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Molecular Orbital Calculations and Raman Measurements for 1-Ethyl-3-methylimidazolium Chloroaluminates

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Raman spectroscopic data are presented for the room-temperature molten salts $(AlCl_3)_x$(1-ethyl-3-methylimidazolium chloride)$_{1-x}$, for x ranging from 0.46 to 0.67. *Ab initio* molecular orbital theory has been used to compute the structure and vibrational frequencies of some of the anionic and cationic species present in these melts; the results are compared with semiempirical calculations and used to interpret the experiments.

Introduction

Mixtures of aluminum chloride with either alkali chlorides ($MCl-AlCl_3$) or organic halides have fascinating chemistry and are used in a variety of applications, such as electrolytes in high-energy, high-density batteries;[1−3] nonaqueous solvents for studying ionic components;[4,5] catalytic solvents for Friedel−Crafts reactions;[6−8] and industrial electrodeposition processes, i.e., deposition of Al on high-quality steel surfaces.[9] These mixtures are referred to as chloroaluminates.

The $MCl-AlCl_3$ mixtures have been thoroughly investigated by a variety of techniques, including electrochemical and thermodynamic,[10−14] infrared and Raman,[15−17] X-ray,[18] and neutron scattering.[19] In basic solutions for $0.33 < x_{AlCl_3} < 0.5$, the dominant anionic species is $AlCl_4^-$. In acidic solutions, $x_{AlCl_3} > 0.5$, more species are reported such as $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, and Al_2Cl_6. It has been shown that $AlCl_4^-$ has a nearly tetrahedral structure, and $Al_2Cl_7^-$ and Al_2Cl_6 are composed of two $AlCl_4^-$ tetrahedra sharing one and two corners, respectively. In the case of $Al_2Cl_7^-$, infrared studies[17] have indicated that Li^+ stabilizes a bent Al−Cl−Al bridge while the larger alkali cations stabilize a linear (or slightly bent) bridge. In crystalline KAl_2Br_7, a bent bridge has been reported in a careful crystallographic investigation;[20] recent neutron scattering results on the structure of liquid KAl_2Br_7 lend support to the persistence of the bent bridge even in the liquid phase.[19] A theoretical study[21] using the semiempirical MNDO (modified neglect of differential overlap) method has indicated that, for $Al_2Cl_7^-$, the Al−Cl−Al bridge is bent with an angle of 125°. This has also been confirmed by *ab initio* molecular orbital calculations[19,22] using the 3-21G basis. Recently, the structure of $Al_3Cl_{10}^-$ was calculated using the MNDO method and found to consist of three $AlCl_4^-$ ions sharing three corners.[19,23]

Mixtures of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride (EMIC) form chloroaluminate salts that are liquid well below room temperature.[24] The chemistry of these systems is quite similar to that of the mixtures with the alkali halides; the stability and relative abundance of the ionic species strongly depend on the acidity or basicity of the melts as shown by numerous experiments including NMR and IR.[25−28]

In this paper, we present results of Raman scattering experiments on selected melts as well as *ab initio* and semiempirical molecular orbital calculations of the structure and the vibrational modes associated with $AlCl_4^-$, $Al_2Cl_7^-$, and EMI^+. As will be discussed, the theoretical calculations are used to assign the absorption bands in the Raman spectra and provide information on the structure of the isolated ions.

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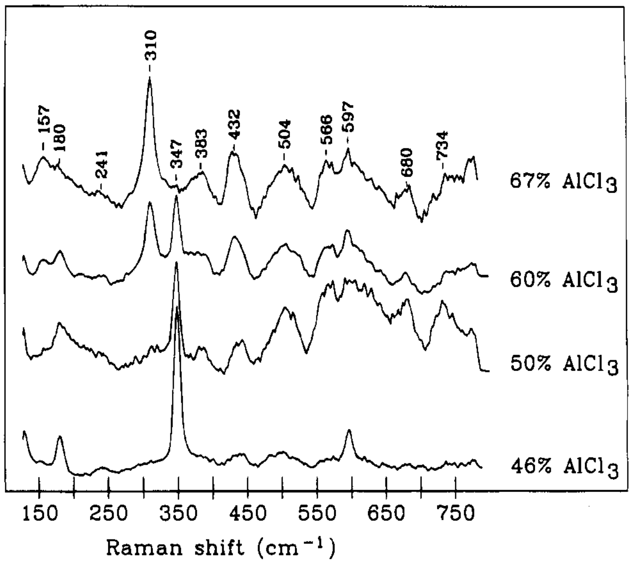

