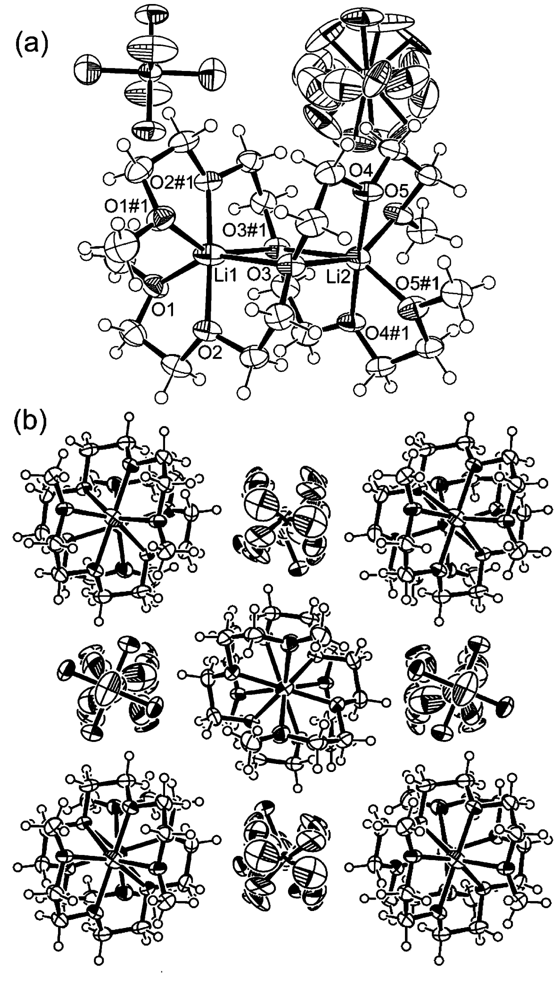

Figure 1. Li^+ cation coordination environment in $(G4)_1$:$LiAsF_6$: (a) double-helix dimer viewed laterally (one of the AsF_6^- anions is disordered over three positions) and (b) packing arrangement of the anions and double-helix dimers (viewed axially). Thermal ellipsoids drawn at 50% probability.

Single-Crystal Structure of $(G4)_{1/2}$:$LiBF_4$. Crystallographic data for $(G4)_{1/2}$:$LiBF_4$ are reported in Table 1. This structure has two different Li^+ cation coordination sites. In the first coordination site, half of the cations are coordinated by the G4 molecules as $[(G4)Li]_2^{2+}$ double-helix dimers very similar to those found in $(G4)_1$:$LiAsF_6$, but with a slightly different symmetry

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(G4)_1$:$LiAsF_6$

Li1−O1	2.072(9)	Li2−O3	2.527(8)
Li1−O2	1.982(3)	Li2−O4	1.997(3)
Li1−O3	2.505(10)	Li2−O5	2.065(7)
O1−Li1−O1#1[a]	102.9(6)	O3−Li2−O3#1	83.6(3)
O1−Li1−O2	80.1(2)	O3−Li2−O4	73.2(2)
O1−Li1−O2#1	97.9(3)	O3−Li2−O4#1	108.5(3)
O1−Li1−O3	150.8(2)	O3−Li2−O5	149.5(2)
O1−Li1−O3#1	92.87(15)	O3−Li2−O5#1	91.13(14)
O2−Li1−O1#1	97.9(3)	O4−Li2−O3#1	108.5(3)
O2−Li1−O2#1	176.9(8)	O4−Li2−O4#1	177.8(6)
O2−Li1−O3	73.4(3)	O4−Li2−O5	80.2(2)
O2−Li1−O3#1	109.0(4)	O4−Li2−O5#1	98.4(3)
O3−Li1−O1#1	92.87(15)	O5−Li2−O3#1	91.13(14)
O3−Li1−O2#1	109.0(4)	O5−Li2−O4#1	98.4(3)
O3−Li1−O3#1	84.4(4)	O5−Li2−O5#1	107.5(5)
O1#1−Li1−O2#1	80.1(2)	O3#1−Li2−O4#1	73.2(2)
O1#1−Li1−O3#1	150.8(2)	O3#1−Li2−O5#1	149.5(2)
O2#1−Li1−O3#1	73.4(3)	O4#1−Li2−O5#1	80.2(2)

[a] Symmetry transformation: (#1) $-x + 1$, y, $-z + {}^1/_2$.

