in the doublet and 11 Hz in the triplet. In the literature no P–P couplings for gold compounds are reported. We have observed a ^3J coupling of 8 Hz in the compound [(Ph₃P)₂C-(AuPPh₃)₂](NO₃)₂ which was prepared by the reaction of Ph₃P=C=PPh₃ with AuPPh₃NO₃ (ratio 1:2).[10]

The fact that the spectra of mixtures of $Au_{11}L'_7(SCN)_3$, $Au_{11}L'_6L(SCN)_3$, and $Au_{11}L'_5L_2(SCN)_3$ can be fitted very well with a singlet, doublet and triplet suggests that the assumption, which was made, i.e., L couples with all L' with the same coupling constant, is reasonable. This would mean that the coupling of L with L' is transmitted equally to all L' ligands even though they are in different positions with respect to L. As mentioned in section a, the temperature-dependent experiments which have been performed on the Au_8, Au_9, and Au_{11} clusters, did not indicate any dynamic behavior to be a probable mechanism for the equivalence of the magnetic environment of the phosphorus atoms. This indicates that the coupling is mainly transmitted through the central gold atom. This is in accord with the conclusions from the single-line $^{31}P[^1H]$ NMR spectra and the Mössbauer results:[6,9] the linearly hybridized peripheral gold atoms have no direct two-center bonds through which the P–P couplings can be transmitted. In this view the P–P couplings over the Au_{11} cluster are to be described as ^4J couplings.

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Registry No. $Au_{11}[PPh_3]_7(SCN)_3$, 12583-03-8; $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7(SCN)_3$, 65982-55-0; $Au_{11}[P(p\text{-}MeC_6H_4)_3]_7(SCN)_3$, 12583-09-4; $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7I_3$, 12582-97-7; $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$, 37871-66-2; $[Au_{11}(PPh_3)_8(SCN)_2]PF_6$, 69787-01-5; $[Au_{11}(PPh_3)_8Cl_2]PF_6$, 69787-02-6; $[Au_9(PPh_3)_8](PF_6)_3$, 38999-04-1; $[Au_9(P(p\text{-}MeC_6H_4)_3)_8](PF_6)_3$, 34754-43-3; $[Au_8(PPh_3)_8](PF_6)_2$, 72271-21-7; $Au(PPh_3)NO_3$, 14897-32-6; $Au(PPh_3)Cl$, 14243-64-2; $Au(PPh_3)SCN$, 14243-61-9; $[Au(PPh_3)_2]PF_6$, 73872-15-8; PPh_3, 603-35-0; $P(p\text{-}ClC_6H_4)_3$, 1159-54-2; $P(p\text{-}MeC_6H_4)_3$, 1038-95-5; $P(p\text{-}FC_6H_4)_3$, 18437-78-0.

(10) F. A. Vollenbroek and J. M. Trooster, to be submitted for publication.


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Negative Oxidation States of the Chalcogens in Molten Salts. 1. Raman Spectroscopic Studies on Aluminum Chlorosulfides Formed in Chloride and Chloroaluminate Melts and Some Related Solid and Dissolved Compounds

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Raman spectroscopic measurements on series of LiCl–CsCl and CsCl–AlCl₃ melts have shown that dissolved tetrachloroaluminate and sulfide ions at temperatures around 400 °C react in a ratio close to 1:1, forming clear solutions sometimes with gel precipitates. Preliminary potentiometric measurements on basic CsCl–AlCl₃ melts have shown the average chloride–sulfide exchange number to be 2.0 ± 0.1. A glassy compound, (CsAlSCl₂)∞, was prepared, indicating in conjunction with other evidence the probable existence of a homologous series of chainlike ions $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ with $n \geq 3$ and polymeric $[AlSCl_2]_n^{n-}$ (for large n). These ions are characterized by a strong polarized Raman band near 325 cm⁻¹, assignable to the AlCl₂–S–AlCl₂ units. In neutral and acidic chloroaluminate melts the ions dissociate, forming dissolved species such as $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ and solid AlSCl. The solutions give a polarized Raman signal near 292 cm⁻¹ which can be assigned to the doubly bridged
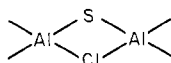
units within the ions. The Raman spectra of AlSCl and some other related solids are reported. The general aspects of the findings are discussed in connection with limited Raman studies on selenium- and bromide-substituted systems, which probably are quite analogous.

Introduction

The nature of sulfur and sulfides dissolved in chloroaluminate melts is rather complex and at present only partially understood. Sulfur reacts with alkali metals and aluminum, forming sulfides and polysulfides often of varying *nonstoichiometric* composition.

A few experiments have previously been conducted on sulfur in molten salt systems. The solubilities and redox reactions of some metal sulfides have been studied in LiCl–CsCl eutectic mixtures at temperatures around 400 °C.[2–8] More recently, the electrochemistry of sulfur and sulfide in sodium tetrachloroaluminate melts was examined[9–11] at 175 °C and found to be highly dependent on the melt composition, according to the proposed reaction (1) in conjunction with the acid–base

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$$AlCl_4^- + S^{2-} \rightleftharpoons AlSCl + 3Cl^- \tag{1}$$

equilibrium (eq 2), occurring near the equimolar composition

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \tag{2}$$
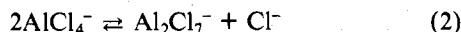
of $AlCl_3$ and NaCl. The equilibrium constant[10] associated with eq 1 showed that the sulfide ion acts as a strong base which is able to compete successfully with Cl^- in its tendency to coordinate to Al^{3+}. The sulfide ion was found to act as a *trichloro* base in acidic melts[11] as indicated by eq 1 or equivalently by eq 3 and as a *dichloro* base in basic melts

$$3Al_2Cl_7^- + S^{2-} \rightleftharpoons AlSCl + 5AlCl_4^- \tag{3}$$

according to eq 4. Solubility studies[12] have shown that the

$$AlCl_4^- + S^{2-} \rightleftharpoons AlSCl_2^- + 2Cl^- \tag{4}$$
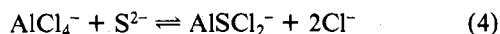
sulfide ion activity is several orders of magnitude smaller in acidic than in basic melts. Proof for the presence of discrete AlSCl molecules in solution has not been given, but the formation of solid AlSCl (with probable polymeric sheet structure[12]) from $AlCl_3$ and metal sulfides under anhydrous conditions at ~ 300 °C is well established.[12,13] Solvation of AlSCl and $AlSCl_2^-$ has been suggested (eq 5 and 6).[10,11] As the melt

$$AlSCl + AlCl_4^- \rightleftharpoons Al_2SCl_5^- \tag{5}$$

$$AlSCl_2^- + AlCl_4^- \rightleftharpoons Al_2SCl_6^{2-} \tag{6}$$
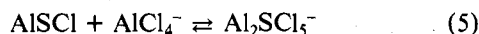
acidity is reduced, eq 7 was assumed to occur with associated pK estimated to be 2.5 (molal scale).[11]

$$AlSCl_2^- \rightleftharpoons AlSCl + Cl^- \tag{7}$$
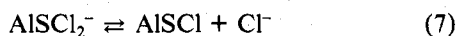
Reactions analogous to eq 5–7 are assumed to occur in oxide-, selenide-, and telluride-containing melts.[14–18]

It appears that there is a lack of information on the kind of species present in sulfide- (or oxide-, selenide-, telluride-) containing tetrachloroaluminate melts. This is because electrochemical measurements[9–11,14–18] do not give information on the structure of the species or their eventual solvation or polymerization reactions.

Since the Raman spectroscopic technique in the past has been successfully used to study complex formation in solution, the work reported here is aimed at a fairly thorough study of the nature of the aluminum–sulfide–chloride complexes in CsCl–$AlCl_3$ binary melts. The eutectic LiCl–CsCl was included because it allowed a convenient dilution of the basic $AlCl_4^-$-rich solutions; a few experiments on selenide- and bromide-substituted melts were done to explore briefly these closely analogous systems.

