a silicate sheet is a main factor in realizing the high resolution of the present clay column in comparison with the previous ion-exchange adsorbents.

The above conclusion is supported by the fact that a montmorillonite column whose cation-exchange sites were replaced with Δ-Ni(phen)$_3^{2+}$ to 50% (or Δ-Ni(phen)$_3^{2+}$–4M$^-$) exhibited much less resolution efficiency (~5%) for Co(acac)$_3$. On such a column, the adsorbed Δ-Ni(phen)$_3^{2+}$ ions are so far apart from each other that the phenanthroline ligands can no longer constitute a hydrophobic region as in the Δ-Ni(phen)$_3^{2+}$–2M$^-$ column.

Probably the manner of chirality recognition by Δ-[Ni(phen)$_3$]$^{2+}$ is not unique; thus the method will be varied immensely by choosing the kind of preadsorbed chiral complex. For example, if a trivalent complex like [Co(phen)$_3$]$^{3+}$ is adsorbed instead of [Ni(phen)$_3$]$^{2+}$, the resultant column may have a wider interlamellar space, allowing for the penetration of a more bulky complex. This is expected because [Co(phen)$_3$]$^{3+}$ occupies three cation-exchange sites per chelate.

Acknowledgment. Thanks are due to Dr. R. Ohnishi of Hokkaido University for permission to use the JEOL ORD spectrophotometer.

Registry No. Co(acac)$_3$, 21679-46-9; Cr(acac)$_3$, 21679-31-2; Ru(acac)$_3$, 14284-93-6; Rh(acac)$_3$, 14284-92-5; Δ-[Ni(phen)$_3$]Cl$_2$, 63985-35-3.

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Negative Oxidation States of Chalcogens in Molten Salts. 2. Raman Spectroscopic, Spectrophotometric, and Electron Spin Resonance Studies on Chloroaluminate Solutions Containing an S_3^- Entity

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The blue solutions produced by reaction between aluminum and sulfur in basic CsCl–AlCl$_3$ melts have been examined by means of Raman spectroscopic, spectrophotometric, and ESR measurements and are mainly attributed to the presence of S_3^- species. The formal absorptivity of the blue solutions, with an absorption maximum near 16 700 cm^{-1}, was measured in the temperature range 390–470 °C and at different sulfur to aluminum formality ratios. The Raman intensity of the ν_1 = 529 cm^{-1} stretching mode was also measured at different sulfur to aluminum formality ratios and in conjunction with the absorption measurements was used to determine the possible number of species formed. The findings have been best interpreted by an equilibrium between the blue S_3^- entity, S(–II) species (present in polymeric chain species of the $[AlSCl_2]_n^{n-}$ type), and molecular sulfur. No direct evidence for the formation of other sulfur species has been found, but there are indirect indications of a possible existence of other sulfur species. ESR measurements show the presence of the paramagnetic S_3^- radical with $g = 2.023$ and a hyperfine splitting into six lines arising from a direct coupling of the S_3^- with the aluminum atom ($I = {}^5/_2$). The data are discussed in terms of the possible formation of $[S_3AlCl_3]^-$ and $[S_3AlCl_4]^{2-}$ species in these melts. Finally a single-line ESR spectrum of blue sulfur species in LiCl–CsCl eutectic was attributed to the presence of S_3^- with $g = 2.028$. This "free" radical had its stretching mode at 527 cm^{-1}.

Introduction

It is now well recognized that sulfur dissolves in a number of condensed media[3–6] including molten-salt systems such as eutectic LiCl–KCl[7] and basic CsCl–AlCl$_3$,[8] forming the blue S_3^- radical. It was, however, found that no blue color could be formed in the most basic NaCl–AlCl$_3$ and KCl–AlCl$_3$ melts in the temperature range up to 400 °C. It was also shown mainly by Raman spectroscopy[9] that, in melts of CsCl–AlCl$_3$ (e.g., 55–45 mol %), sulfur and excess aluminum (i.e., formality ratio Al:S > 2:3) gave no blue species but only polymeric aluminum chlorosulfide chain species of the type $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ ($n \geq 3$).