Figure 1. Raman spectra for four different $\mathrm{AlCl_3}$–EMI melts at 25 °C.

Methods

A. Raman Spectroscopy. The Raman spectra were measured using the 457.9 and 476.5 nm lines from a Laser Ionics 1400-15 ion laser. The scattered Raman signal was collected using a backscattering geometry from samples contained in sealed spinning NMR tubes. The scattered light was recorded with a SPEX Model 1877 triple monochromator and a Photometrics Model CH210 liquid-nitrogen-cooled CCD detector. The spectra taken in the concentration range 46–67 mol % $\mathrm{AlCl_3}$ were recorded in the range 150–750 $\mathrm{cm^{-1}}$. The samples were prepared by mixing anhydrous $\mathrm{AlCl_3}$ with EMIC at 60 °C. The weighing and handling of the samples were done in a glovebox, where the $\mathrm{H_2O}$ and $\mathrm{O_2}$ levels were maintained at less than 2 ppm.

B. Theory. *Ab initio* molecular orbital calculations[29,30] were carried out at the Hartree–Fock (HF) level to determine equilibrium structures and harmonic vibrational frequencies. The polarized split-valence 6-31G* basis was used. This basis set generally gives vibrational frequencies that are about 10% too high on the basis of previous studies.[31,32] The MNDO method,[33] which has done reasonably well in calculations of vibrational frequencies of chloroaluminates,[21] was also used.

Results

A. Raman Spectroscopy. The Raman spectra obtained at 25 °C in the range 150–750 $\mathrm{cm^{-1}}$ are shown in Figure 1, and the band positions are listed in Table 1. The number of bands increases with increasing $\mathrm{AlCl_3}$ content. Two bands (180 and 347 $\mathrm{cm^{-1}}$) show a definite decrease in intensity with increasing content of $\mathrm{AlCl_3}$, while three bands (157, 310, and 432 $\mathrm{cm^{-1}}$) show a definite increase in intensity with increasing content of $\mathrm{AlCl_3}$. The remaining bands (241, 383, 504, 566, 597, 680, and 734 $\mathrm{cm^{-1}}$) were present for nearly every melt but did not show any systematic variations with $\mathrm{AlCl_3}$ content.

Table 1. Raman Frequencies ($\mathrm{cm^{-1}}$) of the $\mathrm{AlCl_3}$–EMIC System

46 mol % $\mathrm{AlCl_3}$– 54 mol % EMIC	50 mol % $\mathrm{AlCl_3}$– 50 mol % EMIC	60 mol % $\mathrm{AlCl_3}$– 40 mol % EMIC	67 mol % $\mathrm{AlCl_3}$– 33 mol % EMIC
		161 dp	157 dp
181 dp	180 dp	180 dp	
241 dp	241 dp	241 dp	241 dp
		310 p	310 p
350 p	347 p	347 p	
383 p?	383 dp?	381 p?	383 p?
445 p	440 p	431 p	432 p
504 dp	506 dp	505 dp	504 dp
	566 p?	557 p?	566 dp?
		571 pd	
597 p	602 p	594 p	597 p
	680 dp	682 dp	680 dp
	733 dp	734 dp	734 dp