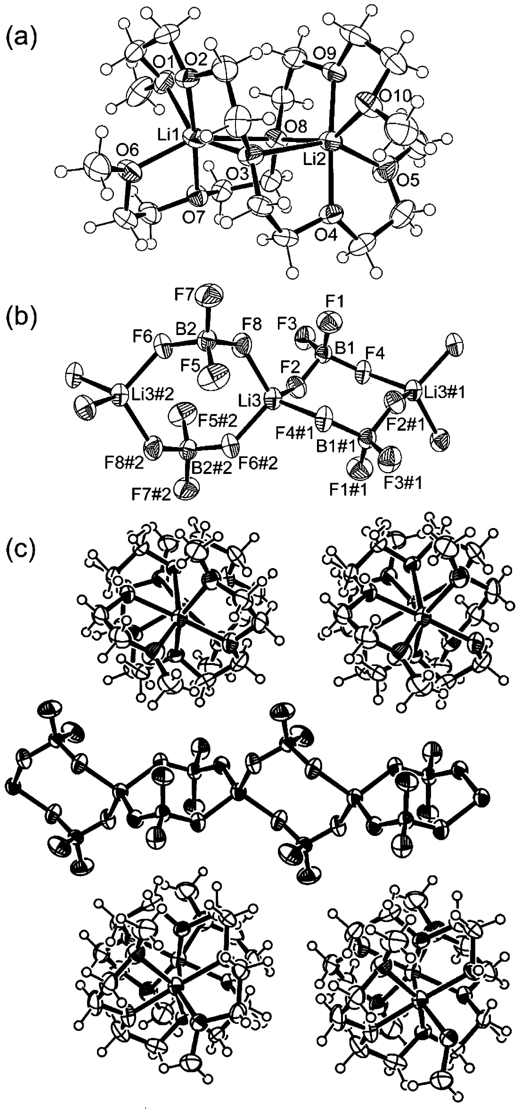

Figure 2. Li$^+$ cation coordination environment in $(G4)_{1/2}$:$LiBF_4$: (a) double-helix dimer viewed laterally, (b) linear $(...(BF_4^-)_2...Li^+)_n$ chain and (c) packing arrangement of the linear $(...(BF_4^-)_2...Li^+)_n$ chains and double-helix dimers (viewed axially) (Li3 and Li4 are in separate ionic chains—not shown). Thermal ellipsoids drawn at 50% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(G4)_{1/2}$:$LiBF_4$

Li1−O1	2.263(4)	Li2−O9	2.015(4)
Li1−O2	1.982(4)	Li2−O10	2.091(4)
Li1−O3	2.279(4)	Li3−F2	1.875(4)
Li1−O6	2.030(4)	Li3−F4#1[a]	1.866(4)
Li1−O7	2.040(4)	Li3−F6#2[b]	1.868(4)
Li1−O8	2.655(4)	Li3−F8	1.883(4)
Li2−O3	2.607(4)	Li4−F9	1.854(7)
Li2−O4	2.033(4)	Li4−F12#3[c]	1.905(8)
Li2−O5	2.075(4)	Li4−F13	1.862(4)
Li2−O8	2.175(4)	Li4−F16#4[d]	1.855(4)
O1−Li1−O2	77.46(15)	O4−Li2−O8	104.38(18)
O1−Li1−O3	146.66(19)	O4−Li2−O9	176.6(2)
O1−Li1−O6	98.42(18)	O4−Li2−O10	100.81(18)
O1−Li1−O7	101.86(18)	O5−Li2−O8	97.45(18)
O1−Li1−O8	92.32(14)	O5−Li2−O9	97.69(19)
O2−Li1−O3	76.59(14)	O5−Li2−O10	104.7(2)
O2−Li1−O6	95.58(18)	O8−Li2−O9	77.14(15)
O2−Li1−O7	176.3(2)	O8−Li2−O10	149.1(2)
O2−Li1−O8	113.58(18)	O9−Li2−O10	78.73(16)
O3−Li1−O6	104.59(18)	F2−Li3−F4#1	104.10(19)
O3−Li1−O7	105.32(18)	F2−Li3−F6#2	111.0(2)
O3−Li1−O8	79.34(13)	F2−Li3−F8	109.0(2)
O6−Li1−O7	80.86(15)	F4#1−Li3−F6#2	108.2(2)
O6−Li1−O8	150.53(19)	F4#1−Li3−F8	116.7(2)
O7−Li1−O8	70.07(13)	F6#2−Li3−F8	107.69(19)
O3−Li2−O4	71.85(13)	F9−Li4−F12#3	107.3(6)
O3−Li2−O5	149.8(2)	F9−Li4−F13	113.0(5)
O3−Li2−O8	82.28(14)	F9−Li4−F16#4	110.2(4)
O3−Li2−O9	111.48(18)	F12#3−Li4−F13	106.6(4)
O3−Li2−O10	88.89(15)	F12#3−Li4−F16#4	115.0(6)
O4−Li2−O5	79.12(16)	F13−Li4−F16#4	104.62(19)