The present investigation was undertaken to study the formation of different sulfur species as a function of the relative amounts of reducing and oxidizing materials (Al and S, respectively) weith CsCl–AlCl$_3$ as solvent (55.7–44.3 mol %) at temperatures near 400 °C. A few experiments using molten LiCl–CsCl (59.3–40.7 mol %) were also performed in which S_3^- was produced by reaction between sulfur and Li$_2$S. A main purpose of this study was to investigate the conditions for the formation of S_3^- from sulfur and aluminum and to determine whether blue species other than S_3^- could be formed.

Experimental Section

General Information. One major problem encountered in these types of experiments was determining the total concentration of sulfur in the melt. In the work with the CsCl–AlCl$_3$ solvent semiaccurate sulfur concentrations have been determined by an essentially simple but experimentally difficult technique. This involved application of sealed cells which were almost completely filled with the melt, keeping the content of the vapor phase to minimum. In the experiments performed with the LiCl–CsCl melt a larger gas volume above the melt was allowed.

Chemicals. The anhydrous AlCl$_3$ used was obtained as described previously.[10] CsCl (Suprapur from Merck) and LiCl (Baker Analyzed reagent) were dehydrated by using our normal procedure for alkali chlorides.[9] Lithium sulfide, Li$_2$S (CERAC/PURE, 99.9%), was obtained in a closed ampule and used without further purification. The sulfur was from Fluka (99.999%). Aluminum metal was used

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(1) Visiting Professor from State University of New York at Old Westbury.

(2) Visiting Professor from Argonne National Laboratory.

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in the form of foil to facilitate very accurate additions of small amounts.

All materials were handled in nitrogen-filled gloveboxes with water contents of ca. 5 ppm. Before use all cells were carefully cleaned in a solution of hydrogen fluoride, rinsed well, and then heated to red-hot under vacuum to eliminate traces of impurities that could otherwise have a strong influence on the measurements. The cells were loaded in the glovebox and finally sealed under vacuum.

Raman Spectroscopic Measurements. The cells used for measuring the Raman spectra were made from 10-mm quartz tubes (~8-mm i.d., ~2-mL volume). Each tube was connected by a 5-mm-o.d. stem to a bulb with larger volume. In a few cases, Raman spectra were obtained with use of ESR cells (described later).

The solid materials were melted under vacuum and equilibriated in the bulb for 1–3 days at 400 °C. Thereafter the melt was transferred to the tube part of the cell by turning the hot cell upside down. By cooling the lower part with liquid nitrogen, it was then possible to sublime all sulfur and remaining salts from the bulb to the bottom of the cell. Then the cell was sealed just above the solidified melt. In this way the volume of the gas phase was reduced to below 2% of the total cell volume at the measuring temperature, and the uncertainty regarding the concentration of sulfur in the melt was kept satisfactorily low. The compact solid in the cell had to be flamed cautiously from one end to minimize the risk of cell cracking during remelting. However, several cells cracked.

For recording of the Raman spectra, the cells were placed and equilibrated in a Kanthal-wire-wound quartz tube furnace with a water-cooled glass jacket. This furnace had greater spacing between the windings where the samples were placed than at the other parts of the furnace, so that the laser beam could pass through the water, the furnace, and the cell and the scattered light could pass into the spectrophotometer. The temperature inside the furnace was regulated within ±5 °C and measured with a calibrated chromel–alumel thermocouple placed at the surace of the cell.

The Raman instrument was a JEOL JRS-400D spectrometer with a cooled (−5 °C) extended S-20 photomultiplier. A Coherent Radiation 4-W argon ion laser served as the light source of the 514.5-nm line (output 500–1000 mW). The signal was amplified in a photon-counting system.

Spectrophotometric Measurements. The absorption cells were made of fused quartz (Ultrasil from Hellma or Spectrosil from Thermal Syndicate) and had an optical path length of 0.5 or 1.0 mm. The filling procedure for these cells was the same as for the Raman cells in order to obtain a very small (less than 2%) vapor space. Again, the cracking of some absorption cells during the remelting procedure was a serious problem, reducing the number of successful experiments.

