

Characterization of Crystalline and Solution Phases of Diglyme–LiSbF<sub>6</sub>Varuni Seneviratne,<sup>†</sup> Roger Frech,<sup>\*,‡</sup> J. E. Furneaux,<sup>†</sup> and Masood Khan<sup>‡</sup>Department of Physics and Astronomy and Department of Chemistry and Biochemistry,  
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Received: September 30, 2003; In Final Form: March 5, 2004

Solutions of lithium hexafluoroantimonate, LiSbF<sub>6</sub>, dissolved in diethylene glycol dimethyl ether (diglyme), CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub>, are used as a model for high molecular weight poly(ethylene oxide), PEO, complexed with LiSbF<sub>6</sub>. During this work, a 2:1 diglyme:LiSbF<sub>6</sub> crystal was discovered and its structure solved by single-crystal X-ray diffraction techniques. The compound crystallizes in the orthorhombic *Pccn* space group with *Z* = 4. In this crystal, the lithium ion is 6-fold coordinated by two diglyme molecules, while the anions are isolated. Raman and FTIR vibrational spectroscopy were used to study both the crystal and a series of diglyme–LiSbF<sub>6</sub> solutions. Similarities in modes sensitive to molecular conformation show that the local conformational structure in the crystal also occurs in diglyme–LiSbF<sub>6</sub> solutions.

## 1. Introduction

To develop new polymer electrolytes with technologically important room-temperature conductivities on the order of 10<sup>−4</sup> S cm<sup>−1</sup>, fundamental factors controlling ionic conductivity have been extensively studied. These factors include ion–ion interactions (ionic association)<sup>1</sup> and ion–polymer interactions (polymer conformation and segmental motion).<sup>2</sup> It has proven useful to study these interactions through their effect on the structures of polymer salt compounds<sup>3</sup> and oligomer–salt compounds.<sup>4</sup> Solved crystal structures have recently become available for a number of compounds comprised of lithium and sodium salts complexed with poly(ethylene oxide), PEO,<sup>5–7</sup> and very short chain oligo PEO (glymes).<sup>4,8,9</sup>

In this paper, we will investigate complexes of lithium hexafluoroantimonate, LiSbF<sub>6</sub>, complexed with diethylene glycol dimethyl ether (diglyme), CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub>. Diglyme has been used as a model compound for high molecular weight PEO<sup>8</sup> and has also been used as a solvent or a cosolvent in electrolytes for secondary lithium batteries.<sup>10</sup> Pure diglyme has several conformations in its liquid state, whereas solid diglyme has the same conformation as found in crystalline high-molecular weight PEO.<sup>11–13</sup> Conformational changes in diglyme are induced by coordinating metal ions that alter the OCCO torsional angles. In the present work, we report the crystal structure of 2:1 diglyme:LiSbF<sub>6</sub> and utilize it to gain a deeper insight into diglyme–LiSbF<sub>6</sub> solutions.

## 2. Experimental Section

LiSbF<sub>6</sub> (Alpha Aesar, 99%) and diglyme (Aldrich, 99.5%) were used as received. Diglyme–LiSbF<sub>6</sub> solutions at various concentrations described by their ether oxygen to cation atomic ratio (EO:Li) were prepared in an N<sub>2</sub>-filled drybox (H<sub>2</sub>O < 1 ppm). Some solutions were stored in the glovebox to allow crystals to form by slow evaporation. From the initial 30:1 solution, millimeter-size crystals were obtained in about two weeks.

A colorless crystal (0.38 × 0.36 × 0.32 mm) of (C<sub>12</sub>H<sub>28</sub>F<sub>6</sub>LiO<sub>6</sub>Sb) complex was used for X-ray diffraction measurement. The data were collected at 153(2) K on a Bruker P4 diffractometer with MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The data were corrected for Lorentz and polarization effects, and an absorption correction based on psi-scans was applied. The (C<sub>12</sub>H<sub>28</sub>F<sub>6</sub>LiO<sub>6</sub>Sb) complex crystallizes in orthorhombic space group *Pccn* (determined from systematic extinctions) with *Z* = 4. Unit cell parameters and the structure are described in detail in the following section. The final R1 = 0.053 is based on 1289 “observed reflections” [*I* > 2 $\sigma$ (*I*)], and wR<sup>2</sup> = 0.148 is based on all reflections (1788 unique data).

