

Vibrational Spectra of Oxide-Contaminated Tetrachloroaluminate Melts

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Infrared and Raman spectra of CsCl–AlCl₃ melts containing oxides are reported and discussed. It was anticipated that several oxide-bearing species exist in chloroaluminate melts, depending on the acidity. A weak Raman band at ~265 cm⁻¹ and several infrared bands of medium intensity were observed and tentatively interpreted. The coordination geometry of oxochloroaluminate complexes is discussed and it is concluded that much experimental work is needed before the complicated chemistry of oxochloroaluminate melts is understood.

The problem of oxide contamination in tetrachloroaluminate melts has been of much concern, since it is difficult both to avoid and detect the presence of *traces* of oxide in such melts.¹ The Raman spectra of alkali-chloride aluminum-chloride molten mixtures are well established;^{2–7} organic chloroaluminate melts have also been studied.^{8–10} No indication of oxide contamination has been evident in these spectra, due either to the weak Raman scattering effect of oxide compounds or, perhaps, the low oxide concentration in the intended pure melts. The complementary infrared (IR) spectra of tetrachloroaluminates have only recently been investigated in the whole range of interest,^{11,12} and some attempts have been made with alkali chloroaluminates^{7,13–15} as well as with organic chloroaluminates.^{9,10,16,17} Again, no obvious indication of oxide contamination has been found, due either to sufficient purity of the investigated melts or, perhaps, a misinterpretation of the experimental results.

The present IR and Raman spectroscopic work on oxide-containing melts was started to determine if oxide bands have been overlooked, since previous results indicated that even the purest chloroaluminate melts contained traces of oxides.¹ The CsCl/AlCl₃ system was selected as the best one to use because the chlorobasicity (excess Cl⁻ relative to Al₂Cl₇⁻) can be varied the most,

and because sharper bands are obtained in the Raman spectra of Cs compounds compared to other alkali metals. It was of course necessary to operate at temperatures above the fusion point of CsAlCl₄. Our aim was to find spectral dependence on the addition of oxides, not to perform a systematic analysis which would require a much longer study. Indeed, it has been qualitatively established that Raman and IR bands dependent on oxide and chloride concentrations do occur, indicating the formation of various unknown aluminum oxochloro species. The well established series of aluminum-chloro species (AlCl₄⁻, Al₂Cl₇⁻, Al₃Cl₁₀⁻,¹⁸ Al₂Cl₆) is used as a basis for discussion of possible structures of the oxochlorides.

Experimental

Materials. Cesium chloride (*p.a.* from E. Merck, AG) and aluminum chloride (Fluka, AG) were purified as described elsewhere.¹⁹ A 1:1 molar mixture was zone-refined in evacuated quartz tubes to give water-clear CsAlCl₄ crystals of typically 99.99% purity, m.p. 387°C. Na₂O (99%, E. Merck, AG) and Cs₂O (99%, Cerac, Inc.) were used directly from the supplied ampoules. AlOCl was prepared as described previously.¹

Because of the extreme moisture sensitivity, all handling of chemicals was done in a N₂ atmos-

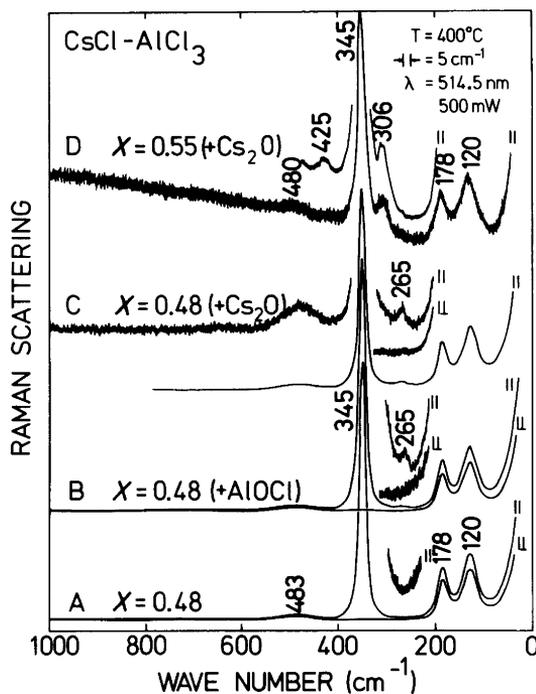


Fig. 1. Raman spectra of $\text{CsCl}-\text{AlCl}_3$ melts as a function of AlCl_3 mole fraction, x , and oxide content. A: "pure" chlorobasic melt; B: with added AlOCl (4 mg/g, i.e. a melt with ca. 0.1 mol oxide *pr.* L). C: saturated with Cs_2O (43 mg/g i.e. ca. < 0.3 M oxide); D: Acidic melt with added Cs_2O (30 mg/g, i.e. ~ 0.2 M oxide), somewhat fluorescing. \parallel and \perp denote a polarized and depolarized spectrum, respectively.