In one case a used Raman cell was placed inside the upper bulb used to fill an absorption cell and sealed off. The Raman cell in contact with the upper bulb was cracked from outside with a very hot flame. After this, all the material was transferred to the cuvette part and sealed off. Vapor-phase losses were minimized due to cooling with liquid nitrogen. In this way the Raman spectrum and the absorption spectrum were obtained from the same melt.

The absorption cells were equilibrated in a furnace of a type previously described.[11] The furnace was regulated to within ±0.1 °C at measurement temperatures and the temperature determined by calibrated chromel–alumel thermocouples. After equilibrium was attained, typically 0.5–1 h after the cell was transferred to the furnace, the furnace was placed in the sample compartment of a Cary 14R spectrophotometer and the spectra were recorded on paper tape with a Datex digital system.

ESR Measurements. The fused-silica cells used for the ESR measurements have been described elsewhere.[12] For optimum sensitivity, a fused-silica tube having an inner diameter of 1.02 ± 0.01 mm (purchased from Wilmad Glass Co. Inc., Bueno, NJ) was used. The filling of the cells was performed in the same way (and with the same cracking problems) as for Raman and spectrophotometric cells. The volume of the gas phase at the measuring temperature was below 1% of the total cell volume (except for the cell containing LiCl–CsCl solvent).

The cells were remelted cautiously with a flame and placed in the TE_{011} cavity of the JEOL JES-ME-IX ESR spectrometer, which operated in the X band. The cells were heated to the measuring temperature of 380–430 °C within ±2 °C by nitrogen gas, which was preheated by passage through a Si–C tube furnace.

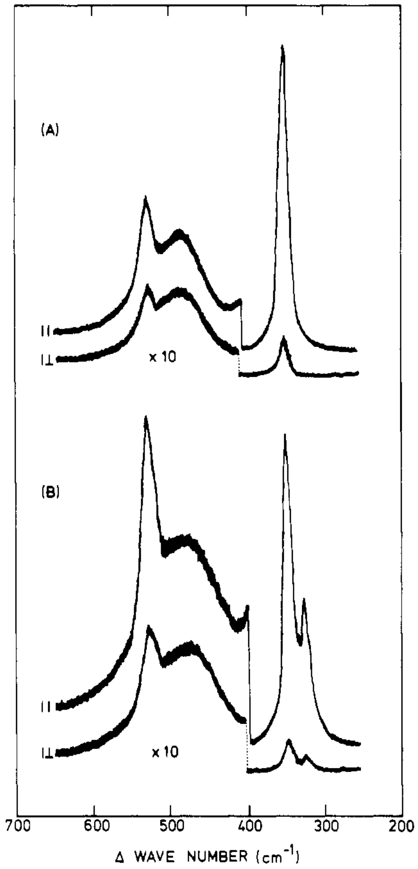

Figure 1. Raman spectra of sulfur species produced by reaction between sulfur and aluminum in CsCl–$AlCl_3$ (55.7–44.3 mol %) at 375 °C. Formality of aluminum and formality ratio $C'_{S(excess)}$:C'_{Al}: A, 0.0336, 3.05; B, 0.753, 0.222. λ_0 = 514.5 nm (500 mW). || and |⊥ denote polarized and depolarized spectra, respectively.

General Considerations. The formality C' is defined as the initial molar amount of one of the added substances (CsCl, $AlCl_3$, sulfur, and aluminum) per 1 L of the melt. In order to account for prior formation of sulfide, we define the excess formality of sulfur, $C'_{S(excess)}$, as the difference between the formality of sulfur (taken as monomeric S) and three-halves of the formality of aluminum. The ratio between the excess formality of sulfur and the formality of aluminum is denoted by R. The formal absorptivity is defined by $A/(C'l)$, where A is the absorbance corrected for the absorbance of cell and solvent and l is the path length. The density of the CsCl–$AlCl_3$ (55.7–44.3 mol %) melt was calculated from the assumption of additivity of the molar volumes of $CsAlCl_4$[13] and CsCl.[14] It was further assumed that the density was unchanged by the addition of sulfur and aluminum since these amounts were below 3% of the total mass. A calculation for all cells showed that the amount of sulfur present at the measuring temperature in the gas phase was below 1% of the added amount of sulfur, and therefore a (uncertain) correction to the R ratio could be avoided.