Fourier transform infrared (FTIR) spectra of diglyme–LiSbF<sub>6</sub> both as crystals and as dilute solutions were collected from 400 to 4000 cm<sup>−1</sup> using a Bruker IFS66V FTIR spectrometer at a spectral resolution of 1 cm<sup>−1</sup>, a KBr beam splitter, and a DTGS detector. (Diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal samples were dispersed in KBr pellets to measure IR spectra. The spectra of diglyme–LiSbF<sub>6</sub> solutions were recorded using a thin layer spread between two ZnSe windows under dry air purge.

Raman scattering spectra were recorded in a backscattering (180°) geometry on an I. S. A. Jobin Yvon T64000 in the triple subtractive mode by adding 10 scans of 16 s each. Spectra of the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal were obtained with the crystal sealed in a cell. To record Raman spectra, the diglyme–LiSbF<sub>6</sub> solutions were put in round glass wells and covered with a microscope cover glass to minimize contact with air.

Differential scanning calorimetry (DSC) thermograms were collected using a Mettler DSC 820 calorimeter. The samples were sealed in 40  $\mu$ L aluminum pans, and data were acquired while sweeping temperature at 5 °C/min with a nitrogen flow of 87 mL/min.

## 3. Results and Discussion

**3.1. (Diglyme)<sub>2</sub>LiSbF<sub>6</sub> Crystal.** First, we report the discovery and structure determination of the 2:1 compound of diglyme with LiSbF<sub>6</sub>, hereafter labeled (diglyme)<sub>2</sub>LiSbF<sub>6</sub>. As noted earlier, the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> compound crystallizes in the orthorhombic *Pccn* space group. Both the SbF<sub>6</sub><sup>−</sup> anion and the Li<sup>+</sup> cation have crystallographic 2-fold symmetry with the Sb

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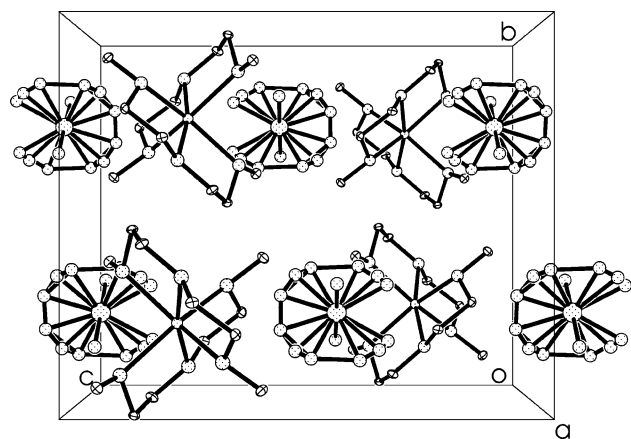


Figure 1. Unit cell of the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal.

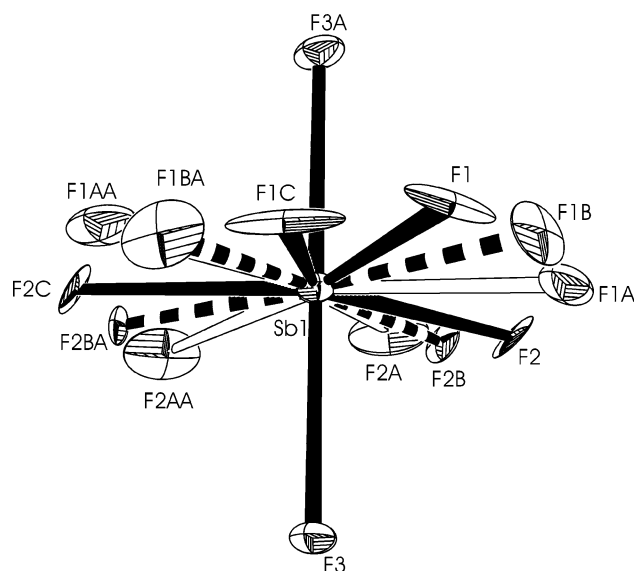


Figure 2. Disorder of the SbF<sub>6</sub><sup>−</sup> anion in the equatorial plane.