Table 2. Frequencies ($\mathrm{cm^{-1}}$) of $\mathrm{AlCl_4^-}$ (T_d Structure) and $\mathrm{Al_2Cl_7^-}$ (C_2 Structure)[a]

species	symm	MNDO	HF/6-31G*
$\mathrm{AlCl_4^-}$	E	107.8	121.1
	T_2	169.1	187.6
	A_1	361.9	353.1
	T_2	528.2	511.4
$\mathrm{Al_2Cl_7^-}$	B	10.5	15.5
	A	13.7	17.3
	A	41.2	39.9
	B	77.7	90.4
	A	78.4	90.6
	A	88.0	98.0
	B	108.2	125.0
	A	135.6	151.3
	B	145.2	162.9
	A	148.7	168.2
	B	162.8	182.9
	B	173.5	196.2
	A	184.5	206.8
	A	316.5	310.5
	B	350.4	332.7
	B	403.1	393.2
	A	448.4	441.6
	B	557.0	553.4
	A	560.7	557.7
	B	573.5	572.4
	A	574.3	572.7

[a] The HF/6-31G* total energies of $\mathrm{AlCl_4^-}$ and $\mathrm{Al_2Cl_7^-}$ are −2080.230 47 and −3700.847 45 hartrees, respectively.

B. Molecular Orbital Calculations. $\mathrm{AlCl_4^-}$. This anion has been studied previously at the HF/6-31G* and MNDO levels of theory.[19,21,33] At the HF/6-31G* level, the anion has a T_d structure with a bond length of 2.17 Å. The HF/6-31G* and MNDO vibrational frequencies were in reasonable agreement with experimental measurements on the anion in various melts.[21] The structure and vibrational frequencies at the two levels of theory used in the present study are reported in Table 2 and Figure 2.

$\mathrm{Al_2Cl_7^-}$. This anion has been the subject of several previous theoretical studies. Davis et al.[21] reported a MNDO study including structure and vibrational frequencies. Curtiss[22] carried out an *ab initio* molecular orbital study using the 3-21G basis set. Both studies found a C_2 structure with a bent Al–Cl–Al angle (MNDO, 124.9°; 3-21G, 132.4°). The HF/6-31G* calculations of the present work yield a C_2 structure and an Al–Cl–Al angle of 123.4° (see Table 2 and Figure 2).

1-Ethyl-3-methylimidazolium Cation ($\mathrm{EMI^+}$). At both levels of theory, the fully optimized cation has a structure with C_1 symmetry. The HF/6-31G* structure is shown in Figure 3. The HF/6-31G* torsion angle of the terminal $-\mathrm{CH_3}$, i.e., $\mathrm{H_6C_4N_2}$

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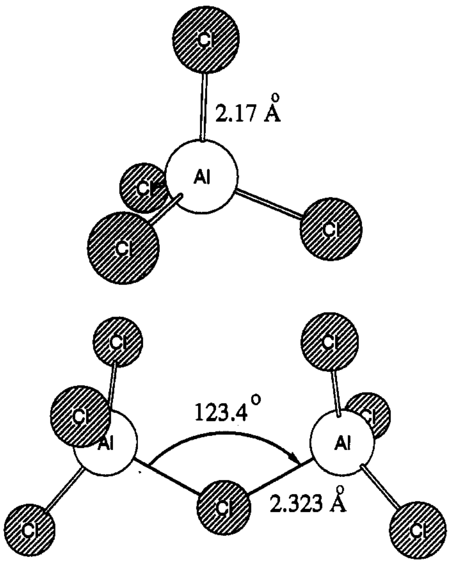

Figure 2. HF/6-31G*-optimized structures for $AlCl_4^-$ and $Al_2Cl_7^-$.