Results and Discussion

Raman Spectra. Figure 1 shows two 375 °C Raman spectra of the blue solutions produced by the reaction between sulfur and aluminum in the CsCl–$AlCl_3$ melt. From previous work[9] it is known that the band at 325 cm^{-1} is due to polymeric species of the type $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ ($n \geq 3$). The bands at 347 and 480 cm^{-1} can be assigned to $\nu_1(AlCl_4^-)$ and $\nu_3(AlCl_4^-)$, respectively, whereas the band at 529 cm^{-1} represents the

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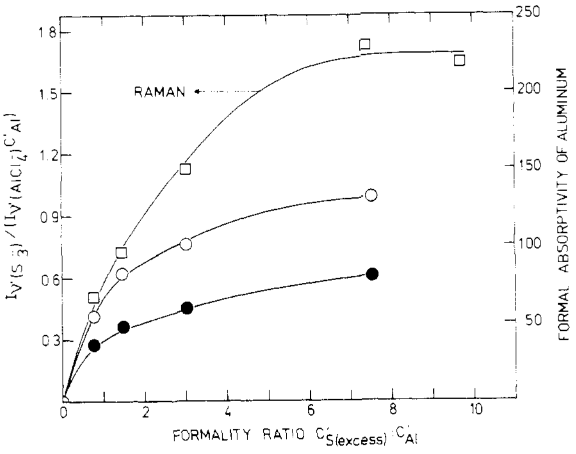

Figure 2. Squares: Relation between the formality ratio $C'_{S(excess)}:C'_{Al}$ and the "formal intensity ratio" $I_{\nu_1(S_3^-)}:(I_{\nu_1(AlCl_4^-)}C'_{Al})$ (left ordinate) calculated from five different Raman spectra obtained at 375 °C with formality of aluminum in the range 0.0325–0.0330. Circles: Relation between the formality ratio $C'_{S(excess)}:C'_{Al}$ and the formal absorptivity of aluminum at 16.7×10^3 cm^{-1} (right ordinate): open circles, 430 °C; filled circles, 390 °C.

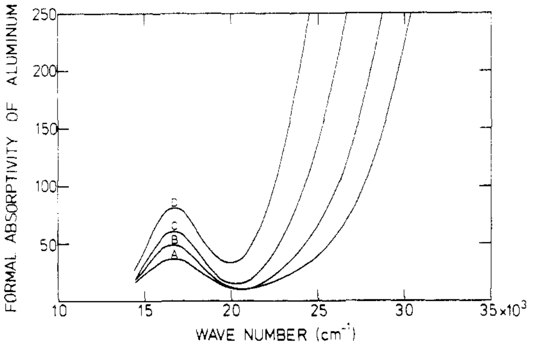

Figure 3. Series of spectra of sulfur species produced by reaction between sulfur and aluminum in CsCl–AlCl$_3$ (55.7–44.3 mol %) at 390 °C. Formality of aluminum was in the range 0.0334–0.0340. Formality ratio $C'_{S(excess)}:C'_{Al}$: A, 0.773; B, 1.48; C, 3.04; D, 7.55.

symmetric stretching mode $\nu_1(S_3^-)$.[8] There seems to be no sign of bands due to other sulfur species.

For a determination of whether other sulfur species could indeed be present, a quantitative examination of the Raman spectra was made. To do so, it is necessary to look at intensity ratios; the most obvious choice is the $I_{\nu_1(S_3^-)}:I_{\nu_1(AlCl_4^-)}$ ratio. Further, so that the plot can be made as similar as possible to the previously used spectrophotometric plots,[10,11,15] this ratio is divided by the formal concentration of aluminum and plotted vs. the formality ratio $C'_{S(excess)}:C'_{Al}$. It has been shown previously[15] that, when such a plot is linear (and independent of total concentration), only two species are formed (e.g., by the reaction between sulfur and aluminum). In Figure 2 is shown such a plot (compared with plots based on visible and ultraviolet spectra, which will be discussed later). It is immediately clear from Figure 2 that there is no well-defined two-species area. This indicates that there must be three or more species formed. Furthermore, it can be seen that there is no sharp break in the curve, indicating that none of the species obtain a high concentration relative to the other species under the present conditions. At the last point (i.e., $R = 9.74$) the melt is saturated with sulfur (the apparent decrease is attributed to the uncertainty in the measurements). An obvious explanation for the observed behavior is the existence of an equilibrium between S_3^-, S(−II), and molecular sulfur, but there are, of course, other possibilities.