and one of the F<sup>−</sup> ions situated along the 2-fold axis. The unit cell dimensions (determined from 50 reflections,  $2\theta = 12.5$ – $40.0^\circ$ ) at 153(2) K are  $a = 11.318(3)$  Å,  $b = 12.196(4)$  Å, and  $c = 14.837(4)$  Å. These data yield a unit cell volume of  $V = 2048(1)$  Å<sup>3</sup> and  $D(\text{calc}) = 1.657$  Mg/m<sup>3</sup>. These dimensions were slightly altered ( $\Delta a = +0.048$  Å,  $\Delta b = +0.051$  Å,  $\Delta c = +0.094$  Å) when the X-ray data were taken at 213(2) K. The asymmetric unit contains one diglyme, 1/2 Li<sup>+</sup> cation, and 1/2 SbF<sub>6</sub><sup>−</sup> anion; thus the unit cell contains four SbF<sub>6</sub><sup>−</sup> anions and four [Li(C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations which pack in the unit cell at 153-(2) K as shown in Figure 1. The SbF<sub>6</sub><sup>−</sup> ion is disordered (indicated by observed peaks in the difference Fourier map) in the equatorial plane, as is more carefully illustrated in Figure 2; the F(1) and F(2) atoms are disordered at three sites. Satisfactory refinement was obtained by using partial occupancy of 40%, 35%, and 25% for the three disordered components. The observed disorder of the anion is essentially identical at 213(2), which suggests that this is static rather than dynamic disorder. A single Li<sup>+</sup> ion is coordinated to six ether oxygen atoms, three from each of two diglyme molecules, as shown in detail for the 153(2) K structure in Figure 3.

It is noteworthy that this crystal structure bears some resemblance to that of the 6:1 compound of high molecular weight PEO with LiSbF<sub>6</sub>, P(EO)<sub>6</sub>LiSbF<sub>6</sub>.<sup>14</sup> In both systems, each cation is “wrapped” by the ethylene oxide units of two organic molecules. More specifically, two diglyme molecules provide

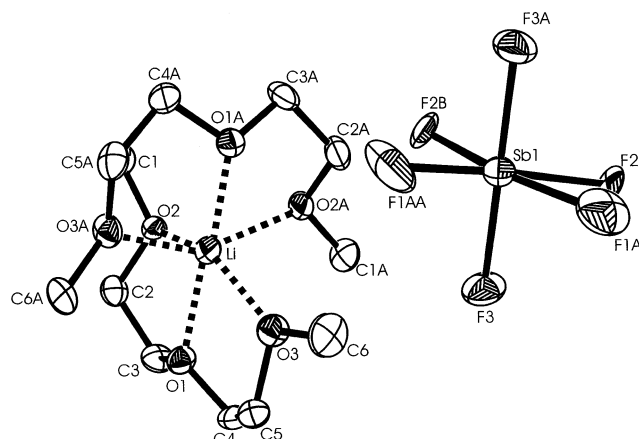


Figure 3. Detail of the lithium ion–diglyme coordination in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal.

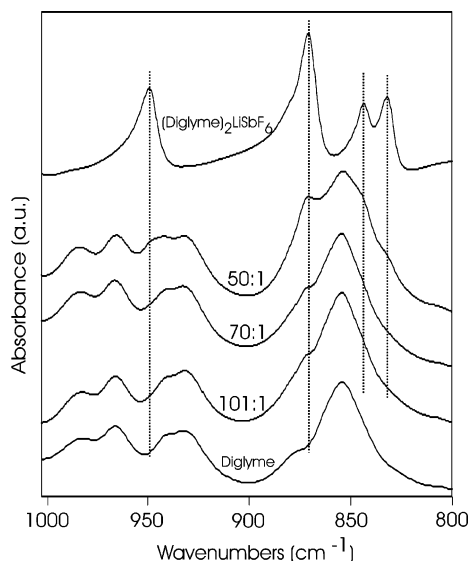
TABLE 1: Dihedral Angles and Li–O Bond Lengths in Crystalline (Diglyme)<sub>2</sub>LiSbF<sub>6</sub> and (Diglyme)LiCF<sub>3</sub>SO<sub>3</sub>