[a−d] Symmetry transformations: [a](#1) $-x$, $-y - 2$, $-z$. [b](#2) $-x$, $-y - 1$, $-z$. [c](#3) $-x + 1$, $-y - 2$, $-z$. [d](#4) $-x + 1$, $-y - 1$, $-z$.

(Figure 2a). The O−Li distances of the noncentral EOs are again short (1.982(4)−2.263(4) Å). The bidentate central EOs, in this case, have one shorter O−Li (2.175(4) and 2.279(4) Å) and one longer O−Li (2.607(4) and 2.655(4) Å) distance (Table 3). It is not clear why the dimer adopts a different symmetry from that found in $(G4)_1$:$LiAsF_6$. In the second coordination site, the other half of the Li$^+$ cations are coordinated by the BF_4^- anions forming linear ionic chains (Figure 2b). These cations have tetrahedral coordination by four fluorine atoms (one each from four anions). The F−Li distances are 1.854(7)−1.905(8) Å (Table 3). Each of the BF_4^- anions is coordinated to two Li$^+$ cations. One of the BF_4^- anions is disordered over three positions of equal occupancy (see Supporting Information). The anions thus form linear $(...(BF_4^-)_2...Li^+)_n$ chains arranged between the $[(G4)Li]_2^{2+}$ double-helix dimers (Figure 2c).

Single-Crystal Structure of $(G4)_{2/5}$:$LiCF_3CO_2$. Crystallographic data for $(G4)_{2/5}$:$LiCF_3CO_2$ are reported in Table 1. This structure also has two different Li$^+$ cation coordination sites (Figure 3). In the first, the G4 molecules are coordinated to two cations (Figure 4a). Each cation is coordinated by three EOs from a G4 molecule with the central EO of each molecule coordinated to both cations in a manner similar to that found in the previously noted $[(G4)Li]_2^{2+}$ dimers in $(G4)_1$:$LiAsF_6$ and $(G4)_{1/2}$:$LiBF_4$. The Li$^+$ cations, however, now have 5-fold coordination by three EOs and two anions. One anion is coordinated to both cations through a single anion oxygen donor atom. The second oxygen donor atom of the anion is coordinated to a cation in the second site. These anions are thus coordinated to three different Li$^+$ cations. The second anion coordinating each cation in the first site also coordinates a cation

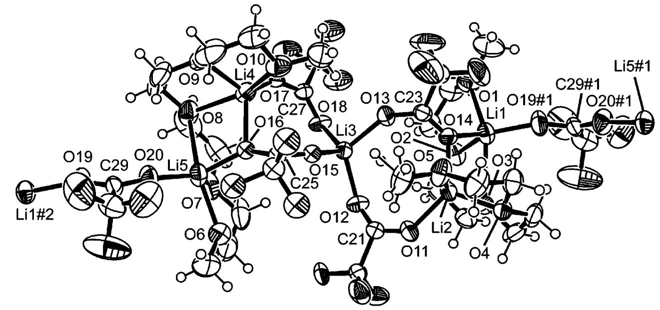

Figure 3. Asymmetric unit of $(G4)_{2/5}$:$LiCF_3CO_2$. Thermal ellipsoids drawn at 50% probability.

