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# Structure of the ambient temperature alkali metal molten salt AICl<sub>3</sub>/LiSCN

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The structure of the ambient temperature alkali metal molten salt system LiSCN/AlCl<sub>3</sub> 1:1 adduct was investigated by neutron diffraction, which demonstrates that the aluminum atom is surrounded by three chlorine atoms and one nitrogen atom, indicating the existence of the AlCl<sub>3</sub>NCS<sup>-</sup> anion, in which the NCS<sup>-</sup> coordinates to the Al center through nitrogen. Molecular orbital calculations using *ab initio* methods are also performed to study the optimized structures of the AlCl<sub>3</sub>NCS<sup>-</sup> and its isomer, AlCl<sub>3</sub>SCN<sup>-</sup>. The results are consistent with the neutron diffraction data and indicate that AlCl<sub>3</sub>NCS<sup>-</sup> is the major anionic complex in the 1:1 LiSCN/AlCl<sub>3</sub> adduct. © 2001 American Institute of Physics. [DOI: 10.1063/1.1344609]

## I. INTRODUCTION

For the applications of high-energy batteries, molten salts are potentially useful electrolytes.<sup>1-4</sup> In the present work we explore complex formation between a Lewis acid and the anion which should delocalize the negative charge of the anion and thereby decrease the Coulombic attractions between cations and anions. These salt/Lewis acid adducts usually result in either ionic liquids or crystalline materials with low melting points. Salts containing large organic catsuch as butylpyridinium chloride or 1,3ions, dialkylimidazolium chloride, interact with AlCl<sub>3</sub> to form ionically conducting liquids at room temperature.<sup>1-3</sup> Organic ionic liquids usually possess high room temperature ionic conductivity, however, these organic liquids have relatively high equivalent weights. Furthermore, the instability of these organic melts when contacted with the electrode surface impedes their applications for energy storage.

Ambient temperature alkali molten salts generally have ionic conductivity that is comparable to that of organic ionic liquids, but with lower equivalent weight and favorable contact with electrodes. Therefore, the development of room temperature alkali metal molten salt systems has been an important research goal. In order to obtain ambient temperature alkali metal molten salts, the choice of alkali metal salts is crucial, and only a few ambient temperature alkali metal molten salt systems possess chemical properties that fulfill the requirements for battery electrolytes.<sup>5–9</sup> The 1:1 LiN (SO<sub>2</sub>Cl)(SO<sub>2</sub>F)/AlCl<sub>3</sub> adduct, reported by Xu *et al.*, has a glass transition temperature of -35 °C and ionic conductivity around  $4 \times 10^{-6}$  S/cm at room temperature.<sup>5</sup> Liu *et al.*<sup>6,7</sup> have shown that the molten system 1:1 LiSCN/AlCl<sub>3</sub> can be supercooled to produce a material with a glass transition temperature of -15 °C and ionic conductivity around 4  $\times 10^{-4}$  S/cm at room temperature. In previous research we found that NaN(CN)<sub>2</sub> and AlCl<sub>3</sub> also form a 1:1 amorphous adduct with a glass transition temperature at 27 °C and room temperature ionic conductivity of  $6 \times 10^{-6}$  S/cm.<sup>8</sup> Zhang et al.<sup>9</sup> prepared a related 1:1 lithium poly(urea-sulfony) imide)/AlCl<sub>3</sub> adduct, which has a glass transition temperature at -22 °C and room temperature ionic conductivity of  $2 \times 10^{-4}$  S/cm. The formation of molten salts in these systems may originate from the ambidentate character of the anions, which offer several configurations when coordinated to AlCl<sub>3</sub> and thereby produce a complicated network that resists crystallization. Among the ambient temperature alkali glassy materials mentioned above, the 1:1 LiSCN/AlCl<sub>3</sub> complex possesses the advantages of easy preparation and high ionic conductivity.

In the present research, we use neutron diffraction to investigate the atomic structure of 1:1 LiSCN/AlCl<sub>3</sub> adducts. Neutron diffraction studies of molten alkali haloaluminates have been carried out extensively.<sup>10,11</sup> These data combined with vibrational spectroscopic data and molecular orbital calculations provide considerable insight into molten salt systems. In Sec. II, the neutron diffraction method is described. The results and discussion are given in Sec. III. Corresponding molecular orbital calculations are presented in Sec. IV.