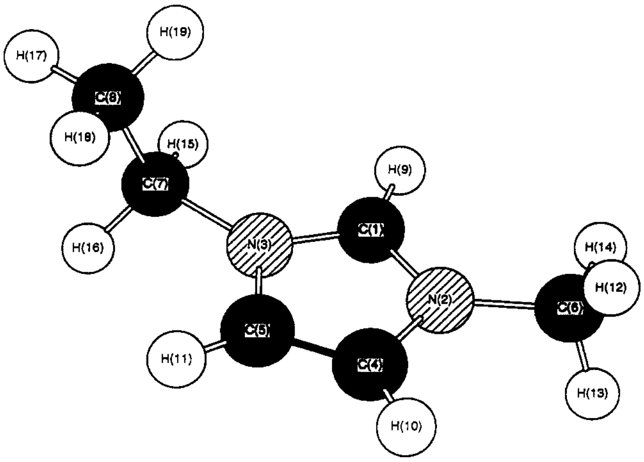

Figure 3. HF/6-31G*-optimized structure for EMI^+.

Table 3. Comparison of X-ray Results and 6-31G* Calculations for the EMI^+ Geometry[a]

geometry	X-ray[b]	6-31G*[c]
C_1N_2	1.30	1.32
C_1N_3	1.27	1.31
N_2C_4	1.39	1.38
N_3C_5	1.41	1.38
C_4C_5	1.38	1.34
N_2C_6	1.48	1.47
N_3C_7	1.55	1.48
C_7C_8	1.43	1.52
$\angle N_2C_1N_3$	110	110
$\angle C_1N_2C_4$	111	108
$\angle C_1N_3C_5$	109	108
$\angle N_2C_4C_5$	104	107
$\angle N_3C_5C_4$	106	107
$\angle C_1N_2C_6$	126	126
$\angle C_1N_3C_7$	130	126
$\angle N_3C_7C_8$	104	112

[a] Bond distances (Å) and bond angles (deg) defined in Figure 3. [b] Taken from ref 34. [c] HF/6-31G* total energy of EMI^+ is −342.313 40 hartrees.

Table 4. Frequencies (cm^{-1}) of EMI^+ (C_1 Structure)

MNDO	HF/6-31G*	MNDO	HF/6-31G*	MNDO	HF/6-31G*
27.1	49.0	1102.7	1105.6	1486.7	1631.0
47.9	88.8	1136.0	1124.0	1518.1	1632.0
122.5	146.7	1150.3	1196.0	1547.5	1650.0
146.8	222.9	1157.3	1203.0	1585.4	1651.0
214.6	249.0	1159.1	1223.9	1675.3	1765.4
290.0	311.2	1190.6	1243.1	1687.0	1772.4
383.9	402.8	1206.7	1261.0	3218.9	3226.1
441.0	455.4	1216.6	1284.6	3259.1	3260.7
510.4	631.9	1276.0	1386.5	3264.8	3275.2
546.5	686.0	1321.7	1435.8	3266.3	3295.6
635.8	714.1	1405.6	1461.8	3276.6	3307.3
725.0	744.3	1407.0	1517.5	3278.2	3332.6
866.4	860.0	1416.4	1537.7	3319.2	3353.9
906.2	864.0	1429.9	1575.8	3348.1	3360.2
945.1	1011.6	1431.1	1585.7	3407.3	3477.8
974.1	1014.6	1446.6	1602.9	3440.5	3480.7
1014.6	1031.8	1478.4	1622.5	3452.5	3497.9

Table 5. Experimental Frequencies (cm^{-1}) for 46 mol % $AlCl_3$−54 mol % EMIC and Corresponding Calculated HF/6-31G* Frequencies

exptl	$AlCl_4^-$(6-31G*)	EMI^+(6-31G*)
181 dp	188 dp	
241 dp		249 dp
350 p	353 p	
383 p?		403 p
445 p		455 p
504 dp	511 dp	
597 p		632 p