phere drybox (water content ≤ 10 ppm) and chemicals were stored in evacuated sealed glass containers. Sample mixtures were preequilibrated in rocking furnaces. For the calculation of molarities, the density of $\text{CsCl}/\text{AlCl}_3$ melts was taken⁵ to be 2.0 g cm^{-3} at $\sim 400^\circ\text{C}$. Specified mole fractions, x , always refer to the solvent only, not including oxides.

Raman spectra. The measurements (Fig. 1) were done in quartz cells as previously described⁵ using 514.5 nm Ar^+ laser radiation and a Jeol JRS 400D spectrometer equipped with a four window furnace. Detection of light was done with a cooled photomultiplier and a photon counting system.

Infrared spectra. Molten, corrosive and hygroscopic salts have posed great experimental diffi-

culties in IR analysis which have recently been overcome by several Norwegian scientists.^{11,12,20-23}

The sample was placed under a circular diamond window (1 mm thick, 8 mm diameter) in a cavity in a nickel block. The cavity, which often contained a polished piston of Ni, was sealed vacuum tight by means of a 0.5 mm diameter wire O-ring of soft gold. Traces of moisture were baked away by preevacuation at 400°C . The filled and assembled cell was transferred to a Kanthal wire-wound, water-cooled electric furnace placed inside the spectrometer. Thick (> 2 mm) or thin ($10-100 \mu\text{m}$) melts were formed, depending on the amount of sample and on the actual presence of the Ni piston which, by gravitation, compressed the film against the window. A detailed description of the technique is given by Hvistendahl^{11,12} and by Rytter *et al.*²⁰

An evacuable ($\sim 10^{-4}$ bar) fast scan Fourier transform spectrometer (Bruker 113C) was used in specular reflection mode, as developed recently.^{22,23} Interferograms were recorded with 4 different combinations of filters, beam splitters and other pertinent parameters, with 100-400 scans and a resolution of 4 to 8 cm^{-1} . After apodization and Fourier transformation, the final spectra were obtained as ratios of single beam reflectance spectra of reference (empty cell or cell with thick film) divided by corresponding thin film spectra of the sample. In this way, spectra looking like absorbance spectra were obtained (Fig. 2). Spectra with empty cell reference could also be plotted as the inverse of the above ratio as done by Hvistendahl *et al.*,²¹ Klæboe *et al.*²² and Rytter *et al.*²³ A comparison of these two methods of representing the data gave, however, the same frequencies and bands as those given in Fig. 2.

Table 1 presents a summary of the observed vibrational bands at different melt compositions, specified by means of x , the mole fraction of AlCl_3 .

Results and discussion

Raman spectra. It is seen from Figure 1 that the addition of either Cs_2O or AlOCl to basic CsAlCl_4 gave rise to a new weak band at $\sim 265 \text{ cm}^{-1}$ (Fig. 1B and C), in addition to the four characteristic bands²⁻⁵ of AlCl_4^- (483 , 345 , 178 , and 120 cm^{-1}). The $\sim 265 \text{ cm}^{-1}$ band, found in melts with additions of Cs_2O or AlOCl , was also

