VAPOCOR COMPLEXATION IN THE CrCl₃-ACl (A= Li, Cs) SYSTEM

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ABSTRACT

High temperature electronic absorption spectroscopy is used in the temperature range 800-1300 K, to study the vapor species, over solid CrCl₃ and molten CrCl₃-ACl (A= Li, Cs) mixtures. In the spectral range 5000 to 40000 cm⁻¹ the vapors of over LiCl-CrCl₃ are characterized by a series of bands, two of which are at high energies and are assigned to charge-transfer transitions. The remaining bands are tentatively assigned to d→d transitions of Cr³⁺ in a distorted tetrahedral coordination (C₂ᵥ: CrCl₄²⁻). In conjunction with the vapor spectra measured for the CsCl-CrCl₃ system and for pure CrCl₃ it is concluded that the vapor complex stoichiometry is 1:1 (i.e. ACrCl₄). With increasing temperatures the relative band intensities change and isosbestic points appear in the spectra suggesting the dissociation reaction:

ACrCl₄(g) ⇌ CrCl₃ (g) + ACl (g)

Due to vapor complexation the apparent vapor pressure of CrCl₃ increases. The volatility enhancement is higher for the LiCl-CrCl₃ than the CsCl-CrCl₃ system reaching values near 60 at ~700 °C.

INTRODUCTION

Metal halide vapors and vapor complexes are important for a variety of applications including chemical synthesis and separations, extractive metallurgy and high efficiency lamps (1). Mixtures of rare earth halides (mainly iodides and bromides) with alkali halides are used in the high temperature metal halide lamps where the formation of vapor complex species according to the reaction:

AX(s/l) + LnX₃(s/l) ⇌ ALnX₄ (g)  [1]

(A= alkali metal; Ln= rare earth; X= halide) leads to an enhancement of the apparent volatility of LnX₃ (2) which in turn increases the lamp spectral efficiency and decreases the required operational temperature.

The formation of the ALnX₄ and other polynuclear vapor species is mainly verified by mass spectrometric studies (3) where the stoichiometry and the thermodynamic function can be established but no structural information can be obtained. In a few cases electronic absorption spectroscopy is used to identify the vapor complex
species from spectral bands due to f→f transitions (2). For certain lanthanides possessing hypersensitive f→f transitions some indirect structural information for the vapor species can also be obtained. It is generally accepted that the ALnX₄(g) is the predominant vapor species over molten AX-LnX₃ mixtures, composed of a LnX₄ "tetrahedral" having (more likely) the A "cation" bound to an edge of the tetrahedral (4). However, no direct spectroscopic/structural information (e.g. Raman spectroscopy) is available due to experimental difficulties arising from the high temperatures needed and the lack of intensity due to the low partial pressures of the vapor complexes.

The present work is aimed to understanding the structure of the vapor complexes formed over AX-LnX₃ mixtures. The rare earth cation Ln³⁺ is substituted by Cr³⁺ which is known to have d→d ligand field sensitive electronic spectra and the vapor complexation over LiCl-CrCl₃ and CsCl-CrCl₃ mixtures is investigated by absorption spectrophotometry.

EXPERIMENTAL

A Perkin-Elmer (Model L-900) NIR-VIS-UV spectrophotometer with reverse optics and an optical fibers attachment was used. A three zone split cylindrical furnace (50 cm long) containing an inconel metal block (20 cm long) used for heating the long path length optical cells (10 cm) up to 1100°C. The spectrophotometer optical fibers were aligned so to focus at the center of the furnace where the optical cell was placed. Due to the fiber absorption the spectra measured with this system covered the region ~900 to 220 nm. For measuring the spectra in the near IR region (2000-900 nm) another home made optical furnace was constructed which could fit in the spectrophotometer compartment (20 cm long). The furnace was water cooled and could be used only for square optical cells (max.1 cm path length). Details of the constructed system can be found elsewhere(5).
Table I. Characteristics of the Spectrophotometric Experiments