Experimental Section

Reagents. Aluminum chloride, $AlCl_3$, was prepared from aluminum metal and HCl gas in a closed system as previously described.[19]

Aluminum bromide, $AlBr_3$, was obtained similarly. The aluminum metal (99.999%) was cleaned in concentrated aqueous NaOH and in a 12:10:3 v/v/v mixture of 89% H_3PO_4 and concentrated H_2SO_4 and HNO_3 acids, respectively. Alkali chlorides (analytical reagents from Merck and Riedel-de Haën) were further purified by first passing dry HCl gas over the solids and then through the melts, flushing with pure N_2, and finally filtering the melt. CsBr (IR spectroscopic grade) was used after being dried at 150 °C for 1–2 days. Sulfur (Merck, Suprapure 99.999%) and selenium (Balzers, 99.999%) were used without further purification. Lithium sulfide, Li_2S (99.9%), was used as obtained from CERAC-PURE in a closed ampule. Aluminum chlorosulfide, AlSCl, was synthesized by using a slightly modified procedure from that previously reported.[12] Aluminum pieces, elemental sulfur, and excess $AlCl_3$ were heated at 300 °C for several days in an evacuated, sealed glass cell. Then, the unreacted $AlCl_3$ and sulfur were condensed at 20 °C in one end of the cell while the other end (containing AlSCl and Al) was maintained at 350–400 °C for 1 h. The pieces of unreacted aluminum were separated mechanically from the white powdery product. Aluminum chloroselenide, AlSeCl, was prepared similarly and had the appearance of fine white needles.[20] White powders of aluminum sulfide, Al_2S_3, and aluminum selenide, Al_2Se_3, were synthesized by heating stoichiometric quantities of the elements to 800 °C for several days.[21–27]

Methodology. Because of the extreme moisture sensitivity of most of the compounds, weighings and transfer operations were done in a drybox. The chemicals were sealed in cells under vacuum, and the melts were equilibrated in rocking furnaces which allowed visual inspection and temperatures up to 630 °C. The cells used for Raman experiments were made of quartz or Pyrex tubing and had a 5 × 5 mm^2 inside cross section in one end. The preequilibrated cells were transferred to the Raman furnace (sometimes several times) and allowed to reach equilibrium prior to measuring.

For the cells containing aluminum and sulfur the reactions (yielding Al(III) + S(–II)) were allowed to proceed at 430 °C for some hours. The yellow color due to dissolved sulfur disappeared, and in general colorless, clear melts appeared, although occasionally a precipitate other than excess aluminum appeared, consisting of alkali chloride or a characteristic gel-like substance. The presence of excess aluminum metal in highly basic melts (i.e., high chloride activity) tended to give brown metallic-like or opaque reaction products in cases of prolonged heating, even when no sulfur was present and the cell was of quartz. Typically, the brown residues (silicon[28]) started to appear 1–2 h after the last visible trace of sulfur disappeared.

The *Raman spectra* were recorded on colorless clear melts whenever possible, by using the 514.5-nm line of a CR argon ion laser. A filtered beam of vertically polarized light of ca. 500-mW intensity was focused to pass horizontally through a 4-mm diameter bore hole in a water-cooled, high-temperature furnace of aluminum bronze of high thermal conductivity, designed in this laboratory and equipped with quartz windows and extra heating around all optical openings. The temperature of the furnace block was regulated to within ca. ±0.1 °C and measured with calibrated chromel–alumel thermocouples. The temperature inside the furnace was constant to within ±2 °C. The scattered light was collected at 90° through a wide ($f/2$) optical opening in the furnace, analyzed with a Polaroid-sheet polarizer (giving polarized ($\parallel$) and depolarized ($\perp$) spectra), and sent through a 90° image rotator and a scrambler into a JEOL-JRS-400-D 0.4-m double monochromator with holographic (Jobin-Yvon) gratings. The signal was recorded with a cooled (0 °C), extended S-20 photomultiplier (Hamamatsu TV) attached to a photon-counting system. The spectrometer was calibrated to an absolute accuracy of ±1 cm^{-1} by using the laser plasma lines and a Ne discharge lamp. The scan rates

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were 10–50 cm^{-1}/min and spectral resolution was about 2–6 cm^{-1}. The photons were counted every 1 cm^{-1} and plotted within a large computer system.

General Considerations and Definitions. In the following, the formality, C', is given in units of F (i.e., the initial molar amount of one of the added substances dissolved in 1 L of the melt). Sulfur is treated as monomeric S. The formalities of the ions dissolved in the melts were determined from the composition by weight (excluding unreacted Al) and the density of the solvent at the particular temperature. $C_{S(-II)}$ and $C_{Al(III)}$ are the molar concentrations of sulfur in the oxidation state –2 and aluminum in the oxidation state +3, respectively. The dependence of the density on composition and temperature is only known for some of the binary solvent mixtures: LiCl–AlCl$_3$,[29] NaCl–AlCl$_3$,[29–31] KCl–AlCl$_3$.[32] For the CsCl–AlCl$_3$, CsBr–AlBr$_3$, and LiCl–CsCl systems interpolation assuming additivity of molar volumes was used. The procedure required knowledge of the densities of the constituent chlorides[33,34] and bromides.[33,35,36] Analogous interpolation in the KCl–LiCl and KCl–NaCl systems where densities of mixtures are known[37] worked accurately, and we expect that similar results are obtained here. Larger errors are probably introduced by assuming the densities of the examined melts equal to those of the pure solvent melts. Even these errors are still small compared to the estimated ~10% standard deviation associated with the total reproducibility of our Raman intensity measurements. It is difficult to improve this accuracy when working with an external standard. The composition of the melts is always given here in either of the notations MCl/AlCl$_3$ or MCl:AlCl$_3$, M being Li, Na, K, Rb, or Cs. The MCl/AlCl$_3$ notation is used to indicate the molar amounts of MCl and AlCl$_3$ which were weighed. This ratio might or might not correspond to the actual molar ratio denoted MCl:AlCl$_3$ which prevails in the melt. This is so because of the occurrence of precipitates (e.g., MCl) in some melts and because of the occasional addition of chemicals (Al, S, etc.) which affects the amount of MCl relative to AlCl$_3$.

Results and Discussion

Initial Experiments in CsCl–AlCl$_3$ Melts. During initial experiments it was noticed that aluminum metal and sulfur reacted according to eq 8 and that the product was completely

$$2Al + 3S \rightarrow products\ (``Al_2S_3") \qquad (8)$$
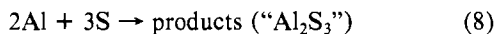
soluble in a melt of CsCl–AlCl$_3$ containing excess CsCl (e.g., of composition 55/45). The sulfur-containing melt dissolved aluminum at 430 °C, going through color changes from initially yellow to blue-green and finally to colorless and clear, without any trace of either aluminum or sulfur when the formality ratio of C'_{Al}:C'_S was equal to 2:3. The Raman spectrum of such melts and melts with excess aluminum (Figure 1) showed a new band near 325 cm^{-1}, where no band is present in the pure solvent,[38] with bands at 483, 344, 178, and 120 cm^{-1}. This new band exhibited a strength which increased with the total concentration of sulfur when an excess of aluminum was present in the melt. From Figure 1, it can be seen that the *weak* bands at 475, 235, and 217 cm^{-1} which probably are due to dissolved S$_8$[39] disappear coincidentally with
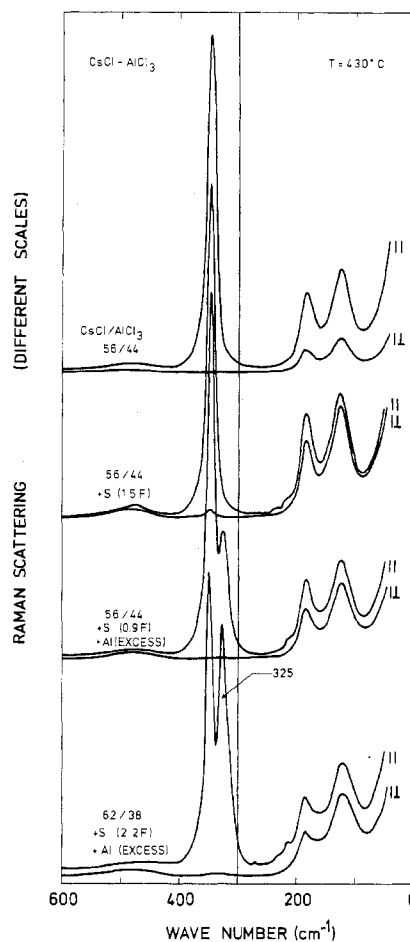

Figure 1. Raman spectra of equilibrated basic CsCl–AlCl$_3$ melts with increasing additions of aluminum and sulfur. The cell with only sulfur was saturated (yellow, with drops of molten S); the others were water clear without precipitate (except for excess Al; resolution 2–4 cm^{-1}). For the meaning of the CsCl/AlCl$_3$ ratios, see the section on definitions.

the yellow color. The clear melts cannot just contain a solution of S^{2-} ions, as expected if eq 9 predominated because "free"

$$``Al_2S_3" + 8Cl^- \rightarrow 2AlCl_4^- + 3S^{2-} \qquad (9)$$

sulfide ions should not give a vibrational Raman spectrum; and in practice they did not (Li$_2$S dissolved in LiCl–CsCl eutectic (0.01 F at 430 °C)). Hence, *a reaction between* AlCl$_4^-$ *and* S^{2-} *must take place.*

Experiments in the LiCl–CsCl Eutectic. It was decided to test the reaction quantitatively by means of Raman spectroscopy in a low-melting mixture which allowed dilution of AlCl$_4^-$. The eutectic mixture of LiCl and CsCl (59.3–40.7 mol %) melting near 323 °C[40,41] proved a convenient solvent.