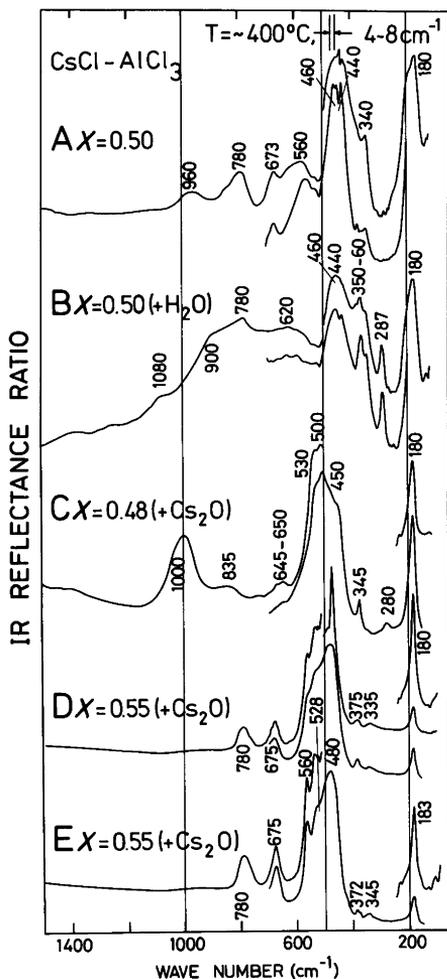


Fig. 2. Infrared reflectance ratio spectra of CsCl-AlCl₃ melts as a function of AlCl₃ mole fraction, x , and oxide content.

- Samples: A: Zone-refined CsAlCl₄ crystal;
 B: Zone-refined CsAlCl₄ crystal powder, exposed to glovebox atmosphere for days;
 C: Chlorobasic mixture saturated with Cs₂O (43 mg/g; i.e. ca. 0.3 M oxide);
 D: Acidic mixture with added Cs₂O (10 mg/g, i.e. 0.07 M oxide);
 E: As D but 30 mg/g, i.e. 0.2 M oxide.

All spectra are given as the calculated ratio of the reflectance of a thick reference divided by the reflectance of thin film samples.

Reference: A-B: Empty diamond/Ni-piston cell; C-E: Similar thick melts with or without oxide. Near 450–550 cm⁻¹, the reliability of the spectra was not high.

observed when Na₂O at 400 °C was added to basic CsAlCl₄ (not shown in Fig. 1), even in an almost neutral CsAlCl₄ melt ($x_{\text{AlCl}_3} \approx 0.5$) and faintly in a highly basic CsCl/AlCl₃ melt ($x_{\text{AlCl}_3} = 0.10$) saturated with Na₂O at 650 °C. A molten mixture of CsCl and Na₂O (at 680 °C) did not show the ~265 cm⁻¹ band.

At high temperatures (≥ 450 °C), or after long periods of heating, a precipitate in the melt and a simultaneous relative decrease in the magnitude of the ~265 cm⁻¹ band were observed. The dissolved oxochloroaluminate complexes seemed to undergo separate transformations to, for example Al₂O₃ or other stable solid phases. Similar observations have been made with NaAlCl₄ and KAlCl₄ melts.²⁴ In a neutral CsAlCl₄ melt, we have, by careful heating, been able to dissolve ~5 mg AlOCl per g of melt, but not ~18 mg Na₂O per g of melt. The oxide solubility is then on the order of 0.1–0.4 mol L⁻¹.

In acidic CsCl/AlCl₃ melts ($x_{\text{AlCl}_3} \approx 0.5$), only bands due to AlCl₄⁻ and Al₂Cl₇⁻ (i.e. the former ones and bands at 425 and 306 cm⁻¹) were seen. Apparently, the solubility of Cs₂O is markedly greater in acidic melts. No oxide band at 265 cm⁻¹ was observed; the problem of fluorescence of AlCl₃ makes the detection of weak Raman signals difficult. In acidic NaCl/AlCl₃ melts at ~200 °C, Torsi *et al.*,³ Mamantov *et al.*⁷ and, more clearly, Gilbert¹⁰ have observed a weak Raman band at ~262 cm⁻¹. This indicates that the species giving rise to the band at ~265 cm⁻¹, may also exist in weakly acidic melts.

All these observations can be understood if it is assumed that the ~265 cm⁻¹ bands are due to oxochloroaluminate species. Obviously, species like (AlOCl)_n · (AlCl₄)_m, with e.g. $n = 2$ and $m = 1$ or 2, which occur in NaAlCl₄ and KAlCl₄ melts according to cryoscopic¹ and potentiometric²⁵ measurements, are likely progenitors for the ~265 cm⁻¹ Raman band. This view is supported by the presence of a medium intensity band at ~253 cm⁻¹ in the spectrum of solid AlOCl reported by Mamantov *et al.*⁷ who also found weak bands at 344 and 625 cm⁻¹.

Infrared spectra. Figure 2 shows the IR reflectance spectra of oxide-containing CsCl/AlCl₃ melts. Four partially overlapping wavenumber ranges were obtained using different beam splitters. Obviously, the spectra depend much on the acidity, and many bands not known to originate

Table 1. Raman and infrared spectral bands of oxide-containing CsCl/AlCl₃ melts at 400 °C (cm⁻¹)^a.