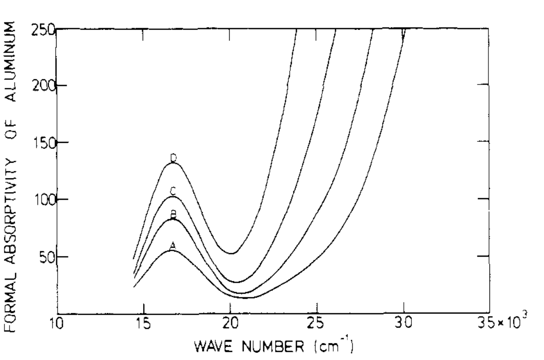

Figure 4. Series of spectra of sulfur species produced by reaction between sulfur and aluminum in CsCl–AlCl$_3$ (55.7–44.3 mol %) at 430 °C. Formality of aluminum was in the range 0.0328–0.0334. Formality ratio $C'_{S(excess)}:C'_{Al}$: A, 0.773; B, 1.48; C, 3.04; D, 7.55.

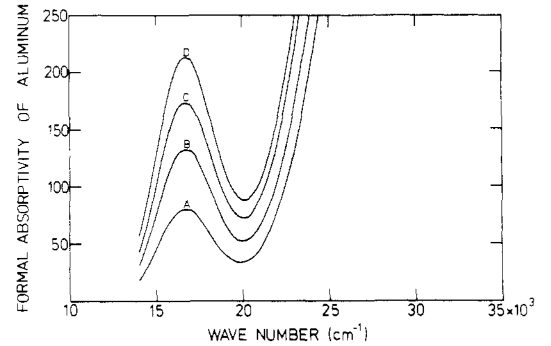

Figure 5. Series of spectra obtained at different temperatures from the cell with formality ratio $C'_{S(excess)}:C'_{Al}$ of 7.55: A, 390 °C; B, 430 °C; C, 450 °C; D, 470 °C. Formality of aluminum was in the range 0.0325–0.0339.

Visible and Ultraviolet Spectra. In Figure 3 is shown a series of spectra of the blue solutions obtained at 390 °C. Here the formality of aluminum is kept almost constant, and the formality ratio $C'_{S(excess)}:C'_{Al}$ is increased. It can be seen from Figure 3 that only one absorption band is present (at 16.7×10^3 cm^{-1}) and that the formal absorptivity is increasing at higher wavenumbers, indicating the existence of at least one more band somewhere in the ultraviolet range. It can also be seen that, as the formality ratio $C'_{S(excess)}:C'_{Al}$ is increased, a rather gradual increase in the formal absorptivity is observed. The spectra obtained at a somewhat higher temperature (i.e., 430 °C) are shown in Figure 4. It can be seen that the shape of the spectra at this temperature is rather similar to the shape at 390 °C. Further, in Figure 5 is given a series of spectra obtained as the temperature is increased while the formality of aluminum and the R value is kept constant. It can be seen that the effect is rather similar to the effect obtained by increasing the formality ratio range at constant formality of aluminum. From Figures 3–5, it is not possible to predict the number of species present. More information can be obtained by examining a formal absorptivity vs. formality ratio plot. Such a plot is given in Figure 2. Here the formal absorptivity measured at 16.7×10^3 cm^{-1} (and for melt temperatures of 390 and 430 °C) is plotted vs. the formality ratio $C'_{S(excess)}:C'_{Al}$. It can be seen that shapes of the visible–UV curves are not much different from that obtained from the Raman spectra. However, something which might be characterized as a break is found around an R value of 1.5, corresponding to the previously[8] mentioned break around a $C'_S:C'_{Al}$ ratio of 3. However, the $C'_S:C'_{Al}$ ratio does not correspond to the formality ratio normally used in such cases and hence should be avoided. The existence of such a break (and the nonlinear curves) indicates that more than three sulfur species should be present