Table 6. Experimental Frequencies (cm^{-1}) for 67 mol % $AlCl_3$−33 mol % EMIC and Corresponding Calculated HF/6-31G* Frequencies

exptl	$Al_2Cl_7^-$(6-31G*)	EMI^+(6-31G*)
157 dp	163 dp	
241 dp		249 dp
310 p	311 p	
383 p?		403 p
432 p	442 p	455 p
566 dp	558 dp	
597 p		632 p
680 dp		686 dp
734 dp		744 dp

dihedral angle, of the ethyl group is 73°. The torsion angle from the MNDO calculation is 89°. Selected geometrical parameters from the HF/6-31G* structure are listed in Table 3 and compared with the X-ray results from the crystal 1-ethyl-3-methylimidazolium chloride obtained by Dymek et al.[34] The bond lengths and bond angles are in good agreement except for N_2C_5, C_5C_6, and $\angle N_2C_5C_6$. The 51 vibrational frequencies of the EMI cation have been calculated using both the HF/6-31G* and MNDO approaches (Table 4). The CH stretching frequencies of the EMI cation were previously reported from an AM1 calculation.[28]

Discussion

The intensities of some of the Raman bands in Figure 1 vary with composition while others remain nearly the same. The assignment of these bands to specific species can be undertaken by analogy with the chloroaluminates and by consideration of the above calculations. The vibrational frequencies in the range 150−750 cm^{-1} from the HF/6-31G* calculations are listed in Tables 5 and 6 along with the observed values for the 46 mol % $AlCl_3$ and 67 mol % $AlCl_3$ melts, respectively. The HF/6-31G*-calculated Raman activities of $AlCl_4^-$, $Al_2Cl_7^-$, and EMI^+ are shown in Figure 4.

The intensities of the bands at 180 and 347 cm^{-1} decrease with increasing $AlCl_3$ content (Figure 1); they are thus assigned to $AlCl_4^-$, since $AlCl_4^-$ is well accepted to be the dominant anionic species in the basic and neutral melts. These two bands are close to those which have been observed for $AlCl_4^-$ in

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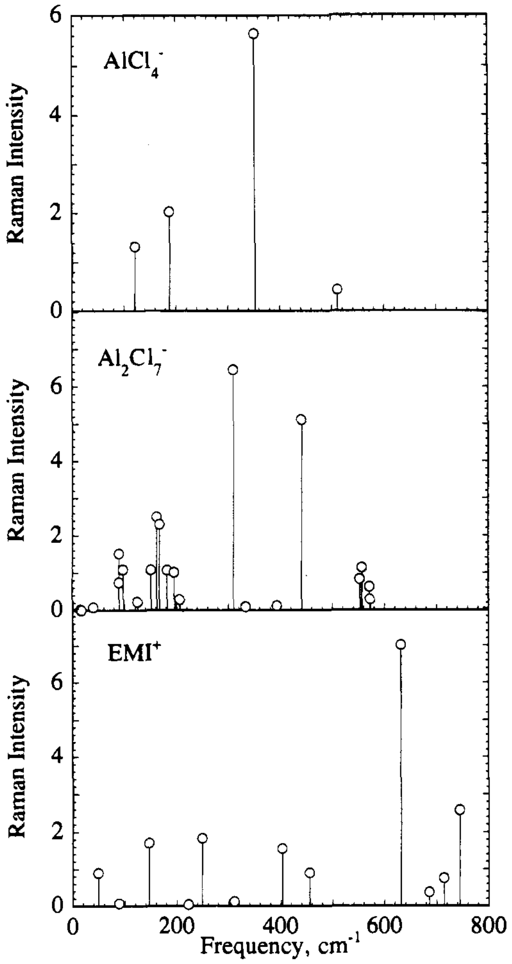

Figure 4. HF/6-31G*-calculated Raman intensities for (a) $AlCl_4^-$, (b) $Al_2Cl_7^-$, and (c) EMI^+.