Assign- ment	This work						Literature results on MCl/AlCl ₃ systems ^b
	Basic, x≅0.48		Neutral, x≅0.50		Acidic, x≅0.55		
	Raman Fig. 1A,B,C	IR Fig. 2C	Raman not shown	IR Fig. 2A,B	Raman Fig. 1D	IR Fig. 2D,E	
v(Al ₂ Cl ₇ ⁻)					120 m		
v ₂ (AlCl ₄ ⁻)	120 m		120 m		120 m		122 ¹⁴ 123 ⁵
v(Al ₂ Cl ₇ ⁻)					178 m	180 s	
v ₄ (AlCl ₄ ⁻)	178 m	180 s	178 m	180 vs	178 m	180 s	182 ^{11,12,14} 185 ⁵
v _a (oxide)	265 w,p		265 vw				262 ^{3,7}
v _b (oxide)		280 w		287 m			
v(Al ₂ Cl ₇ ⁻)					306 w,p		306 ⁵
v(Al ₂ Cl ₇ ⁻)						335 w	326 ¹¹⁻¹²
v ₁ (AlCl ₄ ⁻)	345 vs,p	345 w	345 vsp	340 vw	345 vsp		346-350 ^{5,11,12,14}
v _c (oxide)				360 w			
v(Al ₂ Cl ₇ ⁻)						375 w	381 ¹¹⁻¹²
v(Al ₂ Cl ₇ ⁻)					425 w		
v _d (oxide)		~450 wbsb		~450 vs			464 ¹⁴
v ₃ (AlCl ₄ ⁻)	483 wb	~480 sb	483 wb	~480 vsb	480 vwb	480 vsb	485 ^{5,7,14} 474 ^{11,12,14}
v _e (oxide)		~530 mbsb					
v(Al ₂ Cl ₇ ⁻)						528 msh	517 ^{11,12}
v _f (oxide)				560 wb		560 m	600 ⁷
v _g (oxide)		650 vw		620 wb			630 ¹⁰
v _h (oxide)				673 w		675 m	700 ^{7,14} 675-690 ¹⁰⁻¹²
v _i (oxide)				780 m		780 m	840 ^{7,14} 780-800 ¹¹⁻¹²
v _j (oxide)		835 vwb					
v _k (oxide)				900 w			
v _l (oxide)				960 wb			952 ¹¹⁻¹²
v(OH bend)		1000 m					~1000 ¹⁵
v(OH bend)				1080 vwb			

^aAbbreviations: s = strong; m = medium; w = weak; v = very; b = broad; sh = shoulder; p = polarized. x = mole fraction of AlCl₃.

^bE.g. in a near-neutral NaAlCl₄ melt at ~200 °C, Gilbert *et al.*¹⁰ have clearly observed weak Raman bands at ~262, ~630 and ~690 cm⁻¹.

from AlCl₄⁻ or Al₂Cl₇⁻ fundamentals were seen (Table 1).

The spectra in Figure 2 agree well in coarse features with the CsCl/AlCl₃ spectra obtained by Hvistendahl *et al.*^{11,12} Their bands between 500–1000 cm⁻¹ in neutral melts were weaker (cf. Fig. 2A), but certainly present; also in other, alkali, chloroaluminates. The shape of the v₃ band at ~450–500 cm⁻¹ was, unfortunately, not seen as clearly in our spectrum of CsAlCl₄ as in theirs.^{11,12} In acidic melts such as CsAl₂Cl₇, Hvistendahl *et al.*^{11,12} clearly observed the Al₂Cl₇⁻ bands at 326 and 381 cm⁻¹ and they assigned the bands above

~600 cm⁻¹ to various combinations (cf. Fig. 2D).

We noted that the addition of oxide to the neutral or acidic CsAlCl₄ melts created no strictly new band relative to the Hvistendahl *et al.* spectra, although some bands seemed to grow in intensity. Therefore, we assume that oxide bands were actually present in the Hvistendahl spectra. This view finds support in the work of Mamantov *et al.*⁷ in which IR bands at 840 and 700 cm⁻¹, increasing in intensity with oxide concentration, were observed in NaAlCl₄ melts. It seems reasonable that these bands were due to oxides: AlO stretching and bending group frequencies in

$[\text{Al}(\text{OH})_4]^-$ occur between 950 and 325 cm^{-1} .²⁶ This idea and an alternative explanation involving overtones or combinations has been previously suggested by Smyrl *et al.*,¹⁴ based on data from spectroscopy of oxide-containing Na_3AlF_6 melts.²⁷ Unfortunately, Hvistendahl *et al.*,^{11,12} referring to that work,¹⁴ considered only the view that the 850–700 cm^{-1} bands were due to combinations. Overtone and combination IR bands in KCl/AlCl_3 samples have also been promoted by Russian scientists.¹⁵ Tait and Osteryoung¹⁷ assigned an IR band at 704 cm^{-1} from acidic or basic imidazolium tetrachloroaluminate melts containing water to Al–O stretching, mainly because the band intensity increased on addition of water.