Exploratory Raman spectra of the pure eutectic and solutions of sulfur, CsAlCl$_4$, and Li$_2$S (separately) were recorded at 430 °C (Figure 2). The high temperature was chosen to increase the solubility of Li$_2$S which was of the order of 0.015 ± 0.005 F at 430 °C, on the basis of visual observations on several melts and a density of 2.45 g/cm^3. A solubility of the same order was reported for Li$_2$S in KCl–LiCl.[6]

Solutions containing approximately equal concentrations of S(–II) and Al(III) were then prepared by using three different approaches: (i) Aluminum metal was used (in slightly excess)

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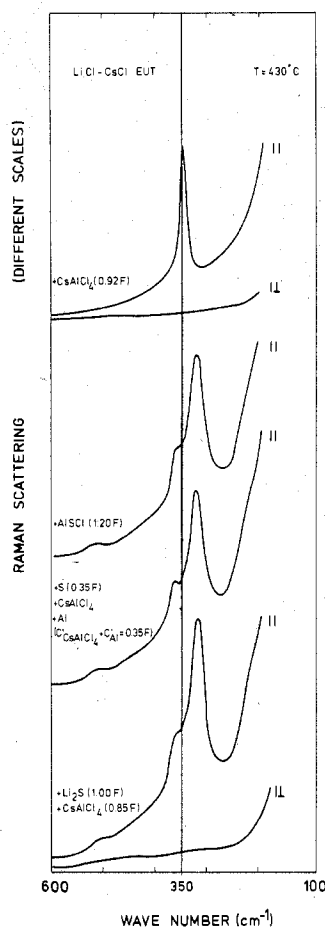(41) Richards, T. W.; Meldrum, W. B. *J. Am. Chem. Soc.* **1917**, *39*, 1816.

Figure 2. Raman spectra of LiCl–CsCl eutectic melts containing aluminate and sulfide prepared by using alternative methods. To the eutectic was added CsAlCl$_4$ (reference), AlSCl, S + Al + CsAlCl$_4$, or CsAlCl$_4$ + Li$_2$S. A suspended gel-like precipitate was present (resolution 4 cm^{-1}).

Figure 3. Raman spectra of LiCl–CsCl eutectic melts with 0.45 F Li$_2$S and decreasing additions of CsAlCl$_4$. Suspended precipitates of Li$_2$S occurred for $C'_{\mathrm{Li_2S}}{:}C'_{\mathrm{CsAlCl_4}} > 1.00$ (resolution 4 cm^{-1}).

Figure 4. Quantitative determination of the stoichiometry in the reaction between S(–II) and Al(III) in the LiCl–CsCl eutectic. The relative Raman signal was obtained as the ratio of the area due to ν_1(AlCl$_4^-$) relative to pure CsClCl$_4$, above estimated hand-drawn base lines. When Li$_2$S precipitates occurred, signals were scaled by using the 325-cm^{-1} band intensity.

to fully reduce sulfur in eutectic melts containing some amount of CsAlCl$_4$. (ii) AlSCl and CsAlCl$_4$ in varying amounts were added to the eutectic. (iii) Varying amounts of CsAlCl$_4$ and Li$_2$S were added to the eutectic. In all cases colorless melts were obtained which were clear (no precipitate) up to high concentrations. In approaches i and ii it is only possible to vary the concentrations of Al(III) and S(–II) such that $C_{\mathrm{S(-II)}}{:}C_{\mathrm{Al(III)}} \leq {}^3/_2$ (i) or ≤ 1 (ii). If the molar ratio of aluminum metal to sulfur in case i was just slightly $\geq{}^2/_3$, the attack of the cell walls and hence formation of the brown residues could be suppressed.

The Raman spectra of the melts depended only on the relative amounts of S(–II) and Al(III) and *not* on the method of preparation. Examples of spectra obtained by using the three methods of preparation are given in Figure 2, for the case of $C_{\mathrm{S(-II)}}{:}C_{\mathrm{Al(III)}} \approx 1$. It can be concluded that the methods are equivalent and that the same kind of aluminum chlorosulfide species occurs. This result shows that other convenient methods exist than electrogeneration of S(–II).[3,6]

It is clear from Figure 2 (and Table I) that the same new Raman band at $\sim$325 cm^{-1} appears as in Figure 1 but now without the presence of AlCl$_4^-$, because of the missing ν_1 band at 347 cm^{-1}. This gives us a chance to study the stoichiometric Al:S ratio by Raman spectroscopy. Two series of LiCl–CsCl eutectic melts were made: one series containing a fixed amount of CsAlCl$_4$ and increasing additions of Li$_2$S and another with the Li$_2$S content fixed and varying amounts of CsAlCl$_4$. The Raman spectra were recorded under standardized conditions ($\sim$10% accuracy). These spectra (Figure 3) clearly show that
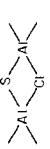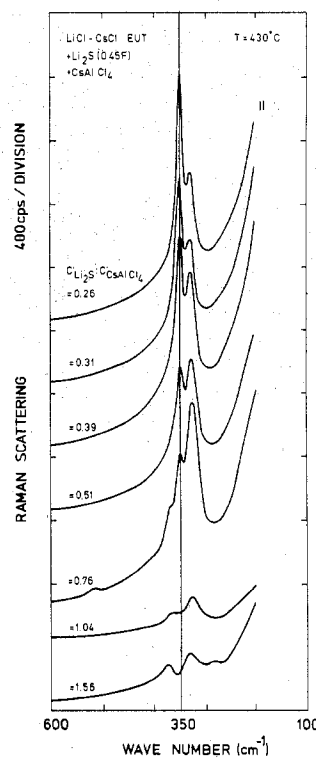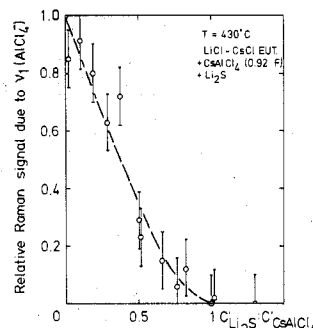
AlCl$_4^-$ reacted with S^{2-}, since the AlCl$_4^-$ band at 347 cm^{-1} steadily decreases as a function of $C_{\mathrm{S(-II)}}{:}C_{\mathrm{Al(III)}}$, while the new $\sim$325-cm^{-1} band (indicating the formation of new species) increases in intensity simultaneously. The association between Li$^+$ and Cl$^-$ within the eutectic solvent makes the Rayleigh wing so broad that, except for ν_1 at $\sim$347 cm^{-1}, the bands due to AlCl$_4^-$ are hardly discernible. When the $C_{\mathrm{S(-II)}}{:}C_{\mathrm{Al(III)}}$ ratio reached a value near or above 1.00, the melts contained suspended precipitates (Li$_2$S or reaction products) which reduced the Raman signals obtained (Figure 3, bottom).