|                      | (Diglyme) <sub>2</sub> LiSbF <sub>6</sub> | (Diglyme)LiCF <sub>3</sub> SO <sub>3</sub> |
|----------------------|---|--|
| Dihedral Angle (deg) |   |  |
| C1–O1–C2–C3          | 175.7                                     | −177.4                                     |
| O1–C2–C3–O2          | 57.3                                      | 56.2                                       |
| C2–C3–O2–C4          | 171.4                                     | −175.9                                     |
| C3–O2–C4–C5          | 177.4                                     | 171.6                                      |
| O2–C4–C5–O3          | −53.5                                     | −55.3                                      |
| C4–C5–O3–C6          | 177.3                                     | 179.6                                      |
| Bond Distance (Å)    |   |  |
| Li–O1                | 2.200                                     | 2.166                                      |
| Li–O2                | 2.071                                     | 2.044                                      |
| Li–O3                | 2.173                                     | 2.113                                      |

a 6-fold coordination of the lithium ion in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal, whereas there is a 5-fold coordination of the lithium ion by two PEO chains<sup>14</sup> in the P(EO)<sub>6</sub>LiSbF<sub>6</sub> compound.<sup>14</sup> In both systems there is no direct interaction of the cation with the heteroatoms of the anion. This is in marked contrast to most crystalline PEO-salt compounds whose structures have been solved to date, where the anions participate in the coordination of the cations.<sup>5,6,15</sup>

The conformation of each diglyme molecule in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal is *tgt* – *tgt*, where *t* is trans ( $180^\circ \pm 30^\circ$ ), *g* is gauche ( $60^\circ \pm 30^\circ$ ), and *g* is gauche-minus ( $-60^\circ \pm 30^\circ$ ). The notation *tgt* refers to the bond sequence O–C–C–O, i.e., the conformation about the O–C bond and C–O bond is trans, and the conformation about the C–C bond is gauche. Thus, the conformation of the two O–C–C–O bond sequences in a diglyme molecule is *tgt* – *tgt*. The published 1:1 diglyme:lithium trifluoromethane sulfonate (LiTf) crystal structure indicates the same *tgt* – *tgt* conformation for its diglyme molecules.<sup>8</sup> In that crystal, lithium is 5-fold coordinated with three oxygen atoms from a diglyme molecule and two oxygen atoms, one each from two triflate ions. Although the packing of the two diglyme molecules around the lithium ion in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal appears to differ from the packing of a single diglyme molecule coordinating a lithium ion in the (diglyme)LiCF<sub>3</sub>SO<sub>3</sub> crystal,<sup>8</sup> the torsional angles and Li–O bond lengths are strikingly similar in both crystals, as shown in Table 1.

Baboul et al. reported an ab initio molecular orbital study of the potential energy surface for the interaction of a single Li<sup>+</sup> cation with two diglyme molecules as a model for two PEO chains.<sup>16</sup> That study examined Li<sup>+</sup>–(diglyme)<sub>2</sub> complexes in configurations where Li<sup>+</sup> was coordinated by 3–6 diglyme oxygen atoms. It was found that the minimum energy structure was obtained with six-coordinated Li<sup>+</sup> (with three-coordination



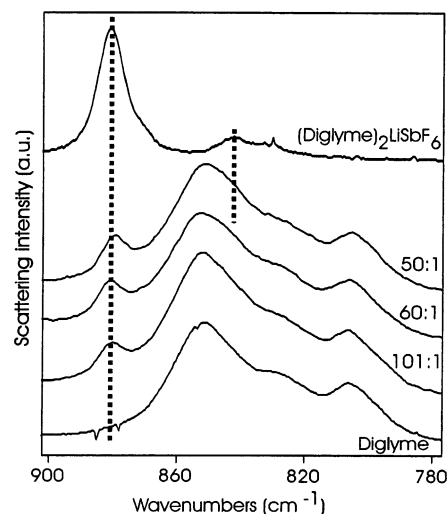
**Figure 4.** IR spectra from 800 to 1000  $\text{cm}^{-1}$  for several solutions of diglyme-LiSbF<sub>6</sub>, crystalline (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, and pure diglyme. The dashed lines mark band positions in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal.