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### **II. EXPERIMENTAL SECTION**

Anhydrous lithium thiocyanate was prepared by a modification of a method published in the literature:<sup>12</sup> lithium hydroxide monohydrate was mixed with an equal molar amount of ammonium thiocyanate and dissolved in water. After filtration, the mixture was heated under 60 °C at 0.2 torr to remove water and ammonia. The crude product was dried under high vacuum ( $< 5 \times 10^{-5}$  torr) at 150 °C for three days and then stored and handled in a dry nitrogenfilled glove box. <sup>6</sup>LiOH·H<sub>2</sub>O (95 atom%), <sup>7</sup>LiOH·H<sub>2</sub>O (97 atom%), NH<sub>4</sub>SCN (99.99+%), and AlCl<sub>3</sub> (99.99%) were purchased from Aldrich Chemical Company. The presence of two Li isotopes was used to separately identify the correlations between lithium, making use of the opposite signs of the scattering length for  ${}^{6}\text{Li}(+)$  and  ${}^{7}\text{Li}(-)$ . Aluminum chloride was sublimed three times following the procedure described in the literature.<sup>13</sup> The AlCl<sub>3</sub> and LiSCN in a 1:1 ratio were pulverized, melted at 120 °C under a dry nitrogen atmosphere, and then loaded into a vanadium container with dimensions of 9.28 mm i.d., 9.52 mm o.d., and 63 mm in height. The neutron diffraction measurements were performed at 300 K using the GLAD facility at the Intense Pulsed Neutron Source at Argonne National Laboratory. Similar measurements were also performed on an empty vanadium container and a vanadium standard was employed for instrument calibration and data normalization. The data analysis was carried out following the standard procedures developed at Argonne National Laboratory for amorphous materials, including multiple scattering, absorption, and inelasticity corrections; an overview is provided in Ref. 14.

The differential cross section per atom  $d\sigma/d\Omega$  can be deduced from measured intensity I(r) and could be expressed as

$$\frac{d\sigma}{d\Omega} = \langle \bar{b} \rangle^2 (S(Q) - 1) + \langle \bar{b}^2 \rangle,$$
$$\langle \bar{b} \rangle = \sum_i x_i \cdot \bar{b}_i, \quad \langle \bar{b}^2 \rangle = \sum_i x_i \cdot \bar{b}_i^2,$$

where  $x_i$  represents the concentration of the *i*th component, and  $\overline{b}_i$  and  $\overline{b}_i^2$  are its mean and mean-square neutron scattering amplitudes, respectively. For a multicomponent system, the average structure factor S(Q) is the weighted sum of partial structural factors  $S_{ij}(Q)$ :

$$S(Q) = \frac{\sum_{i,j} x_i x_j b_i \cdot b_j S_{ij}(Q)}{\langle \overline{b} \rangle^2},$$

Figure 1 shows the S(Q) values for the <sup>6</sup>LiSCN/AlCl<sub>3</sub> and <sup>7</sup>LiSCN/AlCl<sub>3</sub> systems. The intensity differences for the various features in the S(Q)'s measured for the <sup>6</sup>Li and <sup>7</sup>Li samples result from the different Li scattering lengths. The sharp features originate from a small amount of crystallinity, which is not expected to affect the conclusions presented below.

The average correlation function T(r) is defined as

$$T(r) = 4\pi\rho r + \frac{2}{\pi} \cdot \int_0^{Q_{\text{max}}} Q[S(Q) - 1]\sin(Qr)dQ,$$



FIG. 1. Experimental average structure factors for  $^{6}\text{LiSCN/AlCl}_{3}$  and  $^{7}\text{LiSCN/AlCl}_{3}$  systems.

where  $\rho$  is the number density. T(r) was obtained using standard data analysis programs at Argonne, and qualitatively discussed in Ref. 14. From this it follows that

$$T(r) = 4\pi\rho r G(r).$$

The G(r) is known as the total pair distribution function and can be written as

$$G(r) = 1 + \sum_{i,j} w_{ij}(g_{ij}(r) - 1), \quad w_{ij} \equiv \frac{\sum_{i,j} x_i x_j b_i \cdot b_j}{\langle \overline{b} \rangle^2}.$$

The total pair distribution function G(r) is a linear sum of various particular pairs, multiplied by weighting factors  $w_{ij}$ . Tables I and II list these coefficients for each ion pair in the 1:1 LiSCN/AlCl<sub>3</sub> system. To obtain the coordination number for each ion pair, the peaks were fit with Gaussian functions and the coordination numbers calculated as

$$C_i(j) = \frac{\langle \bar{b} \rangle^2}{x_i \cdot \bar{b}_i \bar{b}_j} \cdot A_{ij},$$

where  $C_i(j)$  is the average number of atoms *j* around an atom *i*, and  $A_{ij}$  is the peak area of rT(r) for the *ij* pair.

Raman spectra were obtained with a Biorad FT spectrometer on samples sealed in capillary tubes. The amorphous samples display weak and broad bands in contrast with the more distinct bands of crystalline samples. The spectral resolution of the interferometer was 4 cm<sup>-1</sup>.