The intensities of the observed ν_1(AlCl$_4^-$) bands are plotted against composition in Figure 4. The overall reproducibility of the individual signals is indicated by the error bars. A significant contribution to the error is the low accuracy with which the base lines of the background underneath the ν_1 band could be drawn. Also, the position of the sample and reference cells in the optical system was quite delicate, especially with respect to the focusing of the light onto the entrance slit. With the results in Figure 4, it is clear that the AlCl$_4^-$ signal de-

Table I. Raman Frequencies (cm⁻¹) of Sulfur and Sulfide Dissolved in the LiCl–CsCl Eutectic and in the CsCl–AlCl₃ System at 430 °C (and 370 °C)ᵃ

	LiCl/CsClᵇ		CsCl/AlCl₃ᵇ								
	59/41	59/41	56/44	56/44	56/44	56/44	53/47	50/50	46/54	40/60ᶜ	40/60ᶜ
additions	0.92 M Al(III)	0.35 M S(–II) 0.35 M Al(III)	56/44	56/44	S(satd)	0.9 M S(–II)	1.8 M S(–II)	1.6 M S(–II)	1.4 M S(–II)	1.2 M S(–II)	1.2 M S(–II)
AlCl₂–S–AlCl₂		518 w, p									
AlCl₄⁻										421 m, p	423 m, p
sulfur			485 w	485 w	485 w / 475 w, p	485 w	485 w				
Al₂Cl₇⁻		365 w, p									
AlCl₂–S–AlCl₂		325 s, p									
AlCl₄⁻	347 s, p		347 s, p	347 s, p	347 s, p	347 s, p	348 s, p	348 s, p	348 s, p	348 s, p	346 s, p
AlCl₂–S–AlCl₂						325 m, p	326 m, p	326 m, p			
Al₂Cl₇⁻								294 w, p	292 m, p	306 s, p	306 s, p
(Cl₂Al–S–AlCl₂ structure)										293 s, p	
sulfur		~220 w, p			235 w, p	215 w, p	216 w, p				
sulfur					217 w, p						
AlCl₂–S–AlCl₂			183 m	183 m	183 m	183 m	185 m	185 m	183 m		184 m
AlCl₄⁻											166 w
Al₂Cl₇⁻			123 m	123 m	123 m	123 m	123 m	123 m	122 m		125 w
AlCl₄⁻									100 w		99 m

ᵃ p = polarized, s = strong, m = medium, w = weak. ᵇ Molar ratio. For the meaning of I, see section on definitions. ᶜ Temperature 370 °C.
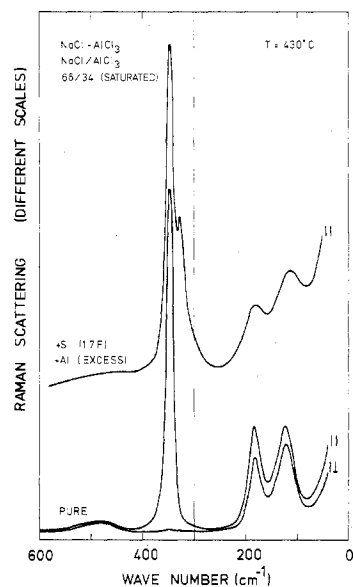

Figure 5. Raman spectrum of S and Al dissolved in basic NaCl–AlCl₃ (resolution 4 cm⁻¹). For the meaning of the NaCl/AlCl₃ ratio, see the section on definitions.

creases as the ratio $C_{S(-II)}$:$C_{Al(III)}$ was increased and finally disappears around a $C_{S(-II)}$:$C_{Al(III)}$ ratio of 1.00, indicating that *one* S²⁻ ion reacts with *one* AlCl₄⁻. We conclude that the schematical reaction (10) occurs. Here, η is the so-called

$$AlCl_4^- + S^{2-} \rightarrow AlSCl_{4-\eta}^{(3-\eta)-} + \eta Cl^- \qquad (10)$$
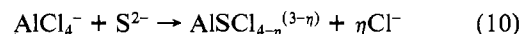
chloro basicity or the average chloride–sulfide exchange number, i.e., the number of chloride ions replaced from coordination to Al³⁺ each time one S²⁻ is added to the melt.[11] η is not known for the LiCl–CsCl eutectic, but it is known for the system NaCl–AlCl₃ from potentiometric experiments.[11] Here, at 175 °C, η attained a value of close to 2 in the basic range with pCl⁻ < 2. Hence, by extrapolating this result to our very basic chloride eutectic, we obtain eq 4 for η = 2, or perhaps (but rather unlikely) if η goes down to 1, we obtain eq 11. The influence of temperature on the spectra was found

$$AlCl_4^- + S^{2-} \rightarrow AlSCl_3^{2-} + Cl^- \qquad (11)$$
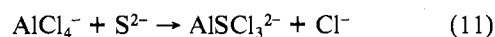
to be very small and can be interpreted as a general temperature insensitivity of equilibria like eq 4.

Potentiometric and Raman Spectroscopic Evidence for the Formation of [AlSCl₂]ₙⁿ⁻ (with n > 2). Having studied the reaction between sulfide and tetrachloroaluminate ions in the basic LiCl–CsCl eutectic solvent, we further investigated the behavior of sulfide in tetrachloroaluminate solvent.

Preliminary potentiometric measurements were made on the CsCl–AlCl₃ system by using a two-chamber potentiometric cell with aluminum electrodes and a saturated reference as previously described.[19] The concentration of chloride in the saturated melt was initially estimated to be roughly ~2.0 M at 400 °C by using the phase diagram data[42] and the interpolated density.[33,34] Potentiometrically, we obtained a value of 2.5 ± 0.1 M, on the basis of a measured potential difference of 63.97 mV between the sample melt (with CsCl/AlCl₃ = 53.98/46.02) and the saturated reference. Two other measurements on pure solvents with CsCl/AlCl₃ = 49.85/50.15 and 47.95/52.05 gave 889.9 and 1106.1 mV, respectively. These values correspond to an equilibrium constant $K = [Cl^-] \times [Al_2Cl_7^-]/[AlCl_4^-]^2 = 10^{-7.60}$ for the equilibrium given by eq 2 at 400 °C with Cs⁺ as counterion. (A value of $K = 10^{-7.4}$

(42) van der Kamp, L. K.; van Spronsen, J. W. *Z. Anorg. Allg. Chem.* **1968**, *361*, 328.

has been given in the literature.[43])

The chloro basicity of S^{2-} was determined potentiometrically for the melt with molar composition $CsCl/AlCl_3$ equal to 53.98/46.02. Sulfur was added to the melt, forming a 0.31 M "sulfide" solution, via reaction with the aluminum electrode (eq 8 and 9). This addition changed the potential difference from 63.97 to 82.64 mV, corresponding to an experimental η equal to 2.0 ± 0.1 considering reactions given by eq 8–10.

This result is equivalent to the η found within the basic range of the $NaCl-AlCl_3$ system at 175 °C by Robinson et al.[11] The obvious conjecture that the same species exist in the sodium and cesium systems was tested by means of Raman spectroscopy. Figure 5 shows the Raman spectrum of a basic (saturated) $NaCl-AlCl_3$ melt to which sulfur and excess aluminum had been added. Again, as in the $CsCl-AlCl_3$ system (Figure 1), a band near ~325 cm^{-1} was seen (here at 327 cm^{-1}). Since the spectrum was almost unchanged at 175 °C (where η = 2 was found[11]), the same kinds of species exist in both systems (giving rise to the ~325-cm^{-1} band) formed via reactions in which S^{2-} behaved as a *di*chloro base. Furthermore, the LiCl–CsCl results show that the S(–II):Al(III) stoichiometry is 1:1. Therefore, the ion $AlSCl_2^-$, suggested by Robinson et al.,[11] in analogy with Trémillon's $AlOCl_2^-$ ion[14,15] at first sight seems to be justified.

Polymeric $[AlSCl_2]_n{}^{n-}$. Following these ideas, we tried to prepare the pure compound "$CsAlSCl_2$" (eq 12). This com-