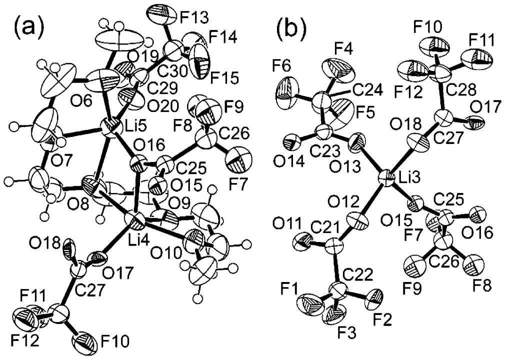

Figure 4. Li^+ cation coordination environment of (a) Li4 and Li5 and (b) Li3 in $(G4)_{2/5}$:$LiCF_3CO_2$. Thermal ellipsoids drawn at 50% probability.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $(G4)_{2/5}$:$LiCF_3CO_2$

Li1−O1	2.077(19)	Li3−O15	1.947(12)
Li1−O2	2.091(15)	Li3−O18	2.00(3)
Li1−O3	2.460(12)	Li4−O8	2.276(7)
Li1−O14	1.916(6)	Li4−O9	2.065(7)
Li1−O19#1[a]	1.868(6)	Li4−O10	2.111(7)
Li2−O3	2.323(12)	Li4−O16	2.021(12)
Li2−O4	2.008(10)	Li4−O17	1.88(2)
Li2−O5	2.056(14)	Li5−O6	2.086(8)
Li2−O11	1.879(6)	Li5−O7	2.062(7)
Li2−O14	1.954(6)	Li5−O8	2.388(7)
Li3−O12	1.920(6)	Li5−O16	1.846(12)
Li3−O13	1.933(6)	Li5−O20	1.859(7)
O1−Li1−O2	79.8(6)	O13−Li3−O15	98.1(6)
O1−Li1−O3	152.8(7)	O13−Li3−O18	106.0(11)
O1−Li1−O14	100.0(12)	O15−Li3−O18	117.5(10)
O1−Li1−O19#1	101.4(10)	O8−Li4−O9	75.7(2)
O2−Li1−O3	73.5(3)	O8−Li4−O10	152.0(3)
O2−Li1−O14	103.9(6)	O8−Li4−O16	82.0(3)
O2−Li1−O19#1	134.2(7)	O8−Li4−O17	99.1(10)
O3−Li1−O14	82.1(3)	O9−Li4−O10	78.5(3)
O3−Li1−O19#1	100.6(3)	O9−Li4−O16	110.4(6)
O14−Li1−O19#1	120.5(4)	O9−Li4−O17	129.2(9)
O3−Li2−O4	77.3(3)	O10−Li4−O16	97.0(4)
O3−Li2−O5	155.0(6)	O10−Li4−O17	105.7(9)
O3−Li2−O11	97.3(4)	O16−Li4−O17	118.9(9)
O3−Li2−O14	85.1(3)	O6−Li5−O7	79.8(3)
O4−Li2−O5	81.2(4)	O6−Li5−O8	153.4(4)
O4−Li2−O11	116.4(4)	O6−Li5−O16	96.5(5)
O4−Li2−O14	114.8(4)	O6−Li5−O20	101.9(3)
O5−Li2−O11	103.6(8)	O7−Li5−O8	74.4(3)
O5−Li2−O14	92.6(8)	O7−Li5−O16	101.5(6)
O11−Li2−O14	127.9(3)	O7−Li5−O20	128.6(4)
O12−Li3−O13	117.6(3)	O8−Li5−O16	82.7(4)
O12−Li3−O15	106.1(5)	O8−Li5−O20	99.1(3)
O12−Li3−O18	111.3(7)	O16−Li5−O20	128.6(7)

[a] Symmetry transformation: (#1) $x - 1, -y + {}^1/_2, z - {}^1/_2$.

in the second site and these anions are coordinated to two different Li^+ cations. The four-coordinate Li^+ cations in the second site are tetrahedrally coordinated by four anions (Figure 4b) and serve as bridges between the G4−Li^+ cation solvates. The cental EOs of the G4 molecules (e.g., O3 and O8) which coordinate two Li^+ cations have longer O−Li distances than the remaining EOs, which coordinate a single Li^+ cation (Table 4). The structure of $(G4)_{2/5}$:$LiCF_3CO_2$ contains several disordered groups including one G4 molecule and several $CF_3CO_2^-$ anions (see Supporting Information).

