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SPECTRAL IDENTIFICATION OF $Al_3Cl_{10}^-$ IN 1-METHYL-3-ETHYLIMIDAZOLIUM CHLOROALUMINATE MOLTEN SALT

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Abstract—The IR specular reflection of molten 1-methyl-3-ethylimidazolium (MEI) Al_3Cl_{10} is reported. After elimination of vibrational bands due to MEI^+, $Al_2Cl_7^-$ and Al_2Cl_6, the following bands were assigned to $Al_3Cl_{10}^-$: 583, 540, 488, 424, 361, 293 and 174 cm^{-1}. MNDO–MOPAC calculations were carried out and the predicted frequencies and intensities agreed remarkably well with the experimental spectrum.

In molten mixtures of $AlCl_3$ with MCl (M^+ being an alkali ion or an organic cation), the anionic species Cl^-, $AlCl_4^-$ and $Al_2Cl_7^-$ are well recognized and the latter two have been characterized spectroscopically.[1-5] Evidence for the existence of minor amounts of higher polymers, $Al_nCl_{3n+1}^-$ with $n \geq 3$ has been found in melts with more than 66 mol % $AlCl_3$.[2,3,5,6,7,8] While $AlCl_4^-$, $Al_2Cl_7^-$ and Al_2Cl_6 are well characterized, only a few weak spectral bands or shoulders have been attributed to higher polymers. The stoichiometry of the higher polymers has also been uncertain. Generally the formation of higher polymers is more likely with larger M^+ cations.[3]

The two components 1-methyl-3-ethylimidazolium chloride (MEICl) and $AlCl_3$ are completely miscible. A recent thermodynamic study[9] of acidic mixtures ($X_{AlCl_3} > 0.5$) of MEICl and aluminum chloride showed a much stronger dependence of the $AlCl_3$ activity on melt composition than for alkali chloride–aluminum chloride mixtures. Vapour pressure measurements gave $AlCl_3$ activity as high as 0.53 at 76.7 mol % $AlCl_3$. However, with the addition of MEICl, the $AlCl_3$ activity drops off sharply to 0.30 and 0.14 for 73.8 and 70.5 mol % $AlCl_3$, respectively. A straightforward explanation of this behaviour is the presence of substantial amounts of $Al_3Cl_{10}^-$ and no other high polymers. Based on a thermodynamic model,[9] the following relative amounts were predicted at 250°C and 75 mol % $AlCl_3$: $Al_3Cl_{10}^- = 50\%$, $Al_2Cl_7^- = 33\%$ and $Al_2Cl_6 = 17\%$. The relative amount of $Al_3Cl_{10}^-$ in the MEICl–$AlCl_3$ melts is substantially higher than in alkali chloride–$AlCl_3$ melts. This melt should then provide an excellent opportunity to characterize the $Al_3Cl_{10}^-$ ion spectroscopically and at the same time serve as a check on the thermodynamic model.

EXPERIMENTAL

A melt with 25 mol % MEICl–75 mol % $AlCl_3$ and a pure MEICl melt were prepared.[10] The melts were added to a cell described in detail earlier[5] and their IR specular reflection spectra were obtained with a Bruker IFS 113v Fourier transform instrument. The spectra of these films (< 10 μm) were recorded after letting a piston press the melt against a diamond window (Type II A, D. Drukker and Zn). Thick samples (2–3 mm) were used as a ref-

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erence to avoid false band splitting.[11,12] The averaged spectra consisted of 400 single scans obtained with a DTGS detector at a resolution of 8 cm^{-1}. A 3.5 μm Mylar beam splitter was used in the frequency range 150–700 cm^{-1}.