$$AlSCl + CsCl \rightarrow \text{"}CsAlSCl_2\text{"} \qquad (12)$$

pound represents AlSCl dissolved in the utmost basic $CsCl-AlCl_3$ system (i.e., when no $AlCl_3$ is added). For the preparation, a sealed quartz cell containing a mixture of 2 molar equiv of aluminum, 3 molar equiv of sulfur, 1 molar equiv of $CsAlCl_4$, and 2 molar equiv of $CsCl$ was heated at 450 °C. The yellow melt soon turned green and deep blue, and after some days of rocking, it had the appearance of a light green, very viscous liquid. After some hours at 600 °C, a colorless, clear, viscous liquid resulted. By then, all sulfur and aluminum had reacted. On being cooled, the liquid became highly viscous until finally a fully transparent glass was formed. The glass–liquid transition temperature was around 200 °C, judging from the disappearance of cracks produced by fast solidification. It might be possible to grow crystals but only with difficulty because of the high viscosity; we had no luck in doing so. Since the melt did not crystallize, it is reasonable to consider it to be polymeric. From the content of the cell, the homogeneous glass must have the composition Cs:Al:S:Cl equal to 1:1:1:2. Since the monomeric repetition unit is $[AlSCl_2]^-$ and aluminum is preferably tetrahedrally four-coordinate, the glass can hardly be anything else than chains or rings of the composition $[AlSCl_2]_n{}^{n-}$ with Cs^+ ions around to counterbalance the charges. The average degree of polymerization (or the ring size) is not known, but three observations point to large values of n, indicating long chains: (i) the lack of crystallization, (ii) the very high viscosity even at 500 °C, and (iii) the shape of the dashed curve in Figure 4. In this figure (as already discussed), the formation of aluminum chlorosulfides must be responsible for the disappearance of the $\nu_1(AlCl_4^-)$ signal. If very short chains like $[Al_2SCl_6]^{2-}$ or $[Al_3S_2Cl_8]^{3-}$ were formed by the addition of S^{2-}, this means that the $\nu_1(AlCl_4^-)$ signal would disappear faster than according to a 1:1 reaction. The observed initial slope of ca. –1.4 in Figure 4 seems to exclude rings like $[Al_2S_2Cl_4]^{2-}$ and $[Al_3S_3Cl_6]^{3-}$, etc. (requiring initial slopes of –1.0), and the shortest chain $[Al_2SCl_6]^{2-}$ (requiring an initial slope of –2), the first chain species likely to be formed in the LiCl–CsCl melt being $[Al_3S_2Cl_8]^{3-}$ and $[Al_4S_3Cl_{10}]^{4-}$ (requiring initial
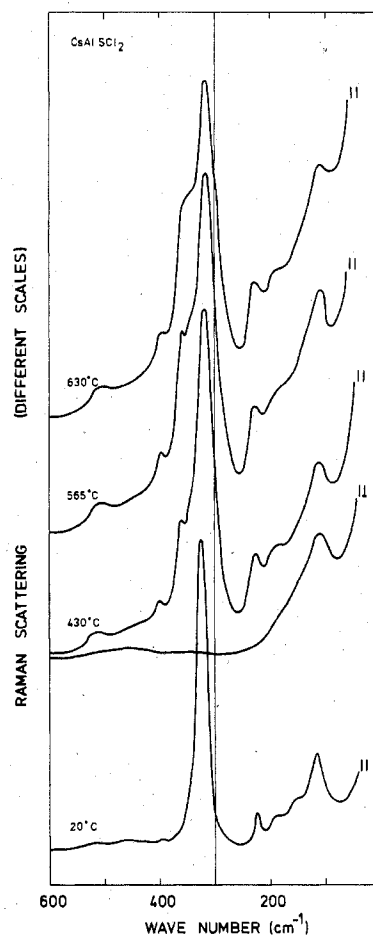

Figure 6. Raman spectra of "$CsAlSCl_2$" at high temperatures (viscous liquid) and at room temperature (clear glass; resolution 2–4 cm^{-1}).

Table II. Raman Frequencies (cm^{-1}) of "$CsAlSCl_2$"

melt (430 °C)	glass (25 °C)	soln^a (430 °C)
510 w, p		518 w, p
398 w, p		
360 w, p		365 w, p
319 s, b	323 s^b	325 s, p
225 m, p	225 m^b	~220 w, p
~185 w	~185 w	
~140 w	~145 w	
111 m	114 m	

^{a} From Table I. ^{b} No polarization measurement.

slopes of –1.5 and –1.3, respectively).

The Raman spectrum of the glassy compound is shown in Figure 6. The most prominent band at 319 cm^{-1} and the weaker features at 360 and 510 cm^{-1} are analogous to bands in Figure 2. Because of the absence of the Rayleigh wing of the LiCl–CsCl eutectic, weaker bands can now be clearly identified also (see Table II).

From the similarity of the spectra in Figures 2 and 6, we deduce that the species formed by the reaction between $AlCl_4^-$ and S^{2-} in the LiCl–CsCl eutectic and the polymeric species $[CsAlSCl_2]_n$ are of similar kind, probably differing only with respect to the degree of polymerization. It is well-known that for homologous series of chainlike molecules the vibrational spectra become more and more alike the longer the chain (compare, e.g., the similarities of the spectra of paraffins, C_nH_{2n+2}, and perhaps more interestingly the series Si_2OCl_6, $Si_3O_2Cl_8$, and $Si_4O_3Cl_{10}$[44]). Therefore, we assume that the

(43) Torsi, G.; Mamantov, G. *Inorg. Chem.* **1971,** *10,* 1900; **1972,** *11,* 1439.

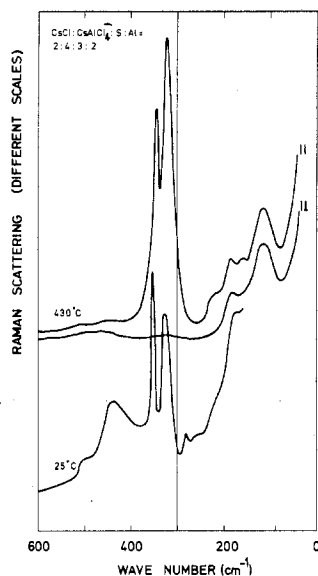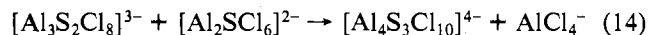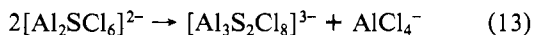(44) Goubeau, J.; Warncke, R. *Z. Anorg. Allg. Chem.* **1949,** *259,* 109, 233.

Figure 7. Raman spectrum of "$Cs_2Al_2SCl_6$". The bands observed from the clear melt at 430 °C indicate a mixture of $CsAlCl_4$ and $Cs_n[Al_nS_{n-1}C_{2n+2}]$ with n approximately equal to 4 (resolution 2–4 cm^{-1}). Bands are 347, 321, 220, ~180, and 115 cm^{-1} at 430 °C and ~500, 440, 351, 323, and 278 cm^{-1} at room temperature.
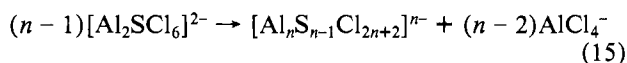
~325-cm^{-1} band is an indication for the $AlCl_2$–S–$AlCl_2$ unit of the $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ species ($n = 2, 3, 4, ...$). Depending on the value of n, the band shifts, $n \simeq 3$ giving ~325 cm^{-1} and $n \rightarrow \infty$ giving ~319 cm^{-1} in the cesium system. For sodium a slightly higher value of ~327 cm^{-1} is obtained (Figure 5).

The high viscosity, the similarity of the Raman spectra, and the other evidence show that $S(-II)$ *dissolved in basic tetrachloroaluminates* (or in solutions containing the $AlCl_4^-$ ion) *exists as chainlike species* $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$. In dilute melts n seems to attain small values like 3–4, and in more "$AlSCl_2^-$"-concentrated solutions higher values of n are reached until finally for $n \rightarrow \infty$ the polymeric compound "$CsAlSCl_2$" is obtained. Small rings do not seem to be formed to any great extent.

The conclusion that $[Al_2SCl_6]^{2-}$ is of minor importance relative to longer chains $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ was confirmed by means of the following experiment. Aluminum, sulfur, Cs-$AlCl_4$, and CsCl were mixed in the molar ratios 2:3:4:2 and equilibrated for some days at 430 °C until a homogeneous clear melt was obtained. The composition would allow the formation of the compound $Cs_2Al_2SCl_6$, but it melted incongruently, starting at ~260 °C, and the Raman spectrum (Figure 7) clearly showed the presence of $AlCl_4^-$, judging from ν_1 (347 cm^{-1}). Accordingly, reactions like

$$2[Al_2SCl_6]^{2-} \rightarrow [Al_3S_2Cl_8]^{3-} + AlCl_4^- \qquad (13)$$

$$[Al_3S_2Cl_8]^{3-} + [Al_2SCl_6]^{2-} \rightarrow [Al_4S_3Cl_{10}]^{4-} + AlCl_4^- \qquad (14)$$

must occur or cumulatively

$$(n-1)[Al_2SCl_6]^{2-} \rightarrow [Al_nS_{n-1}Cl_{2n+2}]^{n-} + (n-2)AlCl_4^- \qquad (15)$$

Approximately 20% of the total aluminum present in the cell occurred as $AlCl_4^-$ and 80% as some kind of $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ species, judging from the intensities of the $AlCl_4^-$ Raman signal combined with a measurement of the density. Hence, eq 14 seems to be the most important one for a description of the species in the "$Cs_2Al_2SCl_6$" melt.