aluminum chloride–alkali chloride melts.[17] They are in good agreement with the HF/6-31G* predictions for $AlCl_4^-$ of 188 and 353 cm^{-1} and with the MNDO values of 169 and 362 cm^{-1}. The HF/6-31G* calculations also predict weaker bands at 121 and 511 cm^{-1}. The band at 121 cm^{-1} is beyond our experimentally accessible range but has been reported in the MCl–$AlCl_3$ melts. The observed band at 504 cm^{-1} is very close in value to the calculated one at 511 cm^{-1} but cannot be unambiguously ascribed to $AlCl_4^-$ since its intensity in the 67 mol % $AlCl_3$ melt is nearly the same as that in the neutral and basic melts. We propose that this band is due to $AlCl_4^-$ in the basic, neutral, and 60 mol % $AlCl_3$ melts. In the 67 mol % $AlCl_3$ melt, this band can be due to higher polymeric ionic species. Indeed, in MCl–$AlCl_3$ for the 67 mol % $AlCl_3$ melt, Rytter et al.[17] found a very weak peak at 496 cm^{-1} only when the counterion was Cs^+; they ascribed it to higher polymers, e.g. $Al_3Cl_{10}^-$. Since EMI^+ is much larger than Cs^+, one would expect that this peak would be present in our melts.

Three bands (157, 310, 432 cm^{-1}) increase in intensity with increasing content of $AlCl_3$ (Figure 1). They are assigned to $Al_2Cl_7^-$ because this anion is known to be dominant in acidic melts. The HF/6-31G* results for $Al_2Cl_7^-$ predict bands at 163, 311, and 442 cm^{-1} in excellent agreement with experiment (Table 2). From Raman spectral measurements in the alkali–aluminum chloride solutions,[16,17] the following frequencies were assigned to $Al_2Cl_7^-$: 110, 159, 312, and 432 cm^{-1} for Li^+; 91, 160, 312, and 433 cm^{-1} for Na^+; 97, 161, 311, and 432 cm^{-1} for K^+; and 96, 161, 306, and 431 cm^{-1} for Cs^+. Remarkably, the vibrational frequencies observed for $Al_2Cl_7^-$ remain essentially unchanged as the size of the counterion changes drastically from that of Li^+ to that of EMI^+.

The bands at 241, 383, 597, 680, and 734 cm^{-1} can be ascribed to the EMI cation since they are close to some of the computed values (see Tables 5 and 6). The remaining band at 566 cm^{-1} is close to 558 cm^{-1} calculated for $Al_2Cl_7^-$ (see Figure 4) but was not previously reported in the study of MCl–$AlCl_3$ melts. This band could be enhanced due to the presence of a large cation, EMI^+.

The present results can be compared to those obtained for other room-temperature melts containing an organic cation. Gale, Gilbert, and Osteryoung[35] have measured the Raman spectra of $AlCl_3$–1-butylpyridinium chloride (BPC); four absorption bands were observed for $AlCl_4^-$ (126, 184, 351, and 484 cm^{-1}) and $Al_2Cl_7^-$ (102, 163, 315, and 434 cm^{-1}) which agree well with experiments in high-temperature melts[16,17] and also with our calculated and experimental data. However, the Raman spectra shown in Figure 1 have more resolved peaks than the corresponding ones in BPC melts, especially bands that we have assigned to the organic cation, EMI^+. The better resolution and the *ab initio* calculations play an important role in assigning the observed bands to specific ionic species.

Conclusion

$AlCl_3$–EMIC melts have been investigated using *ab initio* molecular orbital calculations and Raman spectroscopy. The $Al_2Cl_7^-$ anion has a C_2 structure with an Al–Cl–Al bond angle of 123.4° at the HF/6-31G* level. The Al–Cl distance in the bridge is 2.32 Å, and that of the terminal group is 2.13–2.14 Å. The EMI^+ cation has a C_1 structure with the torsion angle for the terminal CH_3 of the ethyl group of 73°. The measured absorption bands confirm that the vibrational frequencies of $AlCl_4^-$ and $Al_2Cl_7^-$ do not depend significantly on the nature of the countercation (e.g. alkali or organic). Our data support the formation, in very acidic melts, of higher polymeric ionic species: such species have been suggested in earlier studies in high-temperature melts when the size of the countercation becomes large, i.e. Cs^+. We have also been able to observe well-resolved bands due to the EMI^+ cation. The assignment of specific frequencies to individual ionic species has been done on the basis of the calculations as well as their intensities as a function of the composition.

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