RESULTS

Figure 1, curves (a) and (b) show the spectra of the melt having the stoichiometric composition MEIAl$_3$Cl$_{10}$ at 200°C. The melt film was slightly thicker for the lower spectrum. Figure 1, curve (c) gives the spectrum of MEICl at the same temperature. The goal of the present work was to characterize the Al-species, Al$_2$Cl$_7^-$, Al$_3$Cl$_{10}^-$ and Al$_2$Cl$_6$. Although the spectrum of MEICl was recorded over the range 4000–150 cm^{-1}, it is only shown here in the range 700–150 cm^{-1}, with the purpose of eliminating bands in the spectrum of MEIAl$_3$Cl$_{10}$ not belonging to Al-species. By comparing curves (b) and (c), the following bands in curve (b) can be eliminated as due to MEI$^+$: 643, possibly 616, 247, 228, 204 and 154 cm^{-1}. The remaining band frequencies are given in the figure. The following uncertainties in the band positions are estimated for the reflection spectra:

- —2 cm^{-1} for narrow bands with medium or less intensity.
- —5 cm^{-1} for broad bands, well defined shoulders and narrow bands with high intensity.
- —10 cm^{-1} for very strong and broad bands and less defined shoulders.

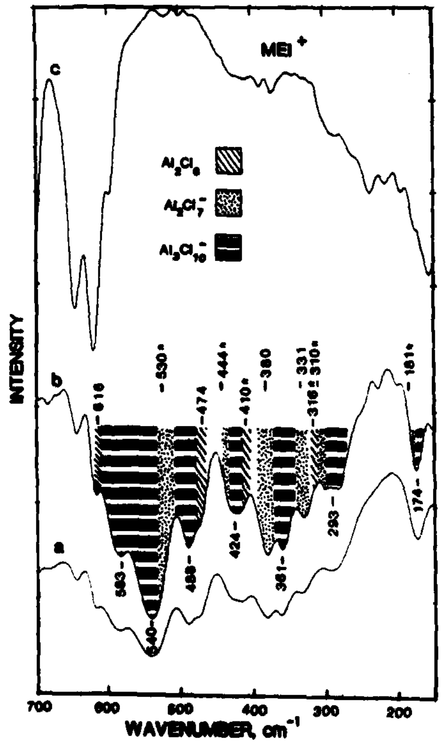

Fig. 1. IR reflectance spectra of a molten mixture of 25 mol % 1-methyl-3-ethylimidazolium chloride (MEICl) and 75 mol % aluminum chloride (a) and (b), and of MEICl (c) at 200°C. The (a) spectrum has been recorded on a melt with a slightly higher thickness than the melt in the (b) spectrum.

The band positions are to some extent dependent upon the melt thickness.

The assignment of peaks (or parts of broad bands) to Al$_2$Cl$_6$ and Al$_2$Cl$_7^-$ are based on previous analyses of inorganic melts.[3,13] The bands assigned to Al$_2$Cl$_7^-$ and Al$_2$Cl$_6$ which do not show up as a peak or a pronounced shoulder, but which are given based on previous evidence,[3,13] are marked with an asterisk.

In a previous IR study,[5] the Al$_3$Cl$_{10}^-$ ion was looked for in a NaCl–AlCl$_3$ melt having the composition NaAl$_3$Cl$_{10}$. Due to the lower stability of Al$_3$Cl$_{10}^-$ in this melt, the strong peak at 540 cm^{-1} only appeared as a shoulder, giving a frequency shift of the maximum to 533 cm^{-1}. A shoulder at 361 cm^{-1} was, however observed in agreement with one of the presently observed peaks.

Several Raman studies[2,3,6] have been performed on melts which are high in AlCl$_3$ content, and bands due to high polymers, i.e. Al$_3$Cl$_{10}^-$, have been reported. All the papers reported a peak in the region 390–395 cm^{-1} which we do not observe, although it may be hidden as a shoulder on the 380 cm^{-1} peak. In addition, peaks at 493 and 177 cm^{-1} [3] and 297 cm^{-1} [6] were reported. These frequencies correspond closely to frequencies found in the present IR study.

SPECTRAL CALCULATIONS

Semi-empirical molecular orbital calculations were carried out on the Al$_3$Cl$_{10}^-$ species to provide guidance in the analysis of the spectrum. The MNDO (Modified Neglect of Diatomic Overlap) model[14] as incorporated in the MOPAC program[15] was used. The MOPAC program has been successfully used in studying chloroaluminate species.[16] It readily calculates optimum geometries, heats of formation, force constants of normal modes and other molecular parameters from the input initial geometries. In this work, we also used MOPAC to calculate vibrational modes along with their frequencies and transition dipoles.