| Cell No | Cell Systems and Composition | Cell Constants\(^{(a)}\) | Moles of \(\text{CrCl}_3\) \(^{\text{at} 900^\circ\text{C}}\) \(\text{(mmHg)}\) | Spectral Region \((\text{nm})\) | Volatility | \(\text{V}_{\text{max}}/\text{T}_{\text{min}}\) \((\text{ºC})\) | \(\text{Pressure}^\text{Volatility} \) |
|---------|------------------------------|--------------------------|---------------------------------|------------------|----------|------------------|-------------------------------|
| 1       | \(\text{CrCl}_3\) \(\text{V}=29; \text{L}=10\) | \(1.28 \cdot 10^4\) | \(320\) | 850-220 | 850-220 | 980/620 | 780ºC~15 |
| 2       | \(\text{CsCl-CrCl}_3\) \(1:1\) | \(1.20 \cdot 10^4\) | \(300\) | 980-220 | 850-220 | 995/625 | 730ºC~12 |
| 3       | \(\text{LiCl-CrCl}_3\) \(1:1\) | \(1.18 \cdot 10^4\) | \(300\) | 980-220 | 850-220 | 1000/635 | 700ºC~9.5 |
| 4       | \(\text{LiCl-GaCl}_3\) \(1:1\) | \(\text{excess}\) | \(-----\) | 850-220 | 850-220 | 800/740 | 730ºC~7 |
| 5       | \(\text{LiCl-CrCl}_3\) \(1:1\) | \(\text{excess}\) | \(-----\) | 850-220 | 850-220 | 1010/625 | 670ºC~45 |
| 6       | \(\text{LiCl-GaCl}_3\) \(2:1\) | \(0.7 \cdot 10^4\) | \(300\) | 810ºC~11 | 750ºC~11 | 1010/625 | 675ºC~437 |

\(^{(a)}\) Cell Volume \(V\) \((\text{cm}^3)\); Cell path length \(L\) \((\text{cm})\). \(^{(b)}\) Calculated ideal gas pressure with all components in the vapor phase.

Chromium (III) chloride was prepared by first dehydrating commercial \(\text{CrCl}_3\cdot 6\text{H}_2\text{O}\) in a stream of gaseous \(\text{HCl/N}_2\) by slowly increasing the temperature to \(700^\circ\text{C}\). The so obtained bright purple powdery material was sublimed in sealed and evacuated fused silica tubes at \(850^\circ\text{C}\) giving deep purple crystalline flakes. Anhydrous \(\text{LiCl}\) and \(\text{CsCl}\) were dried and purified by distillation at \(700^\circ\text{C}\) under dynamic high vacuum \((\sim 10^{-8}\text{ torr})\). The procedures for filling up the fused silica optical cells and for measuring absorption spectra have been described before \((5)\). All operations were carried out in an argon gas filled glove box or/and in sealed glass containers.

Table I lists the characteristics of each experiment. Measurements were started at \(-600^\circ\text{C}\) and the temperature was gradually increased in steps of 30 to 50 \(^\circ\text{C}\). The quoted temperatures for the experiments with the 10 cm path length are at the center of the cell where the melts were condensed and in most cases is 10-15 \(^\circ\text{C}\) lower than those of the cell windows. The absorbance range for measurements with reasonable signal/noise ratio was between 0.05 to 2.

RESULTS AND DISCUSSION

Spectra over \(\text{LiCl-CrCl}_3\)

By combining absorbance measurement from the 1 cm and the 10 cm path length (cells #5 and #3 respectively) we were able to measure the spectra of the vapors over the \(1:1\) \(\text{LiCl-CrCl}_3\) mixture from 2000 to 220 nm \((5000 \text{ to } 45000 \text{ cm}^{-1})\). In cell #3 all the salts placed in the cell were in the vapor phase at temperatures above \(720^\circ\text{C}\) giving an almost constant absorbance at higher temperatures. This permitted the evaluation of the molar absorptivity \(\varepsilon\) (in \(\text{L mol}^{-1} \text{ cm}^{-1}\)) for the vapor species formed in the \(\text{LiCl-CrCl}_3\)
system (Figure 1). The energies of the observed bands are listed in Table II. Possible assignments as well as temperature effects on the spectra are presented in the following subsections.

Figure 1. Electronic absorption spectra of the vapors over LiCl-CrCl$_3$. The band positions are shown by Latin numerals on the lower part of the figure. On the upper part of the figure the vertical arrows attached to the spectroscopic symbols indicate the position of the Cr$^{3+}$ ligand field states in octahedral $[^4\text{A}_2\text{g}(F)$, ground state] and tetrahedral $[^4\text{T}_1\text{(F)}$ ground state] chloride environments. Broken vertical arrows correspond to spin-forbidden transitions (see Table III).