TABLE I. Weighting factors for ion pairs in the 1:1 <sup>6</sup>LiSCN/AlCl<sub>3</sub> system.

Ion pairs	Factor $w_{ij}$	Ion pairs	Factor $w_{ij}$	Ion pairs	Factor $w_{ij}$
<sup>6</sup> Li–S	0.004	S-C	0.013	C-Cl	0.136
<sup>6</sup> Li–C	0.009	S-N	0.019	N-N	0.031
<sup>6</sup> Li–N	0.013	S-Al	0.007	N-Al	0.023
<sup>6</sup> Li–Al	0.005	S-Cl	0.058	N-Cl	0.191
<sup>6</sup> Li–Cl	0.041	C–C	0.016	Al-Al	0.004
<sup>6</sup> Li–Li	0.001	C–N	0.044	Al-Cl	0.070
S-S	0.003	C-Al	0.016	Cl-Cl	0.294

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TABLE II. Weighting factors for ion pairs in the 1:1 <sup>7</sup>LiSCN/AlCl<sub>3</sub> system.

Ion pairs	Factor $w_{ij}$	Ion pairs	Factor $w_{ij}$	Ion pairs	Factor $w_{ij}$
<sup>7</sup> Li–S	-0.005	S-C	0.016	C-Cl	0.160
<sup>7</sup> Li–C	-0.012	S-N	0.022	N–N	0.037
<sup>7</sup> Li–N	-0.017	S-Al	0.008	N-Al	0.027
7Li-Al	-0.006	S-Cl	0.069	N-Cl	0.226
<sup>7</sup> Li–Cl	-0.054	C–C	0.019	Al-Al	0.005
<sup>7</sup> Li–Li	-0.002	C-N	0.052	Al-Cl	0.083
S–S	0.003	C-Al	0.019	Cl-Cl	0.346

#### **III. RESULTS AND DISCUSSION**

The total correlation functions T(r) of <sup>6</sup>LiSCN/AlCl<sub>3</sub> and <sup>7</sup>LiSCN/AlCl<sub>3</sub> are shown in Fig. 2. To obtain the average bond distances and coordination numbers, a series of Gaussian functions were used to fit T(r) up to 4.0 Å. A negative peak, assigned to the <sup>7</sup>Li–Cl pair, is observed in the T(r) of the <sup>7</sup>LiSCN/AlCl<sub>3</sub> sample. Table III lists all the experimental results for bond distances and coordination numbers, as well as the results of the *ab initio* calculation for the AlCl<sub>3</sub>NCS<sup>-</sup> anion discussed below. From Table III, we can see that bond distances and coordination numbers for each pair of atoms are in general reasonable agreement with the *ab initio* calculation results. A disagreement in the coordination numbers of the C–N and S–N pairs in the <sup>6</sup>Li system probably arises from complications caused by the high neu-



FIG. 2. The total correlation functions T(r) for <sup>6</sup>LiSCN/AlCl<sub>3</sub> and <sup>7</sup>LiSCN/AlCl<sub>3</sub> systems. The correlation functions have units of Å<sup>-2</sup>. Each Gaussian fitted curve corresponds to a certain ion pair in the LiSCN/AlCl<sub>3</sub> systems. The dotted line represents the deviation between the experimental result and the total sum of all the fitted Gaussian curves.

TABLE III. Neutron diffraction results for the LiSCN/AlCl<sub>3</sub> system.

<sup>6</sup> Li system	Pair C <sub>ij</sub>	Bond length	Bond length (calc.) <sup>a</sup>	Coord. number <sup>b</sup>	Calc. results <sup>c</sup>
	C–N	1.2	1.15	0.35	1
	C–S	1.64	1.62	0.68	1
	Al–N	1.89	1.86	1.36	1
	Al-Cl	2.17	2.16	3.13	3
	S-N	2.77	2.77	3.42	1
	Li–Cl	2.41		3.96	
<sup>7</sup> Li System	C–N	1.17	1.15	0.77	1
	C–S	1.69	1.62	0.87	1
	Al–N	1.95	1.86	0.58	1
	Al-Cl	2.17	2.16	2.61	3
	S-N	2.83	2.77	0.56	1
	Li-Cl	2.38		3.3	

<sup>a</sup>Calculated bond lengths (in Å) are obtained based on the optimized structure of  $AlCl_3NCS^-$  anion at the HF/6-31G\* level.

<sup>b</sup>Coordination number are for the pair i-j the average number of atoms *j* around an atom *i*.