The initial geometry input for Al$_3$Cl$_{10}^-$ was constructed by simply adding an AlCl$_3$ group to one of the terminal Cls in the geometry of Al$_2$Cl$_7^-$.[16] The most stable configuration was calculated to have a heat of formation of -589.8 kcal mol^{-1} and the structure shown in Fig. 2(a). The characteristic feature of the "stretched" structure is that atoms 1–5–6–7–10 are in a plane, and chlorines 2 and 11 are staggered relative to the central chlorines, 8 and 9. Thus the symmetry is C_{2v}.

It should be noted that the calculation is for an isolated gas phase molecule, while our interest is in $Al_3Cl_{10}^-$ in the liquid phase surrounded by an ionic environment. In previous work,[16] this environment was simulated by arranging ions in a cluster around the ion or ions of interest, significantly lengthening the time required for the computations. Calculations on reaction energetics were improved (by comparison with experimental data) by including surrounding ions. However, the calculated vibrational frequencies and normal modes were virtually unchanged. Therefore, in the present calculations on $Al_3Cl_{10}^-$, we did not attempt to simulate the ionic environment.

In the melt, $Al_3Cl_{10}^-$ is not expected to stay rigidly in the most stable configuration. The activation energies for rotation around the single bridge bond are small (about 1 kcal mol^{-1}) and so the $Al_3Cl_{10}^-$ will twist and be in several different conformations. In order to account for this twisting structure, in predicting the IR spectrum, calculations were performed for two other structures, "winged" and "cart" [Fig. 2(b), (c)]. The "winged" structure was obtained by positioning atoms 6–9–5–1 and 6–9–7–10 each in a plane. In the optimized geometry, the bonds 10–7 and 5–1 are twisted out of plane by 24 and 17°, respectively. The "cart" structure was optimized from an initial geometry in which atoms 1–5–6–7–10 formed a plane. The plane was retained (0.3° deviation), but the central and terminal chlorines were optimized in a staggered structure. The "winged" and the "cart" structures were 0.6 and 1.2 kcal, respectively, less stable than the stretched structure.

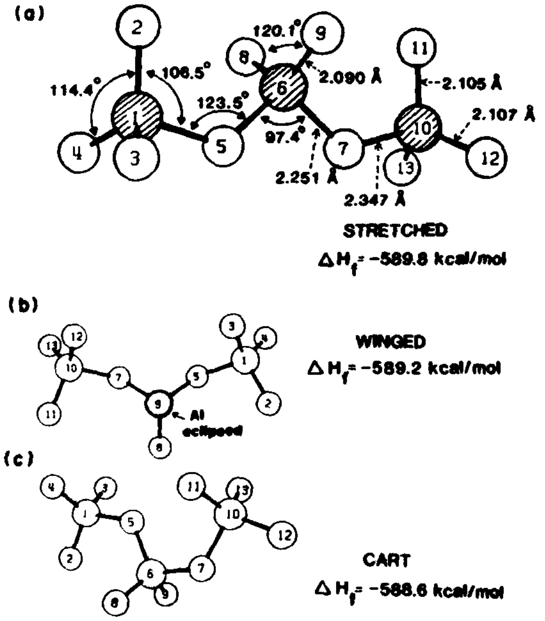

Fig. 2. The three optimized $Al_3Cl_{10}^-$ conformations for which calculations are carried out.

Table 1 gives calculated and experimental frequencies. The calculation is carried out for all three structures. The frequencies are given as bold face numbers in cm^{-1}. The numbers in parentheses refer to intensity. The experimental frequencies are listed as s—strong; m—medium; w—weak and sh—shoulder, while the calculated intensities are given as the square of the transition dipole multiplied by the frequency. Calculated stretching modes which contribute more than 10% to the total vibrational energy are listed. All 12 stretching frequencies are listed, but of the 21 bending modes, only those with intensities greater than one are given. The bonded atoms listed as m_1+m_2 signify stretching, and m_1-m_2 signify compression following the pictorial representations of the normal mode's output by MOPAC. The atom numbers refer to the structures given in Fig. 2.

In Table 1, column 4, the average values for the band locations and intensities are calculated. The values for the different models and the average do not give an exact description of the vibrations, but important features are illustrated. The band locations are found to be quite insensitive to the different conformations, while this is not the case for the intensities. Only for the vibrations that are calculated to be close together, i.e. the terminal antisymmetric and the outer symmetric bridge modes, do cross-overs in band location occur. Experimentally, both bands are found to be broad as expected from the calculations. Another noteworthy feature is the calculated strong increase in intensity for the terminal symmetric stretching modes when the structure is no longer "stretched".