Ionic Association. In ether−salt mixtures, the relatively high donor and low acceptor numbers of the solvents indicate that salt solvation occurs almost exclusively through solvent donor−cation interactions.[14] EOs do not form coordination bonds with anions. The solvate species that form in such mixtures, therefore, are determined by the competitive coordination of the solvent donor atoms and anions to the cations. Various species may thus exist due to ionic association including solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and aggregates (AGGs), depending upon whether no cations, a single cation, or more than one cation is coordinated to each anion. A detailed examination of the phase behavior of various lithium salts in glyme mixtures suggests the following order for ionic association interactions in aprotic solvents:[15]

$$LiCF_3CO_2 \gg LiNO_3 \sim LiBr > LiCF_3SO_3 \gg LiBF_4 > LiClO_4 \sim LiI \gg LiN(SO_2CF_3)_2\ (LiTFSI) \sim LiN(SO_2C_2F_5)_2\ (LiBETI) \sim LiAsF_6 > LiBPh_4$$

The influence of ionic association on phase behavior can clearly be seen from an examination of the phase diagrams of G4 with $LiAsF_6$, $LiBF_4$, and $LiCF_3CO_2$.[15] $LiAsF_6$ forms a SSIP $(G4)_1$:LiX phase with a relatively high melting temperature. The more associated $LiBF_4$ also forms a $(G4)_1$:LiX phase, but with a lower melting temperature (T_m = 35 °C) in addition to a SSIP/AGG $(G4)_{1/2}$:LiX phase. The most associated salt studied, $LiCF_3CO_2$, forms neither a SSIP $(G4)_1$:LiX nor SSIP/AGG $(G4)_{1/2}$:LiX phase. Instead, the first phase to form is a AGG $(G4)_{2/5}$:LiX phase. In addition, phase diagrams indicate that LiBETI, $LiClO_4$, and LiI also form $(G4)_1$:LiX phases while $LiCF_3SO_3$ only forms a AGG $(G4)_{1/3}$:LiX phase (see Supporting Information).[15]

The structure of $(G4)_1$:$LiAsF_6$ appears to resemble that found in the SSIP $P(EO)_6$:$LiAsF_6$ crystal structure.[16] In this latter structure, two PEO chains wrap around the cations, forming cylinders with the anions arranged in rows between the cylinders. The anions do not coordinate the Li^+ cations. The two solvate structures differ, however, in that each PEO chain adopts a nonhelical conformation, forming a half-cylinder. Only five of the six EOs in the $P(EO)_6$:$LiAsF_6$ crystal structure are strongly coordinated to the cation (O−Li distances are 1.9−2.2 Å). The sixth EO is >3.0 Å from the cation. In $(G4)_1$:$LiAsF_6$, however, the chains adopt a helical conformation which interlocks to form double-helix dimer solvates (Figure 1). Six EOs are coordinated to each cation—four are coordinated strongly and two more weakly. The double-helix dimers represent a new

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form of polyether−Li$^+$ cation coordination with some similarities to that found in diglyme $(G2)_2$:LiX solvates.[17−20] As two of the EOs coordinate both cations, the EO/Li ratio of the double-helix dimer solvates is actually 5/1 rather than 6/1.

It is assumed that the $(G4)_1$:$LiBF_4$ phase resembles $(G4)_1$:$LiAsF_6$ from the similarity of the SSIP $[(G4)Li]_2^{2+}$ dimers found in both structures. The formation of a SSIP $(G4)_1$:$LiBF_4$ dimer phase is surprising since a SSIP $P(EO)_6$:$LiBF_4$ crystalline phase does not form.[15] $LiClO_4$, which is somewhat more dissociated than $LiBF_4$ in ether solvents, forms a $(G4)_1$:$LiClO_4$ phase, a $(G4)_{1/2}$:$LiClO_4$ phase, and a $P(EO)_6$:$LiClO_4$ phase. The latter is isostructural to the SSIP $P(EO)_6$:$LiAsF_6$ phase in which the anions are not coordinated to the Li$^+$ cations.[6,21−23] The ClO_4^- and BF_4^- anions have the same geometry and nearly identical sizes.[24] The difference in phase formation may therefore be related to the subtle difference in the ionic association strength (e.g., electrostatic interaction between the Li$^+$ cations and anions) of the two salts. The possible higher coordination of a $(G4)_1$:$LiBF_4$ phase relative to a two-chain $P(EO)_6$:$LiBF_4$ phase may account for the formation of the former. The crystallization kinetics of the $(G4)_1$:LiX phase with $LiBF_4$ are very slow (even at −5 °C), as might be expected if many of the ions remain associated in the amorphous phase whereas the same phase formed much more readily with $LiClO_4$. The $LiClO_4$ and $LiBF_4$ salts thus have borderline or intermediate phase behavior between the highly dissociated (e.g., $LiAsF_6$) and highly associated (e.g., $LiCF_3CO_2$) salts.[15]