from each diglyme molecule). Both molecules were in a *tgt* - *tgt* conformation. The total dissociation energy of this structure was 121.5 kcal/mol, and the Li-O bond lengths were in the range of 2.11–2.23 Å. Their calculated structure of six-coordinated Li<sup>+</sup>-(diglyme)<sub>2</sub> is very similar to the experimentally determined crystal structure of (diglyme)<sub>2</sub>LiSbF<sub>6</sub> reported here.

DSC was used to study the melting and recrystallization processes in the crystal. The thermograms show that (diglyme)<sub>2</sub>-LiSbF<sub>6</sub> melts with a sharp endothermic peak (onset at 25.6 °C, maximum at 28.5 °C). Recrystallization occurs at 21 °C. In a second temperature sweep, there were no observable changes in the melting or recrystallization peaks, indicating very good reversibility of the thermal transitions.

**3.2. Vibrational Spectroscopy-Conformation Region.** Figure 4 shows IR spectra from 800 to 1000  $\text{cm}^{-1}$  for several diglyme-LiSbF<sub>6</sub> solutions at different compositions, crystalline (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, and pure diglyme. The analogous Raman spectra are shown in Figure 5 for the same systems. Modes in this region are a mixture of CH<sub>2</sub> rocking and CO stretching motions.<sup>17,18</sup> These mode frequencies and intensities are dependent on the OCCO torsional angles and, consequently, backbone conformations. When a salt is dissolved in an ethylene oxide-based system, the interactions between the cations and the ether oxygen atoms change the torsional angles and thus the backbone conformation. Spectral-structural correlations developed in this region for the crystalline compound can then be applied to solutions of diglyme-LiSbF<sub>6</sub> as the salt concentration is changed.

In the IR spectrum of the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal (Figure 4), there are bands at 832, 844, 871, and 949  $\text{cm}^{-1}$ . The Raman spectrum of this crystal (Figure 5) reveals a strong band at 880  $\text{cm}^{-1}$  and a weak band at 842  $\text{cm}^{-1}$ . Because the crystal structure is known from X-ray analysis, these modes can be attributed to two diglyme molecules coordinated by a lithium ion, with the dihedral angle sequence of each diglyme molecule *tgt* - *tgt*, where each C-C bond is in a gauche or gauche-minus conformation. Previous studies have shown that ethylene oxide units with gauche OCCO torsional angles have bands in the range from 825 to 890  $\text{cm}^{-1}$ .<sup>17</sup> Therefore, the IR and Raman bands observed in this study are consistent with the reported structure. It is possible to carry this analysis further. The Raman



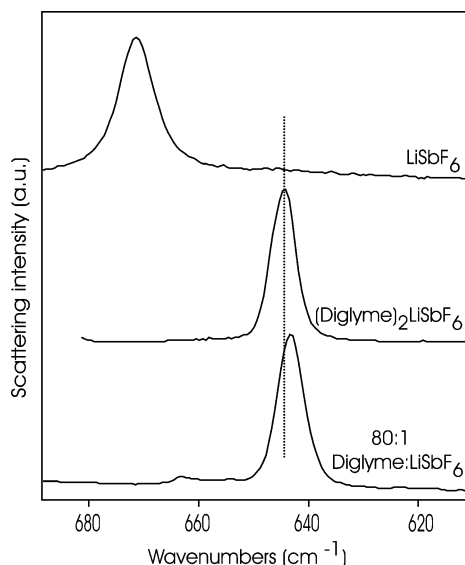
**Figure 5.** Raman spectra from 780 to 880  $\text{cm}^{-1}$  for several solutions of diglyme-LiSbF<sub>6</sub>, crystalline (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, and pure diglyme. The dashed lines mark band positions in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal.