It is instructive to compare these results for "$CsAlSCl_2$" with the chemistry of some analogous polymeric systems. First of all, we note the existence of homologous series of chloro-
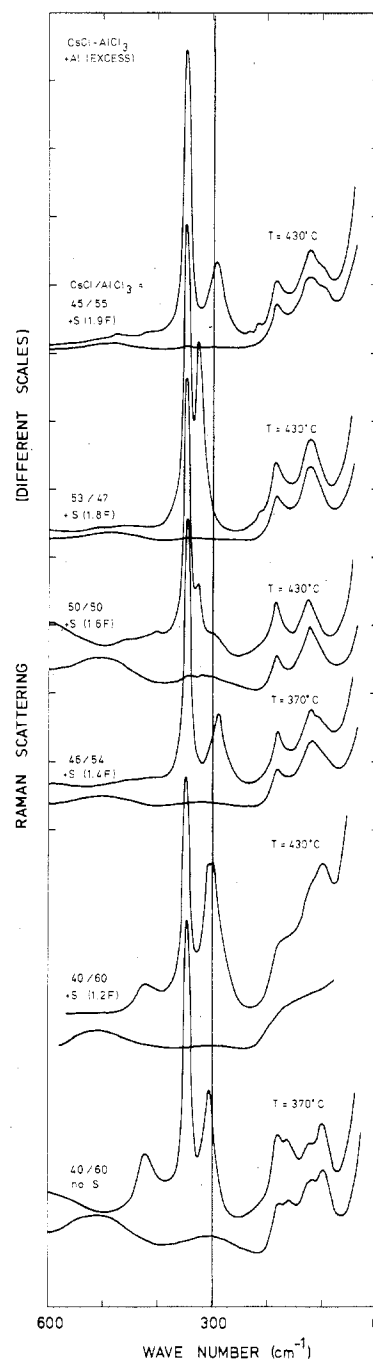

Figure 8. Raman spectrum of $CsCl$–$AlCl_3$ melts with different additions of aluminum, sulfur, CsCl, and $AlCl_3$. All unreacted sulfur disappeared when the acidic melt (containing sulfides, S, and Al) was made basic and then acidic. Neutral or acidic melts tended to give fluorescence (resolution 4 cm^{-1}). For the meaning of the $CsCl/AlCl_3$ ratio, see the reaction on definitions.

silthianes (Si_2SCl_6 and polymeric $(SiSCl_2)_\infty$[45–47]) and halosiloxanes (Si_2OX_6, $Si_3O_2X_8$, etc., identified up to $Si_7O_6X_{16}$ with X = Cl or Br[48,49]), but also the metasilicate and metaphosphate glasses (e.g., $(Na_2SiO_3)_\infty$ or $(NaPO_3)_\infty$) are of interest in this context.[50] In all these cases, the liquids or melts containing

(45) Schumb, W. C.; Bernard, W. J. *J. Am. Chem. Soc.* **1955**, *77*, 862.
(46) Panckhurst, D. J.; Wilkins, C. J.; Craighead, P. W. *J. Chem. Soc.* **1955**, 3395.
(47) Gaubeau, J.; Hirsemann, W. D. *Z. Anorg. Allg. Chem.* **1957**, *290* 292.
(48) Schumb, W. C.; Klein, C. H. *J. Am. Chem. Soc.* **1937**, *59*, 261. Schumb, W. C.; Holloway, D. F. *Ibid.* **1941**, *63*, 2753. Schumb, W. C.; Stevens, A. J. *Ibid.* **1950**, *72*, 3178.
(49) Chambers, D. W. S.; Wilkins, C. J. *J. Chem. Soc.* **1960**, 5088.

polymeric chains form transparent glasses by rapid cooling, though in some cases crystals with chains or small rings can be obtained.

Acid–Base Properties of $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ and Evidence for $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$. In the basic part of the CsCl–AlCl$_3$ system the chain species, $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$, are saturated with respect to an excess of Cl$^-$ ions. We considered next what happened under acidic conditions. The principal acid–base equilibrium of the solvent near the neutral point is eq 2,[43,51,52] with $K \simeq 10^{-7.6}$ for a system containing Cs$^+$ at 400 °C. On the acidic side (i.e., with the CsCl/AlCl$_3$ molar ratio < 1.00) Al$_2$Cl$_7^-$ becomes more abundant according to the acid–base equilibrium (eq 2).

As the CsCl/AlCl$_3$ molar ratio approaches 1.00 on the basic side, no effect on the Raman spectra was found until near the 50/50 ratio. Here the Raman spectra changed markedly (Figure 8 and Table I). The ~325-cm^{-1} band disappeared, and a new band appeared at ~292 cm^{-1}. This band cannot be the strong polarized 306-cm^{-1} band due to Al$_2$Cl$_7^-$ because of the different position and because of the complete absence of the Al$_2$Cl$_7^-$ band at ~430 cm^{-1}. These two bands were not seen until the CsCl/AlCl$_3$ ratio was considerably below 1.00. Apparently the added aluminum and sulfur released chloride ions by reaction with the solvent.
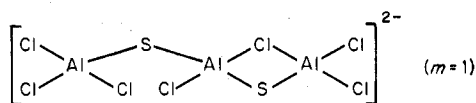
The 292-cm^{-1} band must be due to sulfide-containing species since the band occurred only when S(−II) was present. It cannot be due to the $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ ions, since their characteristic ~325-cm^{-1} band disappeared at the same time as the 292-cm^{-1} band appeared. Hence, $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ type species can only be stable at high Cl$^-$ concentrations. Below some threshold value in Cl$^-$ activity (pCl$^-$ ≈ 3.8) the chloro basicity, η, of S^{2-} changed from ca. 2 to ca. 3 in the NaCl–AlCl$_3$ system at 175 °C,[11] and presumably the same thing happens in the cesium system. The release of chloride happens by elimination of coordinated Cl$^-$ from $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$, forming an increasing number (m) of sulfide–chloride double bridges of the type
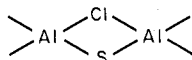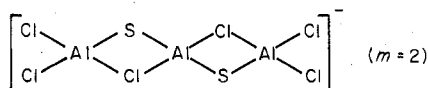

Assuming no change in polymerization, we obtain the reaction

$$[Al_nS_{n-1}Cl_{2n+2}]^{n-} \rightleftarrows [Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-} + mCl^- \rightleftarrows$$
$$[Al_nS_{n-1}Cl_{n+3}]^- + (n-1)Cl^- \quad (16)$$
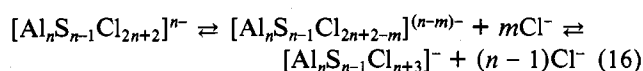
E.g., for $n = 3$ ions like

and

would be formed.

For large n and high acidity the previously proposed formation of "AlSCl" is approached (eq 7). An isolated "AlSCl" molecule is not likely to be soluble in acidic melts per se (aluminum being preferably four-coordinate) and might precipitate as the solid AlSCl,[12,13] which has an orthorhombic layered structure with four-coordinate Al (presumably a

two-dimensional Al–S network with terminal Cl as in GaOCl[50]). In fact, a white precipitate was seen in the neutral and acid melts; and distinct Raman bands at 273 and 202 cm^{-1} were found in spectra from these samples quenched to room temperature. The solid AlSCl has its strongest Raman bands exactly here (obtained on powder at room temperature), so the precipitate can be due to AlSCl. On the other hand, some "sulfide" must be in solution because of the ~292-cm^{-1} band.

We assign this band to the occurrence of
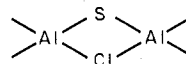
doubly bridged skeletons in $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ ions (varying numbers of single and double bridges). The band position around ~292 cm^{-1} is quite independent of n and m ($n > 2$, $n > m > 0$), in the same way as the ~325-cm^{-1} band of the $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ ions was found to be independent of n, except for small shifts in position. All these ions have been referred to as AlSCl and AlSCl$_2^-$, respectively, in recent literature,[10,11,16,17] and the authors pointed out that the structures might be more complicated. AlSCl in solution probably is $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ and AlSCl$_2^-$ is $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$.

We are unable to estimate n and m here and in eq 16 (n might even change during the reaction or depend on the ratio $C_{S(-II)}:C_{Al(III)}$, the chloride activity, and the temperature). We note that a mixture of Na$_2$S and excess AlCl$_3$ apparently did not react at 330 °C to form NaAl$_2$SCl$_5$ (the $n = 2$, $m = 1$ member of the $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ series) but gave only solid AlSCl,[12] perhaps due to the special procedure applied. Also, we note that the existence of an Al$_2$OCl$_5^-$ ion has been suggested by Letisse and Trémillon[14] for an analogous oxide. However, nothing can be said yet on the quoted dissolved species "AlOCl", "AlO$^+$", and "AlOCl$_2^-$".[14,15,18]

Dependence on Alkali Metal. The influence of the alkali metal was studied in two series of mixtures with molar ratios MCl/AlCl$_3$ equal to 54/46 and 52/48. To the melts were added equal amounts of sulfur and an excess of aluminum such that formalities within each series were identical except for the kind of alkali metal. The amount of sulfur was chosen such that the 54/46 series was inevitably basic and such that the 52/48 series could be neutral, taking into account that "Al$_2$S$_3$" must act as an acid substance when $\eta = 2$ (in basic melts) and as a basic substance when $\eta = 3$ (in acidic melts): 2Al + 3S + 8Cl$^-$ → 2AlCl$_4^-$ + 3"S^{2-}"; "S^{2-}" + AlCl$_4^-$ → product + ηCl$^-$. Hence, for $\eta = 2$, $^2/_3$ Cl$^-$ is consumed totally per S, and for $\eta = 3$, $^1/_3$ Cl$^-$ is liberated per S.