The solvate structure of $(G4)_{2/5}$:$LiCF_3CO_2$ in which the cations are coordinated to three EOs and two anions bears a close resemblance to that found in $P(EO)_3$:LiX crystal structures,[23] but differs slightly due to one of the EOs being coordinated to two cations. In all three of the $(G4)_n$:LiX crystal structures reported, the G4 molecules adopt a similar conformation when coordinated to two Li$^+$ cations (Figure 5). The EOs coordinate a single Li$^+$ cation except for the central EO, which is coordinated to two cations. In contrast, all of the EOs in the $P(EO)_3$:LiX crystal structures are reported to be coordinated to a single Li$^+$ cation. A partial structure solution for the $(G4)_{1/3}$:$LiCF_3SO_3$ phase (see Supporting Information), however, suggests that a different form of coordination is possible with a G4 molecule coordinating three Li$^+$ cations instead of two.

The $(G4)_n$:LiX crystal structures differ significantly from $(G4)_n$:NaX solvate structures with the larger Na$^+$ cation. An AGG $(G4)_1$:$NaCF_3SO_3$ complex has been reported in which all five EOs from a single G4 molecule coordinate a Na$^+$ cation in addition to two oxygen donor atoms (one each from two anions).[25] Each anion, in turn, is coordinated to two Na$^+$ cations, resulting in a linear polymeric structure. Other CIP $(G4)_n$:NaX crystal structures have also been reported.[26−28] The Na$^+$ cations in these structures are coordinated to a single anion and all five EOs of the G4 molecules with the G4 molecules adopting a crown ether-like (i.e., 15-crown-5) conformation.

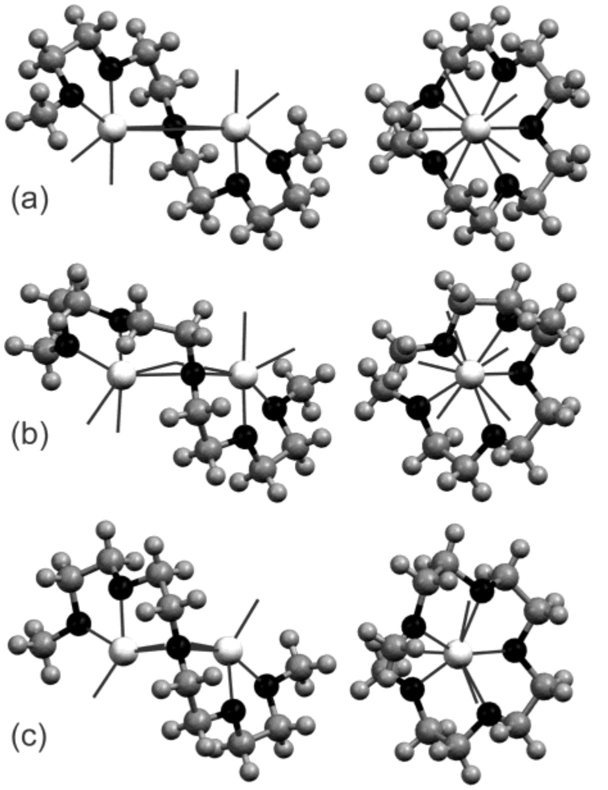

Figure 5. G4 molecular conformations in (a) $(G4)_1$:$LiAsF_6$, (b) $(G4)_{1/2}$:$LiBF_4$, and (c) $(G4)_{2/5}$:$LiCF_3CO_2$.

Li$^+$ Cation Transport Mechanisms in Highly Associated PEO Electrolytes. The Li$^+$ cation coordination found in $(G4)_{1/2}$:$LiBF_4$ and $(G4)_{2/5}$:$LiCF_3CO_2$ in which the cations are coordinated solely by four BF_4^- or $CF_3CO_2^-$ anions, respectively, offers a clue to ionic transport mechanisms in highly concentrated liquid and polymer electrolytes. Such 4-fold Li$^+$ cation coordination by anions was also observed in the crystalline solvate structures of $(G3)_{1/2}$:$LiCF_3SO_3$,[25] $(G2)_{1/2}$:$LiCF_3SO_3$,[29] and $(G2)_{1/3}$:$LiCF_3CO_2$.[29] Molecular models of a concentrated amorphous $P(EO)_n$−LiI (EO/Li = 8) electrolyte at 127 °C indicated that the Li$^+$ cations were coordinated by three to five EOs and one or two I$^-$ anions. Transition states were found in which the cations lost coordination to the polymer EOs and became coordinated by four (or five) anions following which a new polymer chain would coordinate the cations (in addition to one or two anions).[2] The anomalously high coordination numbers may be attributed to the method by which