spectrum of the (diglyme)LiCF<sub>3</sub>SO<sub>3</sub> crystal has a strong band at 877  $\text{cm}^{-1}$  and a weaker band at 842  $\text{cm}^{-1}$ .<sup>8</sup> As previously noted, the diglyme molecules in both crystals exhibit the same conformation with strikingly similar values of the dihedral angles. However, in (diglyme)<sub>2</sub>LiSbF<sub>6</sub> there are two diglyme molecules coordinating a single lithium ion, whereas in the (diglyme)LiCF<sub>3</sub>SO<sub>3</sub> crystal, there is only one diglyme molecule coordinating each lithium ion (along with two triflate oxygen atoms, one from each of two triflate anions). This observation strongly argues that the vibrational pattern in the conformation region arises from a single diglyme molecule in a *tgt* - *tgt* conformation coordinated with a lithium ion. Apparently in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal, the vibrations of each diglyme molecule are decoupled. This phenomenon has been previously described in (diglyme)LiCF<sub>3</sub>SO<sub>3</sub> crystals.<sup>19</sup>

The OCCO torsional angles calculated by ab initio methods for the pure diglyme in a *tgt* - *tgt* conformation are about  $\pm 79^\circ$  and  $\pm 72^\circ$ .<sup>20</sup> The relatively high frequencies revealed in the Raman band at 880  $\text{cm}^{-1}$  and in the IR band at 871  $\text{cm}^{-1}$  for the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal compared to both Raman and IR frequencies of pure diglyme indicate smaller OCCO torsional angles (Table 1) present in the crystal. The OCCO torsional angles in the compound are reduced upon coordination with a Li<sup>+</sup> cation.

The vibrational modes originating in the *tgt* - *tgt* conformation of a diglyme molecule coordinating a lithium ion can be unambiguously identified in the spectra of the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal. A careful examination of the IR absorbance spectra of the diglyme-LiSbF<sub>6</sub> solutions (Figure 4) shows the growth of a band at 871  $\text{cm}^{-1}$  whose intensity increases with salt concentration. This band occurs at the same frequency as the most intense band of crystalline (diglyme)<sub>2</sub>LiSbF<sub>6</sub> in this region. It is noteworthy that this band can be seen in the 101:1 sample, the most dilute composition in this study. The bands at 844 and 832  $\text{cm}^{-1}$  seen in the crystal can also be seen in the 50:1 solution. The diglyme bands at 854, 931, 941, 965, and 983  $\text{cm}^{-1}$ , which are present in the solutions, disappear upon formation of the crystal.

Similarly, a Raman band at 880  $\text{cm}^{-1}$  can be seen in the solution spectra in Figure 5, even at very dilute salt concentrations. This band corresponds to the most intense band in the Raman spectrum of the crystal in this region. The broad band at 852  $\text{cm}^{-1}$  in pure diglyme and the solutions completely



**Figure 6.** Raman spectra of pure microcrystalline LiSbF<sub>6</sub>, crystalline (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, and a dilute solution of diglyme–LiSbF<sub>6</sub>. The dashed line marks the band position of the  $\nu_1(A_{1g})$  mode in the (diglyme)<sub>2</sub>LiSbF<sub>6</sub> crystal.

disappears in the crystal. However, a very weak shoulder at 842 cm<sup>−1</sup> in diglyme and the salt solutions persists in the crystal. These data and the IR absorbance data, taken together, show that with the addition of salt the lithium ions coordinate diglyme molecules, forming local structures similar to those in the crystalline phase.

**3.3. Vibrational Spectroscopy–Anion Modes.** The isolated SbF<sub>6</sub><sup>−</sup> anion belongs to the O<sub>h</sub> point group. The six normal modes of vibration can be described by the irreducible representations of the O<sub>h</sub> point group as follows:

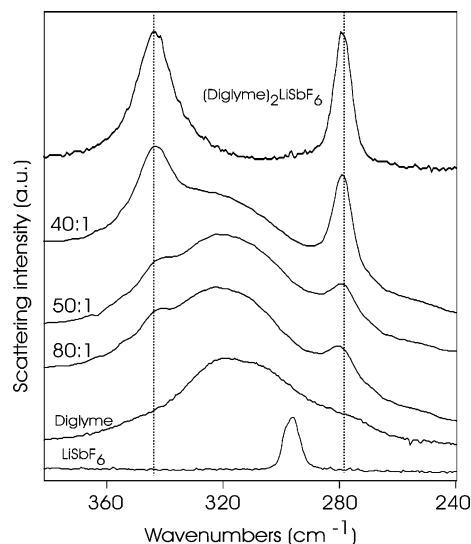
$$\Gamma(\text{SbF}_6^-) = A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$$