In Fig. 3 calculated and experimental frequencies are compared. The strongest single mode, the 595 cm^{-1} "cart" mode, is set equal to 100 and the other intensities are given relative to this. A close correspondence is found between calculated and experimental values with respect to both band location and intensity. The calculated frequencies tend, however, to be a little higher than the experimental values.

The following comments apply to the bands given in cm^{-1} assigned to $Al_3Cl_{10}^-$:

Table 1. Calculated and experimental vibrations for $Al_3Cl_{10}^-$ as well as experimental vibrations for $Al_2Cl_7^-$ and Al_2Cl_6

I. "Stretched"		II. "Winged"		III. "Cart"		Ave. I, II, III	Experimental frequency	Main vibrational stretch modes
							616 (w)	Al_2Cl_6, terminal antisym.
605 (17.5)	6+9, 6−8	**601** (34.7)	6+9, 6−8	**595** (39.6)	6−9, 6+8	**600** (30.4)	**583** (m)	Central antisym.
581 (24.7)	10−11, 1−2 10+12, 10+13 1+3	**574** (14.9)	10+13, 10−11 10−12	**580** (18.3)	10+13, 1−2 10−11, 1+3			
578 (0.8)	1+2, 10−11 1−3, 1−4 10+13, 10+12	**577** (11.2)	1+2, 1−3 10+12	**579** (17.6)	1−2, 10+11 10−13, 1+3 1+4	**576** (55.4)	**540** (s)	Terminal antisym.
573 (10.0)	10+12, 10−13	**580** (26.8)	10+12, 10−11	**573** (16.9)	10+12, 10−11 10−13, 10+7			
570 (6.7)	1+4, 1−3	**571** (11.6)	1−4, 1+3 1+2	**574** (6.8)	1+4, 1−3 1−2, 1+5			
505 (5.0)	6+8, 6+9 6−7, 6−5	**510** (10.3)	6−8, 6−9 6+7, 6+5	**503** (11.3)	6−8, 6−9 6+5, 6+7	**506** (8.9)	**488** (m)	Central sym.
							474 (sh)	Al_2Cl_6, terminal sym.
425 (0.0002)	6−7, 6+6	**429** (0.6)	6−7, 6+5	**440** (5.1)	6−7, 6+5	**431** (1.9)		Inner, antisym. bridge w/outer Al-atoms counteracting

408 (0.1)	10+11, 10+12 10+13, 1+2 1+4, 1+3	**407** (4.5)	10+11, 10+13 10+12, 1+2 1+4, 1+3	**407** (8.0)	1−2, 1−3 1−4, 10−12	**407** (4.2)	**424** (m)	Terminal sym.
							380 (m)	$Al_2Cl_7^-$, terminal sym.
373 (27.0)	6+5, 6−7	**376** (32.4)	6+5, 6−7	**381** (24.8)	6+7, 6−5 10+13, 10+11	**377** (28.1)	**361** (m)	Inner, antisym. bridge w/reinforcement from outer Al-atoms
352 (0.4)	6+7, 6+5 10−7, 1−5	**353** (2.1)	6+5, 6+7 1−5, 10−7	**352** (4.8)	6+7, 10−7 6+5, 1−5	**352** (2.4)		Mainly inner sym. bridge
							331 (m)	$Al_2Cl_7^-$, antisym. bridge
311 (0.2)	1−5, 10−7	**306** (2.4)	1−5	**294** (3.6)	1+5			
						299 (14.2)	**301** (m) **293** (m)	Mainly outer sym. bridge
293 (13.5)	10+7, 1−5	**290** (14.3)	10−7, 1+5	**302** (10.2)	10−7, 1+5 6−5		**287** (m)	Outer antisym. bridge
				176 (3.1)				
160 (0.4)		**163** (1.6)		**159** (1.2)		**161** (4.3)	**174** (w)	Bending mode mainly involving bridge
154 (1.8)		**160** (3.7)		**153** (1.2)				