Cell #4 contained excess of the 1:1 mixture and thus, the absorbance was measured over the formed liquid from ~650 to near 850 °C where optical saturation occurred due to the high concentration of the absorbing species. These measurements in combination with the molar absorptivity values permitted for each temperature the calculation of the vapor complex partial pressure $P_C$ and the volatility enhancement ratio:

$$\rho = \frac{P_C}{P_{\text{CrCl}_3}} \tag{2}$$

where $P_{\text{CrCl}_3}$ is the vapor pressure over CrCl$_3$ solid (6) at the same temperature. Values of $\rho$ are listed in Table I.

Spectra over CrCl$_3$

Spectra measured with cell #1 at temperature below 700°C show a strong charge transfer (CT) band in the UV region and a rather weak band (marked as T) in the region of ~12500 cm$^{-1}$ where the main absorption band of the Li-Cr-Cl vapor complex (band IV) occurs (Figures 2a and 3a). The thermodynamic function of vaporization of CrCl$_3$ have been measured over the years and critically evaluated (6). Monomeric CrCl$_3$(g) are formed but the simultaneous appearance of CrCl$_4$(g) has been argued to exist (7). At

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temperatures above 900 °C all the CrCl₃ in cell #1 was vaporized and the only band observed was at 13200 cm⁻¹ (marked as C). Due to optical saturation no CT band(s) could be measured at these temperatures. Detailed temperature dependent measurements shown in Fig. 3a indicate an isosbestic point, a decrease of the T band intensity and a simultaneous increase of the C band intensity. We consider all this as an indication that the vapors over CrCl₃ are predominated by dimmer-monomer equilibrium:

\[ \text{Cr}_2\text{Cl}_6 (g) \rightleftharpoons 2 \text{CrCl}_3 (g) \]  

[3]

The dimmer is presumably of the Al₂Cl₄(g) type composed of edge bridged “CrCl₄” tetrahedral and having an absorption band (T) near to that of the Li-Cr-Cl vapor complex. Band C due to the monomer is a d→d transition of Cr³⁺ in a trigonal or pyramidal coordination.

**Spectra over CsCl-CrCl₃ and temperature effects**

At low temperatures (<800 °C) and in the region 850 to 500 nm (~11500 to 20000 cm⁻¹) the spectra of the CsCl-CrCl₃ vapors taken from cell #2 are very similar to those of LiCl-CrCl₃ (Figs 2b and Table II). The molar absorptivity values of the 12500 cm⁻¹ bands are also close but the near UV spectra show marked differences. Measurements over excess CsCl-CrCl₃ liquid mixtures shows that the volatility due to vapor complexing is somewhat lower than that of the LiCl-CrCl₃ system (Table I).

By increasing the temperature of cell #2 above 800 °C where all condense phases were evaporated the ~12500 cm⁻¹ band shifted gradually to the blue reaching at 1250 K an energy close to the 13200 cm⁻¹ band of the CrCl₃ monomer (Fig. 2b). This would imply that an equilibrium is established where the Cs-Cr-Cl vapor complex dissociates to CrCl₃ and CsCl. Assuming that the vapor complex has the 1:1 stoichiometry then the spectra in Fig. 2b suggest the dissociation:

\[ \text{CsCrCl}_4 (g) \rightleftharpoons \text{CsCl} (g) + \text{CrCl}_3 (g) \]  

[4]

In support of this dissociation is the analogous behavior of the Li-Cr-Cl vapor complex spectra at high temperatures Fig. 3b. The intensity of the 12500 cm⁻¹ band decreases with increasing temperature, a blue shift occurs towards the CrCl₃ (g) band and an isosbestic point is present. This accounts for a similar to the above (reaction 4) equilibrium:

\[ \text{LiCrCl}_4 (g) \rightleftharpoons \text{LiCl} (g) + \text{CrCl}_3 (g) \]  

[5]

In other words it appears that the spectral behavior of the vapor complexes formed by the 1:1 ACl-CrCl₃ (A= Li, Cs) systems are similar suggesting that species of the same stoichiometry are formed which at high temperatures dissociate to the component salts. In contrast the spectra measured over the 2:1 LiCl-CrCl₃ mixture (cell #6) suggest somewhat different systematics. The data indicate that relative to the 1:1 mixture the vapor complexes formed in the 2:1 system dissociate at lower temperatures and this is followed by an increase in volatility enhancement (i.e. compare the \( p \) values at 800°C for the 1:1 and 2:1 LiCl-CrCl₃ systems, Table I). It seems that the accepted assumption that the predominant vapor species over the AX-LnX₃ systems is the ALnX₄...
might not be general. Thus, additional systematic studies are needed where the effect of the condense phase composition on the vapor phase stoichiometry is examined.