The equilibrated melts were all colorless with varying amounts of precipitation at 430 °C. Raman spectra of the 52/48 series are shown in Figure 9 and bands given in Table III. Besides the four bands due to the AlCl$_4^-$ ion (occurring at approximately the same position, ~490, ~350, ~180, and ~120 cm^{-1} for all M[38]) only the familiar bands at ~325 and ~292 cm^{-1} are seen in Figure 9: the ~325-cm^{-1} band alone for Cs and Rb, both bands for K and perhaps Na, and the ~292-cm^{-1} band alone for Li, now occurring at ~300 cm^{-1}. The Raman spectra of the 54/46 series had much the same appearance except for a systematic trend by which the ~292-cm^{-1} bands were observed less pronouncedly (Li looked like Na in Figure 9, etc.). We conclude from this, in connection with the results of Figure 8, that the chloride activity of especially the Li-containing melts is much lower than that for the Cs melts with the same composition. This is due to the well-known association among Cl$^-$ and the smaller more polarizing alkali metal ions. The fact that the 52/48 spectra were different from the 54/46 ones means that the precipitates of the former series cannot be merely MCl, because if the melts in the 52/48 series had already been saturated with MCl, the 54/46 series would have been unchanged. The phase diagrams

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Table III. Raman Frequencies (cm^{-1}) of Bands at 430 °C Observed in ~1.2 M Sulfide Melts with MCl/AlCl$_3$ = 52/48 (M Being Alkali Metal)

	Li	Na	K	Rb	Cs
AlCl$_4^-$	488 w	485 w	482 w	482 w	482 w
AlCl$_4^-$	347 s, p	349 s, p	348 s, p	348 s, p	347 s, p
AlCl$_2$-S-AlCl$_2$		~327 w, p	326 w, p	325 m, p	325 m, p
>Al<$^S_{Cl}$>Al<	300 m, p	300 w, p	~300 w, p		
AlCl$_4^-$, AlCl$_2$-S-AlCl$_2$	170 m	181 m	182 m	182 m	182 m
AlCl$_4^-$, AlCl$_2$-S-AlCl$_2$	119 m	118 m	119 m	122 m	122 m
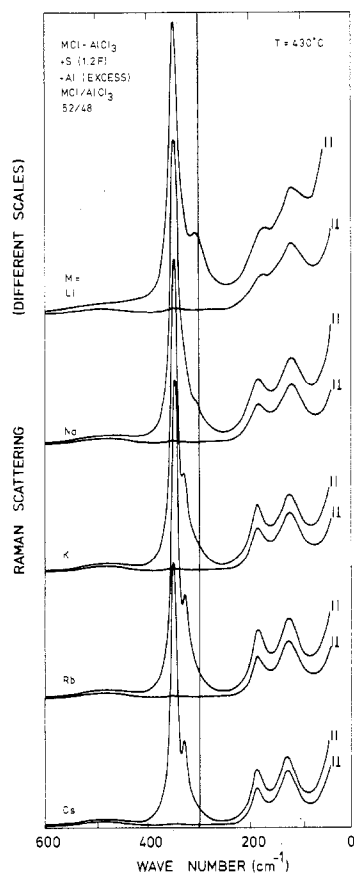
Figure 9. Raman spectra of ~1.2 M sulfide in tetrachloroaluminate melts depending on the kind of alkali metal (resolution 4 cm^{-1}). For the meaning of the MCl/AlCl$_3$ ratio, see the section on definitions.

of the MCl–AlCl$_3$ mixtures show beyond any doubt that no solid phase exists in any neutral MAlCl$_4$ melt at 430 °C (in accordance with that, the approximately neutral 52/48 series are unsaturated with respect to MCl). Further, it appears that MCl saturation is close to occur for the 54/46 series (where the actual molar ratio MCl:AlCl$_3$ in the melt is approximately equal to 52:48 by taking the chloro acidity of "Al$_2$S$_3$" into account (i.e., eq 8–10)). The MCl saturation temperatures (including uncertainty) for the MCl–AlCl$_3$ melts with molar composition ratio 52:48 all seem to be below 430 °C[19,29,42,53–56] except for the LiCl–AlCl$_3$ system where the LiCl saturation temperature can only be estimated to be 430 ± 100 °C.[29,53] Therefore, even the Li melt of the 54/46 series might not be saturated. The precipitates were more or less gel-like, consisting of M$_n$[Al$_n$S$_{n-1}$Cl$_{2n+2}$] or M$_{n-n}$[Al$_n$S$_{n-1}$Cl$_{2n+2-m}$].

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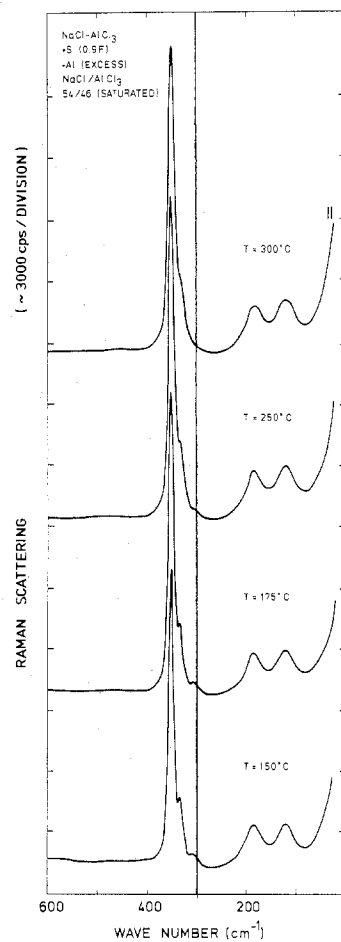
Figure 10. Temperature dependence of the Raman spectrum of sulfide in a basic NaCl–AlCl$_3$ melt (resolution 4 cm^{-1}). Bands are 351, 333, 304, 184, and 118 cm^{-1} at 150 °C. For the meaning of the NaCl/AlCl$_3$ ratio, see the section on definitions.

The dependence of the Raman spectra on temperature was small except for the cases where the ~325- and ~292-cm^{-1} bands were both present. Figure 10 illustrates the situation for Na in the 54/46 series: the ~292-cm^{-1} band diminished notably at higher temperatures. Figure 10 gives evidence for an increasing chloride activity due to higher solubility of NaCl at higher temperatures, whereby eq 16 is shifted to the left. The

>Al<$^S_{Cl}$>Al<
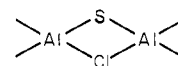
rings are opened, reducing the "concentration" of the units responsible for the 292-cm^{-1} band. Similar, though less pronounced, results were obtained for Li and K.

Related Systems. In an attempt to see how general these results are, we extended this study to analogous selenide and
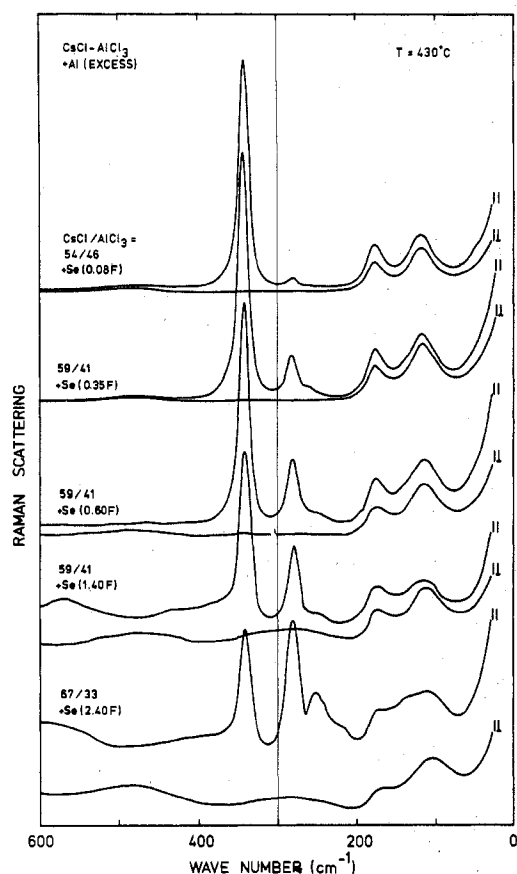
Figure 11. Raman spectra of clear basic CsCl-AlCl₃ melts with increasing additions of aluminum and selenium. Gel precipitates occurred in the most basic melts when selenide formality exceeded ~ 1 F (resolution 4 cm⁻¹). For the meaning of the MCl/AlCl₃ ratio, see the section on definitions.

bromide basic melts as well as the solids AlSCl, AlSeCl, Al_2S_3, and Al_2Se_3.