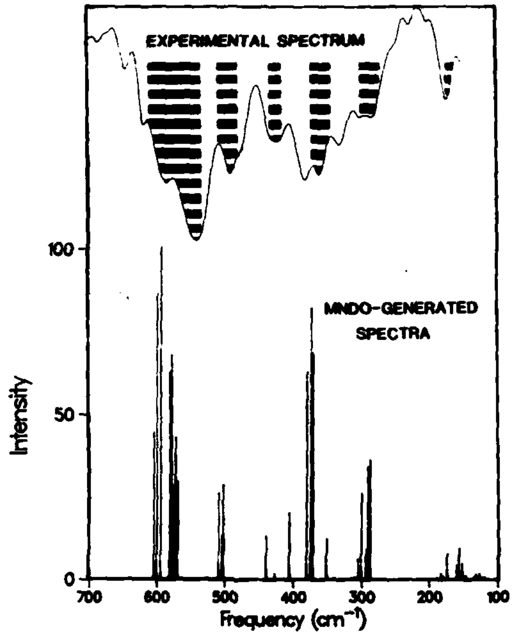

Fig. 3. Comparison of the experimental reflection spectrum with combined MNDO-generated spectra for the three structures given in Fig. 2.

583: the central antisymmetric stretching mode is found at the highest frequency as expected.

540: the four terminal antisymmetric stretching modes are calculated to be strong and close together with partial cross-overs. The experimental band is found to be broad and strong as expected.

488: the central symmetric stretching mode is also strong in accordance with calculations.

424: the terminal symmetric band is the only stretching mode for which the calculations predict a lower frequency. This mode is, however, expected to give the strongest interaction with the surroundings, with all six terminal chlorines vibrating. This interaction may well result in an increase of the experimental frequency relative to the calculated values. An alternative explanation is to assign the 424 cm^{-1} band to a combination of Al_2Cl_7, Al_2Cl_6 and the weak $Al_3Cl_{10}^-$ mode predicted at 431 cm^{-1}. The symmetric stretching mode is unobserved in the region, 390–395 cm^{-1}, where a Raman band has been reported.[2,3,6]

361: three inner bridge modes are predicted at 431, 377 and 352 cm^{-1}. Of these, the 431 and 352 modes are predicted to be weak. In accordance with this, only the inner antisymmetric bridge with intensity reinforcements from the outer Al atoms are clearly observed, while the two weak bands may be hidden by the 424 and 331 cm^{-1} bands, respectively.

293: this may be only one band, the splitting being
(304) caused by electronic noise. The band is due to
(287) outer symmetric and antisymmetric stretching, the cross-overs giving a broad band.

174: this band is due to bridge bending frequencies. The calculated frequencies are a little lower than the experimental.

CONCLUSION

The MNDO–MOPAC calculations predict the observed frequencies and intensities remarkably well, in spite of the fact that the model considers an isolated $Al_3Cl_{10}^-$ ion and has no adjustable parameters. The vibrational modes were assigned based on the empirical rules and comparison with $AlCl_4^-$, $Al_2Cl_7^-$ and Al_2Cl_6 before the MNDO model was applied. The MNDO vibrational analysis confirmed the results. This generally good agreement indicates that discrepancies between the theoretical and experimental spectra may be due to shifts in the experimental frequencies caused by interactions with surrounding ions, rather than to imperfections in the MNDO method.

The $Al_3Cl_{10}^-$ ion having low symmetry and shifting conformations is particularly rewarding to study by IR spectroscopy because all the modes become allowed. We were indeed able to assign 10 of the 12 calculated stretching modes and can probably also see the modes predicted at 432 and 352 cm^{-1} as part of the 424 and 331 cm^{-1} bands.

The present method of calculating intensity as the mean of three arbitrary but carefully chosen models can be improved. A future development of the MNDO–MOPAC calculation may be to generate conformations statistically and give the conformations weight according to their Boltzmann energy.

Finally, the spectra give a qualitative check on the conclusion of the thermodynamic study where the ratio of the species $Al_2Cl_7^-/Al_3Cl_{10}^-/Al_2Cl_6$ were predicted to be 2/2/1.[9] By comparing the present spectrum with the spectra for 67 and 100 mol % $AlCl_7$ in Fig. 6 in ref. 5 the predicted ratios are confirmed within the limits of uncertainty.

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