The  $\nu_1(A_{1g})$ ,  $\nu_2(E_g)$  and  $\nu_5(F_{2g})$  modes are only Raman active,  $\nu_3(F_{1u})$  and  $\nu_4(F_{1u})$  are only infrared active, and  $\nu_6(F_{2u})$  is inactive in both Raman and IR.<sup>21</sup> The  $\nu_1(A_{1g})$  mode is nondegenerate and gives an intense, symmetric band at 671 cm<sup>−1</sup> in LiSbF<sub>6</sub> (Figure 6). The Raman spectra of (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, dilute solutions of diglyme–LiSbF<sub>6</sub>, and P(EO)<sub>6</sub>LiSbF<sub>6</sub> have a band at 644 cm<sup>−1</sup>, which is assigned to the  $\nu_1(A_{1g})$  mode. These peaks are highly symmetrical, showing that the SbF<sub>6</sub><sup>−</sup> is a “spectroscopically free” anion in the crystal as well as in the solutions. If ionic association were present to a significant extent, then multiple bands would be expected in this region.

Figure 7 shows Raman spectra from 240 to 380 cm<sup>−1</sup> for LiSbF<sub>6</sub>, diglyme, (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, and solutions of diglyme–LiSbF<sub>6</sub> with different EO:Li ratios. The triply degenerate  $\nu_5(F_{2g})$  mode of SbF<sub>6</sub><sup>−</sup> in crystalline LiSbF<sub>6</sub> is at 296 cm<sup>−1</sup> and in diglyme–LiSbF<sub>6</sub> solutions is at 279 cm<sup>−1</sup>. The broad diglyme band centered at about 320 cm<sup>−1</sup> decreases as the salt concentration increases in (diglyme)<sub>2</sub>LiSbF<sub>6</sub> while a new band appears at about 342 cm<sup>−1</sup> in the 80:1 solution. The intensity of this new band grows with increasing salt concentration. Although this is most likely a diglyme band, it is also possible that this is the infrared-active  $\nu_4(F_{1u})$  mode of SbF<sub>6</sub><sup>−</sup>, which has become Raman active due to the change in vibrational potential energy environment.

#### 4. Summary

The 2:1 compound of diglyme with LiSbF<sub>6</sub>, (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, was found to crystallize with four asymmetric units



**Figure 7.** Raman spectra from 240 to 380 cm<sup>−1</sup> for LiSbF<sub>6</sub>, diglyme, (diglyme)<sub>2</sub>LiSbF<sub>6</sub>, and solutions of diglyme–LiSbF<sub>6</sub>.

in a unit cell described by the space group *Pccn*. Each lithium ion is 6-fold coordinated by two diglyme molecules, with each oxygen atom of the two molecules fully participating in the coordination sphere as evidenced by the relatively uniform Li–O distances. The SbF<sub>6</sub><sup>−</sup> anion is solvent-separated from the lithium ion. The conformation of the diglyme molecule is *tgt* – *tgt* which is the same conformation seen in crystals of (diglyme)LiCF<sub>3</sub>SO<sub>3</sub>. In that system the crystal is composed of discrete (diglyme:LiCF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> dimers. The striking similarity of the values of the dihedral angles and Li–O distances in these two systems, and the remarkable similarity of the vibrational modes in spectral regions sensitive to conformation suggests that the frequencies of these modes can be used as a specific spectral marker for the particular local structure common to both crystals: a single lithium ion coordinating a single diglyme molecule resulting in a *tgt* – *tgt* conformation of the diglyme.