Further support for our assignment of the 840–700 cm^{-1} bands to oxide can be derived from the IR spectra of various solids. Novak and Potier²⁸ examined a solid sample of AlOCl in the 600–3800 cm^{-1} range and found bands at 825, 725, and 690 cm^{-1} , but no bands in the OH stretching range. This indicates that AlO and/or AlCl stretchings occur in the 1000–600 cm^{-1} range. Al–OCl was examined independently by Mamantov *et al.*⁷ in the range 1000–200 cm^{-1} with essentially similar results (bands at 825, 710, and 680 cm^{-1}).

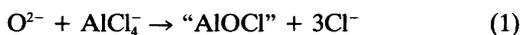
For a deeper understanding of Figure 2 and the influence of traces of water vapor on the chemicals, it is instructive to note previous spectroscopic results^{26,29,30} obtained on concentrated aqueous solutions of Al(III). IR bands due to deformations of Al–OH, Al–OH₂, and Al–OH–Al bonds in $[\text{Al}(\text{OH})_6]^{3+}$, $[\text{Al}(\text{OH})(\text{OH})_5]^{2+}$, $[\text{Al}_2(\text{OH})_2(\text{OH})_8]^{4+}$, and other Al species are found^{29,30} in the 1100–900 cm^{-1} range, whereas unassigned bands occur in the frequency region from ~830 to ~630 cm^{-1} . In basic solutions,²⁶ the tetrahedral $[\text{Al}(\text{OH})_4]^-$ ion is infrared-active at ~950 and ~725 cm^{-1} and Raman-active at ~725, ~625, and ~325 cm^{-1} . For high concentrations of $[\text{Al}(\text{OH})_4]^-$, new bands arise at ~900 (IR) and ~705 and ~540 cm^{-1} (Raman), which have been interpreted²⁶ to originate from discrete $[\text{Al}(\text{OH})_3\text{--O--Al}(\text{OH})_3]^{2-}$ ions (in conjunction with NMR data and deuteration studies). Most interestingly, these ions are known from X-ray crystal structure of potassium aluminate crystals in the solid state.³¹ From all this, we suggest that the neutral and basic melts which produced the spectra in Fig. 2A, B, and C may have contained Al–O–H groups, since these

spectra have bands near 1000 cm^{-1} . AlOCl does not show such bands.²⁸ Fig. 2D and E (acidic melts) do not seem to show bands from Al–OH groups; probably instead, the melts contained solvated H^+ and Al–O–Al groups, formed because of the great oxide affinity of AlCl_3 .

Tentative interpretations of the observed bands are given in Table 1. We arrived at these assignments using first the well known fundamentals of the AlCl_4^- and Al_2Cl_7^- ions and then assuming that the rest of the bands were due to oxides (labelled ν_a to ν_i in Table 1). The most distinct oxide bands occurred near ~270, ~450, ~530, ~560, ~675, and ~780 cm^{-1} , in reasonable agreement with the results from aqueous solutions. The ν_3 (AlCl_4^-) band at ~483 cm^{-1} (Fig. 1) in Raman and at ~474 cm^{-1} in IR^{11,12} was not distinctly observable in our IR spectra. This may have been due to new Al–O bands arising and noise from ratioing of small sample and reference signals. Accordingly, in Table 1, the ν_3 band has been given the value 480–483 cm^{-1} for all the CsCl--AlCl_3 melts investigated, even though a band was not seen.