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cation coordination was determined (if an EO or I^- anion was within 4 or 5 Å of a Li^+ cation, respectively, it was reported as coordinated to the cation). Li^+ cation transport between polyether chains in concentrated electrolytes, therefore, does not require that the cations remain coordinated to one or more polyether chains. The anions may serve as a "bridge" between the chains by creating a favorable transition state with 4-fold Li^+ cation coordination.

Li^+ Cation Transport Mechanisms in Dissociated PEO Electrolytes. The double-helix dimer solvates found in $(G4)_1$:$LiAsF_6$ and $(G4)_{1/2}$:$LiBF_4$ represent a novel form of Li^+ cation coordination not previously reported. These solvates differ from those observed in the $P(EO)_6$:LiX (X = PF_6, AsF_6, SbF_6) crystal structures, which also contain Li^+ cations coordinated by two polyether chains.[16,30] It is unclear whether longer PEO chains could adopt the same conformations as found in $(G4)_1$:$LiAsF_6$ and $(G4)_{1/2}$:$LiBF_4$, enabling the formation of a $P(EO)_5$:LiX crystal structure. No such crystal structures have yet been reported, although a phase diagram for P(EO)−$LiBPh_4$ [31] and P(EO)−$LiN(COCF_3)_2$ [32] indicate that these salts may form $P(EO)_5$:LiX phases.

No crystal structures have yet been determined in which all five of the G4 EOs are coordinated to a single Li^+ cation, although molecular models have indicated that this should be possible.[33,34] These calculated structures are SSIPs in which the polyether chains fully encapsulate the cations. Such solvates may not form crystalline phases because the higher coordination (6-fold) in the $[(G4)Li]_2^{2+}$ dimers is more favorable. Thus, Li^+ cations may be fully coordinated to five or six EOs from a single PEO chain in an amorphous $P(EO)_n$−LiX phase.

Molecular models of amorphous $P(EO)_n$−LiI electrolytes indicate that there is a strong preference for Li^+ cation coordination to a single rather than two PEO chains.[2,3] The transfer of the single-chain coordinated cation to a new chain, required for macroscopic ionic transport, may occur when a second chain coordinates the Li^+ cation in a manner resembling the dimers in $(G4)_1$:$LiAsF_6$ and $(G4)_{1/2}$:$LiBF_4$ or that found in the $P(EO)_6$:LiX (X = PF_6, AsF_6, SbF_6) structures. These transition states would retain a high coordination number for the cations without requiring anion coordination (i.e., the formation of CIPs or AGGs). Alternatively, the cations may be coordinated to two chains and simply move along the two chains if the neighboring EOs are uncoordinated. Note that although the dimers in $(G4)_1$:$LiAsF_6$ and $(G4)_{1/2}$:$LiBF_4$ and the cylinders in the $P(EO)_6$:LiX (X = PF_6, AsF_6, SbF_6) structures appear to offer a facile means of Li^+ cation transport "down the tubes or cylinders" to neighboring vacant sites, the polyether chain conformations creating such tubes or cylinders are unlikely to be retained if the EOs are not coordinating a cation. This would result in multiple EO lone pairs oriented toward one another without the positive charge shielding effect from a cation. Thus, these forms of polymer chain orientations probably exist only around the solvated cations (in either crystalline or amorphous solvates).

Acknowledgment. W.A.H. is indebted to the National Science Foundation for the award of a NSF Graduate Research Fellowship and the University of Minnesota for a Graduate Research Fellowship.

Supporting Information Available: X-ray crystallographic data (CIFs) for $(G4)_1$:$LiAsF_6$, $(G4)_{1/2}$:$LiBF_4$, and $(G4)_{2/5}$:$LiCF_3CO_2$. Structure refinement and additional drawings for structures $(G4)_1$:$LiAsF_6$, $(G4)_{1/2}$:$LiBF_4$, and $(G4)_{2/5}$:$LiCF_3CO_2$. Partial structure solution for $(G4)_{1/3}$:$LiCF_3SO_3$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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