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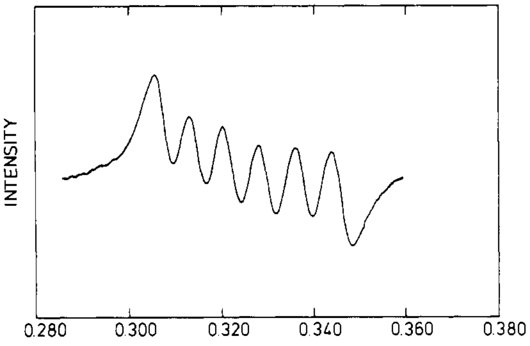


Figure 6. ESR spectrum of the radical species produced by reaction between sulfur and aluminum in CsCl-$AlCl_3$ (55.7–44.3 mol %) at 380 °C. The formality of aluminum and the formality ratio $C'_{S(excess)}:C'_{Al}$ were 0.753 and 0.222, respectively.

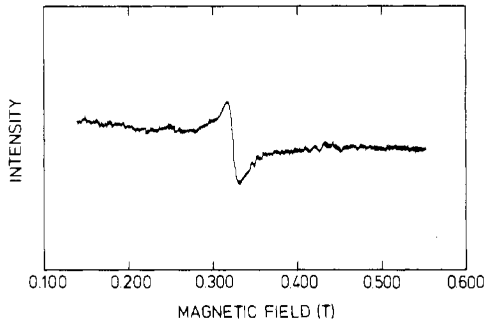


Figure 7. ESR spectrum of the radical species produced by reaction between sulfur and Li_2S in LiCl–CsCl (59.3–40.7 mol %) at 375 °C. Since the melt was saturated with sulfur and Li_2S, the formalities could not be calculated. The weighed mole ratios of LiCl/CsCl/S/Li_2S were 0.5793/0.3978/0.0040/0.0188.

in the examined range. The R value of 1.5 is unfortunately too uncertain to predict any particular species besides S_3^-, S(−II), and molecular sulfur. At the actual temperatures examined, sulfur is known to consist of a mixture of different sulfur molecules, so that the observation of more than three species is not unexpected. Another possibility is formation of polysulfides, S_n^{2-} (n = 1, 2, ...). However, the existence of more than one free radical can be ruled out, on the basis of the ESR measurements.

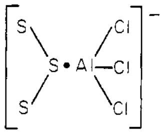
ESR Measurements. In Figure 6 is shown an ESR spectrum of one of the blue solutions. This is the only signal observed over the entire range of the instrument (0.002–0.730 T). Further the shape of the spectrum is virtually independent of the formality of aluminum and the formality ratio $C'_{S(excess)}:C'_{Al}$. From the spectrum given in Figure 6, a gyromagnetic ratio (g value) of 2.023 (3) (i.e., 2.023 ± 0.003) can be calculated. This spectrum should be compared with the ESR spectrum of S_3^- in LiCl–CsCl (59.3–40.7 mol %) obtained at almost the same temperature (Figure 7). From the spectrum in Figure 7 a g value of 2.028 (3) (and a line width of 14 (1) mT) can be calculated. To our knowledge no ESR spectrum of negatively charged sulfur radicals in solution has been reported previously. Attempts to obtain spectra from solutions of S_3^- etc. in hexamethylphosphoramide and dimethylformamide at 25 °C have failed. However, the average of the g components for S_3^- in solid hexamethylphosphoramide (at −196 °C),[16] alkali halide crystals,[17] $SrCl_2$ crystals,[18] and ultramarines[19,20] are in all cases ca. 2.028, which is in excellent agreement with the value found above.

The observed splitting of the ESR signal for the S_3^- entity in CsCl–$AlCl_3$ into six separate lines indicates that S_3^- in this melt must be coupled in one way or another to the Al atom and not to the Cl atom. The only natural Al isotope known has a nuclear spin of $^5/_2$, which should give a six-line splitting, in contrast to the normal Cl isotopes with nuclear spins $^3/_2$, which should give a four-line splitting. The hyperfine coupling constant, A_{iso}, can be calculated from Figure 6 to be 7.6 mT. This is a rather high value.