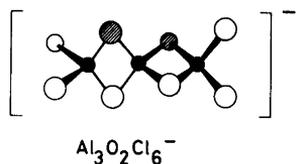
Oxochloroaluminate model structures

As previously seen, we observed that some oxide bands, present in the spectra of basic melts (ν_a , ν_b , ν_c , ν_g , and ν_j) disappeared under acidic conditions, and vice versa (for ν_f , ν_h , ν_i). This is in agreement with the expectation, derived from potentiometric and cryoscopic evidence of analogous sodium and potassium systems,^{1,25} that more than one oxide-bearing species (at least) occurs when the $\text{CsCl}/\text{AlCl}_3$ ratio or the acidity is varied. It is certain that practically no free oxide ion, O^{2-} , is present in chloroaluminate melts,^{32,33} because it could react with the melt according to eqn. 1:



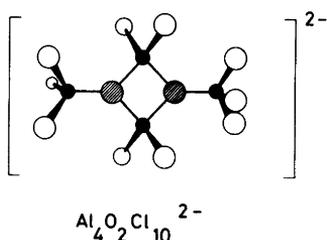
The exact nature of the solute(s), designated “AlOCl”, is not known, and the possibilities are not few. In previous studies^{1,25} on oxides in NaAlCl_4 and KAlCl_4 melts, evidence was found for oxo-dimeric “AlOCl”, i.e. the formation of species like $(\text{AlOCl})_2$, or possibly solvated species like $(\text{AlOCl})_2 (\text{AlCl}_4^-)_m$. For the case where $m = 1$, a simple structurally satisfactory ion can be imagined, shown below.

This ion fulfills the requirement of tetrahedral



coordination around aluminum and has bridging oxide ions between aluminum ions. Recently established crystal structures^{34,35} of two salts containing $\text{Al}_4\text{O}_2\text{Cl}_{10}^{2-}$ ions show that the formula $(\text{AlOCl})_2(\text{AlCl}_4)_2$ is a realistic possibility as illustrated below.

Further we note that "AlOCl", having a con-

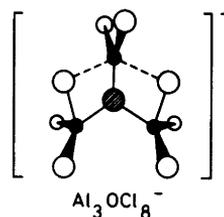


siderable stability in nearly neutral NaAlCl_4 melts,^{25,36} is considered to be a chloroamphoteric substance:



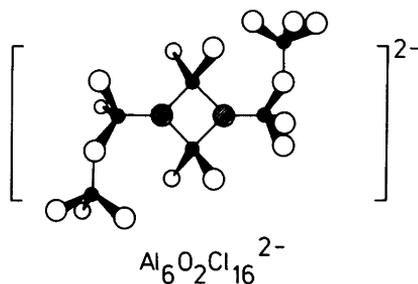
Acidic melt	Neutral melt	Basic melt
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Support for the existence of "AlOCl₂⁻" comes indirectly. Recently, a salt of composition $(\text{NO})_2\text{-}[\text{Al}_2\text{OCl}_6]$, was prepared from AlCl_3 and $\text{CCl}_3\text{-NO}_2$ in CH_2Cl_2 solution and characterized by chemical analysis and IR spectroscopy.^{37,38} Other oxychloroaluminates like KAlOCl_2 ,³⁹ $\text{K}[\text{Al}_4\text{O}_4\text{Cl}_3]$,⁴⁰ and $\text{K}_m(\text{Al}_3\text{O}_4\text{Cl})_n(\text{AlCl}_4)_m$,²⁴ have been found, indicating that "AlOCl" is indeed able to associate further chloride ions under certain circumstances. Also, "AlOCl₂⁻" is related to the AlO_2^- ion through solvation with AlCl_4^- . Regarding evidence for the existence of "AlO⁺", it must be mentioned that the ion $[\text{Al}_3\text{OCl}_6]^-$ was found in a metalloorganic chromium salt and characterized by X-ray structure determination.³⁴ This ion can be taken as a disolvated "AlO⁺" ion, $(\text{AlO}^+)(\text{AlCl}_4)_2$. The chloroacidity of "AlOCl" in the



formation of "AlO⁺" via eqn. 2 has recently been further confirmed in acidic $\text{NaCl}/\text{AlCl}_3$ melts by means of potentiometry.²⁵ Also, Einarsrud and Rytter⁴¹ have proposed the existence of an $\text{Al}_6\text{O}_2\text{Cl}_{16}^{2-}$ or $(\text{AlO}^+)_2(\text{AlCl}_4)_4$ ion, based on infrared spectroscopy of $\text{NaCl}-\text{AlCl}_3$ melts.

The true structure of oxochloroaluminate en-



ties is probably a complicated mixture of smaller ionic species and larger clusters of molecules and ions of a semimolecular type. An increase in association of ionic species should be observed when the melts become more acidic due to the stronger covalent character of these melts. Much work is needed before the complicated chemistry in these melts is understood.

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