It has been shown by electrochemical methods[3,11,17] that *selenide* can be dissolved in chloride and tetrachloroaluminate melts with a behavior much like that of sulfide. In our experiments elemental selenium reacted with excess aluminum in basic CsCl-AlCl₃ melts, forming colorless, clear solutions. High concentrations of selenide and chloride gave gel-like precipitates. The Raman spectra (Figure 11) exhibited new bands which are certainly not due to AlCl₄⁻ and must be associated with the formation of selenide-containing species. Since selenide has been found to behave as a *di*chloro base in basic and as a *tri*chloro base in acidic NaCl-AlCl₃ melts at 175 °C,[11] these species are presumably $[Al_nSe_{n-1}Cl_{2n+2}]^{n-}$ in analogy with the sulfide results. In our experiments (Figure 12), the basicity of the melts was made to increase as the concentration of Se(-II) increased such that any possible formation of partially doubly bridged $[Al_nSe_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ species was avoided.

We also briefly wanted to see the effect of replacing chloride with *bromide*. The phase diagrams of the binary systems MBr-AlBr₃ are known[53,57] as is the Raman spectrum of the AlBr₄⁻ ion.[58,59] Again, as in the chloride system, we found that elemental sulfur or selenium in basic CsBr-AlBr₃ melts reacted with excess aluminum metal at 430 °C, forming clear
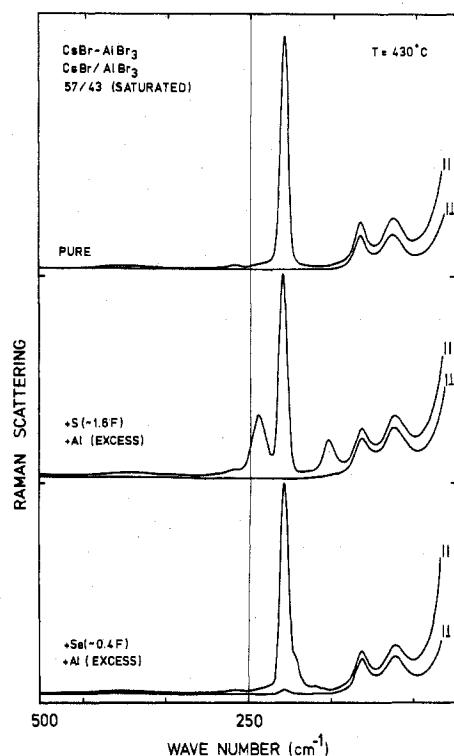

Figure 12. Raman spectra of basic CsBr-AlBr₃ melts, in the pure form and with additions of excess aluminum and sulfur or selenium. The melts had precipitates of CsBr and for selenium a gel substance. Also for sulfur a gel was formed at lower temperatures (resolution 4 cm⁻¹). The 267-cm⁻¹ band is presumably an impurity. The bands at 396, 208, 116, and 77 cm⁻¹ are due to AlBr₄⁻. For the meaning of the CsBr/AlBr₃ ratio, see the section on definitions.

Table IV. Raman Frequencies (cm⁻¹) of Aluminum Chlorosulfide Ions $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ and Presumably Analogous Species with Selenide and/or Bromide Substitution

S, Cl[a]	Se, Cl[b]	S, Br[c]	Se, Br[c]
510 w, p			
398 w, p			
360 w, p			
319 s, p	287 s, p	235 s, p	~190 m, p
	~270 w, p[d]		
	~250 w, p[d]		
225 w, p	~147 w, p[d]	154 s, p	~168 w, p[d]
111 m	~113 m[d]	~73 w[d]	~73 m[d]

[a] See Figure 6. [b] Figure 11. [c] Figure 12. [d] These bands are not well resolved.

Table V. Raman Frequencies (cm⁻¹) of Solid Compounds at Room Temperature

AlSCl	AlSeCl	Al_2S_3	Al_2Se_3
			~450 w
		498 w	433 w
		440 w	425 w
		380 w	315 w
		353 w	296 w
273 s	190 m	~252 w	208 w
	159 s	248 s	158 s
202 m	145 w	211 m	135 m
	137 w	191 m	130 w
	129 w	174 m	
	119 m	154 w	
142 m	113 w	141 m	114 m
	100 m	130 w	99 w
	90 w	120 w	87 w
110 w		101 m	65 w
		67 w	
		58 w	

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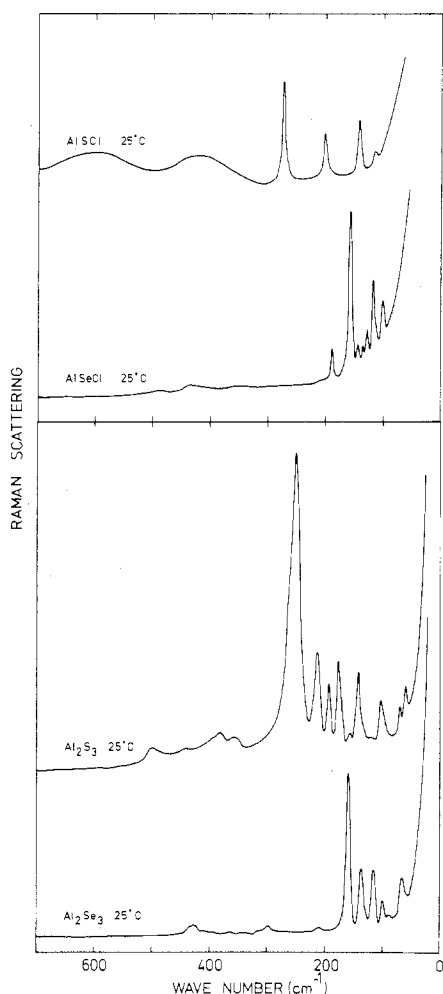
Figure 13. Raman spectra of powder samples of AlSCl, AlSeCl, Al$_2$S$_3$, and Al$_2$Se$_3$ at 25 °C. The AlSCl tended to give fluorescence. The spectrum of AlSeCl showed orientational effects, depending on the orientation of the fine needles (resolution 3 cm^{-1}).

melts. In the Raman spectrum of the AlBr$_4^-$ ion with Cs$^+$ as cation, the bands occurred at 396, 208, 116, and 77 cm^{-1} (Figure 12), in accordance with previous results.[58,59]

The sulfide- or selenide-containing tetrabromoaluminate melts gave new bands (e.g., at 235 and 154 or 190 cm^{-1}, respectively) with intensities proportional to concentrations,

indicating the existence of complexes. The occurrence of gel-like precipitates suggests that also in these bromide melts chainlike ions [Al$_n$X$^{-II}_{n-1}$Br$_{2n+2}$]$^{n-}$ can be formed (X^{-II} = S or Se). Evidence for this formula is missing, but it is not unreasonable to expect the bromide systems to be analogous to the chloride systems as has been found in numerous other cases. The vibrational data are given in Table IV. The only chance for making assignments is that the strong polarized bands are caused by analogous motions in analogous species. From the trend in frequencies it is obvious that both the particular halogens and chalcogens are involved in determining the frequency of these bands. Hence, the bands cannot be assigned to simple motions like Al–X stretchings, etc., and the spectra must be regarded as "fingerprints" of the species existing in the melts.

Finally, we obtained room-temperature Raman spectra of the white solids AlSCl, AlSeCl, Al$_2$S$_3$, and Al$_2$Se$_3$ (Figure 13 and Table V). Data on the vibrational spectra of these hygroscopic substances have never been reported. Also for these spectra, it appears that no simple assignment is possible. In the AlX^{-II}Cl spectra the bands must be due to phonons characteristic of the extended layer/chain structures of which AlSCl and AlSeCl probably consist.[12,20] Al$_2$S$_3$ and Al$_2$Se$_3$ have slightly different structures at room temperature both being closely related to the Wurtzite structure[50] and with cation-deficient disordered three-dimensional Al–X^{-II} networks.[21-27] As would be expected, the phonons in the sulfur compounds generally occur at higher frequencies than in the selenium compounds (Table V).

Concluding Remarks. The coordination chemistry within the AlCl$_4^-$–S^{2-} system in molten salts cannot be considered as solved. The major achievement via Raman spectroscopic results reported here is the establishment of the chain species [AlSCl$_2$]$_n^{n-}$ which seem to be formed in basic systems.