Concluding Remarks. In the CsCl–$AlCl_3$ melt sulfur, besides being present as S(−II) and molecular sulfur, is present as an S_3^- entity bound to an Al atom. There is no indication of the presence of the radical ion S_2^-, which is believed to exist in ultramarines[3,5] and alkali halide crystals.[6,21,22] S_2^- is normally taken to be responsible for a Raman band located in the range 590–610 cm^{-1} and an absorption band located at 25 × 10^3 cm^{-1}. None of these features have been observed in the CsCl–$AlCl_3$ melt under the present experimental conditions. The ESR signals assumed to be due to S_2^- vary considerably with the host crystal; however, no average of the g components for the various crystals comes close to the g values 2.023 and 2.028 found in the present systems. It is possible that the break observed in Figure 2 results from mixtures of different sulfur polymers (probably no larger than S_8). However, the existence of polymeric sulfide species, S_n^{2-} (n = 2, 3, ...), cannot be excluded, because such species will only have a small absorptivity in the visible range and they will therefore not exhibit the resonance Raman effect, which is found for the S_3^- entity.

A full account of the coupling observed, by the ESR measurement, between the S_3^- radical and the aluminum atom is rather difficult. A possible interpretation may be given by assuming the formation of molecular ionic species in the melt. In this respect, we have considered the two ions $[S_3AlCl_3]^-$ (ion A) and $[S_3AlCl_4]^{2-}$ (ion B).

It is noteworthy that the $\nu_1(S_3^-)$ stretching frequency at 529 cm^{-1} in the CsCl–$AlCl_3$ melt is close to that measured for S_3^- in LiCl–CsCl eutectic (i.e., 527 cm^{-1})[23] and/or in room-temperature organic solvents (i.e., 535 cm^{-1} for DMF solutions[3]). This seems to indicate that the attachment of the bent[3] triatomic S^{3-} radical to the aluminum does not occur with a terminal sulfur atom. Thus from a structural point of view ion A is probably similar to the $NH_3{\cdot}AlX_3$ (X = F, Cl, Br, I) adduct type molecules[24,25] as shown in **1**. For the $NH_3{\cdot}AlX_3$ molecules it has been found that the N–H stretching frequency is also close to that of the free ammonia and that weak bonding (bond order ∼0.25) occurs between the nitrogen and aluminum atoms. Presumably by adopting ion A as the species in the melt, we can propose a reasonable molecular structure, which also accounts for the proximity of the $\nu_1(S_3^-)$ frequency to that in other liquid media.



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As already mentioned the blue S_3^- entity can be formed in CsCl–$AlCl_3$ melts but not in NaCl–$AlCl_3$ and KCl–$AlCl_3$ melts. the most obvious reason for this difference is the higher chloride activity in the basic CsCl–$AlCl_3$ melts than in the NaCl–$AlCl_3$ and KCl–$AlCl_3$ melts (under comparable conditions). This perhaps makes ion B a more likely candidate. Also, S(–II) in basic melts is strongly bound to aluminum in polymeric structures of the $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ type (which for large values of n could be looked upon as $[AlSCl_2]_n^{n-}$). If we assume that the compound formed is $[S_3AlCl_4]^{2-}$ (ion B), the reaction giving this compound must be

$$[AlSCl_2]_n^{n-} + (5n/m)S_m + nAlCl_4^- + 2nCl^- \rightleftarrows 2n[S_3AlCl_4]^{2-} \quad (1)$$

where m and n are integers, and most likely m is no larger than 8. It can immediately be seen that this reaction is favored by increasing basicity of the melt whereas a corresponding reaction involving ion A instead of ion B will be independent of the acidity–basicity of the melt.

The formation of $[S_3AlCl_4]^{2-}$ instead of the formation of $[S_3AlCl_3]^-$ is very surprising from a structural point of view since it involves a coordination number higher than 4 for Al(III). Therefore the question of the nature of the sulfur species formed cannot be considered to be completely settled.