However, this conclusion is incomplete without considering pure diglyme. A calculation results in a *tgt* – *tgt* conformation, but with OCCO angles of 79 and −72°, considerably larger in magnitude than either (diglyme)<sub>2</sub>LiSbF<sub>6</sub> (57.3°, −53.5°) or (diglyme)LiCF<sub>3</sub>SO<sub>3</sub> (56.2°, −55.3°). The coordination of the diglyme molecule by the lithium ion therefore plays a critical role, and the local structure specific to the vibrational mode pattern in the conformation region is a lithium ion–diglyme moiety in which the diglyme molecule has a *tgt* – *tgt* conformation whose dihedral angles are similar to those observed in the two crystals. One might further expect that the Li–O distance of the moiety should be roughly similar to yield the same frequencies and band intensities.

As noted in the Results section, these local structures persist in solutions of LiSbF<sub>6</sub> in diglyme at surprisingly (to us) low salt concentrations. Evidence of local structures is also observed in solutions of LiCF<sub>3</sub>SO<sub>3</sub> in diglyme. Finally, the SbF<sub>6</sub><sup>−</sup> anion appears to be spectroscopically “free” in diglyme–LiSbF<sub>6</sub> solutions at all concentrations.

**Acknowledgment.** This work was supported by a grant from the Research Corporation, RA0306, and a grant from NASA EPSCoR. We would like to acknowledge useful conversations with Prof. Peter Bruce and Dr. Yuri Andreev, University of St. Andrews.



## References and Notes

- (1) Bruce, P. G.; Vincent, C. A. *Faraday Discuss. Chem. Soc.* **1989**, 88, 43.
- (2) Bruce, P. G.; Vincent, C. A. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 3187.
- (3) Frech, R.; Chintapalli, S.; Bruce, P. G.; Vincent, C. A. *Macromolecules* **1999**, 32, 808.
- (4) Rhodes, C. P.; Khan, M.; Frech, R. *J. Phys. Chem B* **2002**, 106, 10330.
- (5) Lightfoot, P.; Mehta, M. A.; Bruce, P. G. *Science* **1993**, 262, 883.
- (6) Andreev, Y. G.; Lightfoot, P.; Bruce, P. G. *J. Chem. Soc. Chem. Commun.* **1996**, 2169.
- (7) Andreev, Y. G.; MacGlashan, G. S.; Bruce, P. G. *Phys. Rev. B* **1997**, 55, 12011.
- (8) Rhodes, C. P.; Frech, R. *Macromolecules* **2001**, 34, 2660.
- (9) Henderson, W. A. Ph.D. Thesis, University of Minnesota, Twin Cities, MN, 2002.
- (10) Geoffroy, I.; Willmann, P.; Mestar, K.; Carre, B.; Lemordant, D. *Electrochim. Acta* **2000**, 45, 2019.
- (11) Matsuura, H.; Fukuhara, K.; Tamaoki, H. *J. Mol. Struct.* **1987**, 156, 293.
- (12) Matsuura, H.; Miyazawa, T.; Machida, K. *Spectrochim. Acta* **1973**, 29A, 771.
- (13) Takahashi, Y.; Tadokoro, H. *Macromolecules* **1973**, 6, 672.
- (14) Gadjourova, Z.; Marero, D. M. y.; Andersen, K. H.; Andreev, Y. G.; Bruce, P. G. *Chem. Mater.* **2001**, 13, 1282.
- (15) Andreev, Y. G.; Lightfoot, P.; Bruce, P. G. *J. Appl. Crystallogr.* **1997**, 30, 294.
- (16) Baboul, A. G.; Redfern, P. C.; Sutjianto, A.; Curtiss, L. A. *J. Am. Chem. Soc.* **1999**, 121, 7220.
- (17) Matsuura, H.; Fukuhara, K. *J. Polym. Sci. B: Polym. Phys.* **1986**, 24, 1383.
- (18) Murcko, M. A.; DiPaola, R. A. *J. Am. Chem. Soc.* **1992**, 114, 10010.
- (19) Frech, R.; Rhodes, C. P. *Solid State Ionics* **2002**, 147, 259.
- (20) Gejji, S.; Johansson, P.; Tegenfeldt, J.; Lindgren, J. *Comput. Polym. Sci.* **1995**, 5, 99.
- (21) Begun, G. M.; Rutenberg, A. C. *Inorg. Chem.* **1967**, 6, 2212.