<sup>c</sup>Based on the AlCl<sub>3</sub>NCS<sup>-</sup> anion.

tron absorption of <sup>6</sup>Li nuclei. The peak at 1.9 Å, assigned to the Al-N bond distance, indicates that the thiocyanate anion is coordinated to the AlCl<sub>3</sub> molecule through the N instead of the S. Atwood et al.<sup>15,16</sup> investigated a series of adducts made of Al(CH<sub>3</sub>)<sub>3</sub> and the thiocyanate ion and they concluded that the Al(CH<sub>3</sub>)<sub>3</sub> molecule coordinates to the N end with an Al-N bond distance around 1.94 Å. The Al-S bond distances reported in the literature<sup>17,18</sup> are longer (about 2.32 Å). These observations are in accord with the concept of hard and soft acids and bases (HSAB).<sup>19</sup> The S end of thiocyanate anion is a soft base while the N end is hard. When complexed with Al<sup>3+</sup>, the hard-hard Al-N bond should be preferred. The present data show the coordination numbers  $C_{Al}(Cl) \sim 3$  and  $C_{Al}(N) \sim 1$ , indicating a tetrahedral coordination environment for each Al atom.<sup>20</sup> The tetrahedral coordination geometry of aluminum in molten haloaluminates has been observed and reported in the literature.<sup>10,11</sup> The C<sub>Li</sub>(Cl) value of  $\sim$ 3.6 indicates the predominance of tetrahedral coordination environment for the lithium cation as well.

#### **IV. MOLECULAR ORBITAL CALCULATIONS**

*Ab initio* methods were employed to determine the optimized structures of AlCl<sub>3</sub>NCS<sup>-</sup> and AlCl<sub>3</sub>SCN<sup>-</sup> anions. Initial calculations were performed at the Hartree–Fock level and split-valence plus polarization 6-31G\* basis sets were used. Local minima were obtained by full geometrical optimization and both anionic structures have all positive frequencies. All calculations were carried out using the computer program GAUSSIAN 94.<sup>21</sup>

Two isomers, AlCl<sub>3</sub>NCS<sup>-</sup> and AlCl<sub>3</sub>SCN<sup>-</sup> anions, were studied and geometry optimizations were performed at the HF/6-31G<sup>\*</sup> level and are shown in Fig. 3. The AlCl<sub>3</sub>NCS<sup>-</sup> anion, in which N is bonded to the Al atom, has a linear Al–N–C structure, while the AlCl<sub>3</sub>SCN<sup>-</sup> anion, in which S is bonded to the Al atom, has a bent Al–S–C structure with a bond angle of 101°. Selected bond distances and bond



FIG. 3. Optimized structures of  $AlCl_3NCS^-$  and  $AlCl_3SCN^-$  anions at the HF/6-31G\* level.

angles are also illustrated in Fig. 3. From Table III, we can see that the neutron diffraction experimental data obtained from the condensed phases are in general agreement with the *ab initio* results calculated in the gas phase. This indicates the structural perturbation of the anions by the surrounding environment in the condensed phase is quite small. At the HF/6-31G\* level, the AlCl<sub>3</sub>NCS<sup>-</sup> anion is more stable than AlCl<sub>3</sub>SCN<sup>-</sup> by 16.6 kcal/mol. At a higher level of theory, MP2/6-31G\*, in which electron correlation is included by Møller–Plesset perturbation theory to second order, the energy difference between two anions is 15.5 kcal/mol. These results suggest that the N-bonded complex is the dominant species, consistent with the experimental data, which showed no Al–S coordination peak.

In addition to geometrical optimization of both anions, we also calculated the vibrational frequencies of both anions and compared with experimental data. FT Raman spectra show peaks at 2138 cm<sup>-1</sup> in the C $\equiv$ N stretching region and at 344 cm<sup>-1</sup> when LiSCN is complexed with AlCl<sub>3</sub>. The theoretical results show that, at the HF/6-31G\* level scaled by a factor of 0.89, the AlCl<sub>3</sub>NCS<sup>-</sup> anion has Raman active bands at 2121 cm<sup>-1</sup> and 338 cm<sup>-1</sup>, in reasonable agreement with the experimental data.

#### **V. CONCLUSIONS**

The structures of ambient temperature molten salt system  $\text{LiSCN/AlCl}_3$  were investigated using neutron diffraction. Molecular orbital calculations based on *ab initio* methods were also performed. The neutron diffraction results show that the Al atom maintains a tetrahedral coordination environment and the SCN<sup>-</sup> anion coordinates to the Al through the N end instead of S end. The bond distances obtained from neutron diffraction are in reasonable agree-

ment with the calculation results on the  $AlCl_3NCS^-$  anion. The  $AlCl_3NCS^-$  is more stable than its isomer  $AlCl_3SCN^-$  by 16.6 kcal/mol at the HF/6-31G\* level. The calculated frequencies of the  $AlCl_3NCS^-$  are also consistent with the optical data.

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