Acknowledgment. R. W. Berg and S. von Winbush are grateful for support from the Danish Natural Science Research Foundation, which also provided funds for equipment. This work was partially supported by the Division of Basic Energy Sciences, U.S. Department of Energy. We are also grateful to E. Pedersen (Chemistry Department I, H. C. Ørsted Institute, University of Copenhagen) for his kind advice and help with the ESR investigations.

Registry No. S_3^-, 12597-04-5; CsCl, 7647-17-8; $AlCl_3$, 7446-70-0.

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Polarized Electronic Absorption Spectra of Tetrakis(μ-trifluoroacetato)dimolybdenum(II) and Tetrakis(μ-trifluoroacetato)bis(pyridine)dimolybdenum(II)

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Polarized spectra are reported for the 010 faces of $Mo_2(O_2CCF_3)_4$ and $Mo_2(O_2CCF_3)_4{\cdot}2C_5H_5N$ at 300 and 5 K. At 5 K bands at about 23 000 cm^{-1} exhibit rich vibrational structure. The evidence available from earlier studies with $Mo_2(O_2CCH_3)_4$ provides a justification for assigning the transitions as weak electric dipole allowed with molecular z polarization under the local D_{4h} symmetry. The intensities are sufficiently low that Franck–Condon progressions based on vibronic origins have intensities comparable to the 0–0 progression. The polarization of the transition is that expected for the $^1A_{1g} \rightarrow {}^1A_{2u}$ (δ–δ^*) transition. The presence of a second electronic transition in this vicinity is also indicated.

Introduction

The dimeric complexes of molybdenum(II) possess the interesting quadruple bond between the Mo atoms. Generally, the recent scattered-wave Xα calculations[1-5] have indicated that the lowest energy electronic excitation in such dimers should be the $\delta \rightarrow \delta^*$ transition. A local symmetry of D_{4h} applies to a number of these dimeric complexes. Under this symmetry the spin-allowed $\delta \rightarrow \delta^*$ transition can be characterized as $^1A_{1g} \rightarrow {}^1A_{2u}$ ($b_{1g} \rightarrow b_{2u}$). It is therefore predicted to be an electric-dipole-allowed transition for the absorption of light polarized in the z direction; i.e., along the metal–metal bond.

Polarized optical absorption measurements[6,7] for single crystals containing $Mo_2Cl_8^{4-}$ and $Mo_2(SO_4)_4^{4-}$ with bridging sulfate ligands have indicated that the lowest energy observed absorption bands were z polarized, consistent with the $\delta \rightarrow \delta^*$ assignment. Also, the polarized spectra for $K_3Mo_2(SO_4)_4{\cdot}4H_2O$[8], for which there should be only one electron in the δ orbital, were consistent with a $\delta \rightarrow \delta^*$ assignment.

The assignment of the lowest energy band in the electronic absorption spectra of the tetrakis(μ-carboxylate) complexes has involved more controversy. A number of crystals have provided low-temperature spectra with rich vibrational detail so that from three to seven Franck–Condon progressions, with five to seven lines each, have been resolvable. For tetragonal crystals of tetrakis(μ-glycine)dimolybdenum(II) sulfate tetrahydrate, where z- and x,y-polarized lines were indicated unambiguously, the presence of lines in both polarizations of comparable intensity originally led to the conclusion that this band should not be assigned as a $\delta \rightarrow \delta^*$ transition.[9] This conclusion was apparently supported by the spectra recorded for tetrakis(μ-formato)dimolybdenum(II),[6] where the polarization ratio for the lowest observed line in the spectra was opposite to that expected for a z-polarized transition. In addition, Trogler et al.[10] reported single-crystal spectra for tetrakis(μ-acetato)dimolybdenum and a multicrystal unpolarized spectrum for tetrakis(μ-trifluoroacetato)dimolybdenum(II). They assigned the observed band as $\delta \rightarrow \pi^*$ ($^1A_{1g} \rightarrow {}^1E_g$). However, Martin et al.[11] were able to measure polarization ratios for the sharp line at longest wavelength for two different crystal faces of $Mo_2(O_2CCH_3)_4$, which was the origin of the most intense Franck–Condon progression. From this information the orientation of the transition moment for this line could be determined. It was

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