Figure 2. Electronic absorption spectra of vapors over the CrCl$_3$(s) and CsCl-CrCl$_3$ melt systems. (a) At 975 K the spectra on the left are predominated by the CT transitions in the equilibrium vapor mixture CrCl$_3$-Cr$_2$Cl$_6$; at 1250 K band C of the spectra on the right corresponds to a d←d transition of Cr$^{3+}$ in a trigonal field. No baseline could be established for the spectra but the molar absorptivity can be estimated from the magnitude of the scale $\Delta c = 10$ L mol$^{-1}$ cm$^{-1}$. (b) Vapors over CsCl-CrCl$_3$ (1:1) melt; with increasing temperature band C due to CrCl$_3$ (g) appears in the spectra suggesting the dissociation reaction $4$; the molar absorptivity can be estimated from the magnitude of the scale $\Delta b = 10$ L mol$^{-1}$ cm$^{-1}$. 

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Figure 3. Temperature dependence of the electronic absorption spectra. (a) The chromium (III) chloride vapors; the relative change of the T to C bands and the isosbestic point suggest a dimmer-monomer equilibrium; absorptivities can be estimated from the magnitude of the scale: $\varepsilon = 10 \text{ L mol}^{-1} \text{ cm}^{-1}$. (b) The LiCl-CrCl$_3$ 1:1 vapors; the isosbestic point and the appearance of the CrCl$_3$(g) band C suggest the dissociation reaction 5.
Table II. Observed Bands for Cr(III) Vapor Species and Tentative Assignments.

| LiCrCl₄ (T= 1030 K) | C₆ᵥ(Tₐ) symmetry |
|----------------------|------------------|
| Band | Energy (cm⁻¹) | ε (L mol⁻¹ cm⁻¹) | Tentative Assignments |
| I | (7000) | (10) | ⁴T₂(F) and ⁴E(G) |
| II | (8500) | (20) | |
| III | 10000 | 30 | ⁴A₂(F) |
| IV | 12500 | 41 | ⁴T₁(F) |
| V | (14000) | | ⁴A₁(F) |
| VI | (16500) | | ⁴A₁(F) |
| VII | 24000 | 90 | CT |
| VIII | 31000 | 200 | CT |

CsCrCl₄ (T = 1050 K) ; C₆ᵥ(Tₐ) symmetry

| Band | Energy (cm⁻¹) | ε (L mol⁻¹ cm⁻¹) | Tentative Assignments |
| IV | ~12500 | ~40 | ⁴T₁(P) |
| V | (14000) | | B |
| VI | (16500) | | A |
| VII | 27000 | 220 | CT |

CrCl₃ (T= 1250 K) ; D₃h or C₃ₐ symmetry

| Band | Energy (cm⁻¹) | ε (L mol⁻¹ cm⁻¹) | Tentative Assignments |
| IV | (10) | (−13.5) | d→d |
| V | (14000) | | B |
| VI | (16500) | | A |
| VII | 26000 | 1370 | CT |
| VIII | 35000 | 2500 | CT |

Electronic spectra and structure of the vapor complexes

The d→d spectra of Cr³⁺ (d³ configuration) in different ligand field environments and coordination geometries have been extensively studied (8). Due to the high octahedral field stabilization energy of the d³ configurations the predominant coordination geometries of Cr³⁺ are mainly octahedral. Table III lists the expected transition for the CrCl₆²⁻ (O₆h) and CrCl₄²⁻ (Tₐ) species calculated from the Tanabe-Sugano (9) diagrams using the values of the Racah (B) and crystal field splitting (Dq) parameters, given in the Table. The estimated energies are also marked on the top of the Li-Cr-Cl vapor spectra in Fig. 1. All the spin allowed transitions of the tetrahedral are below 14000 cm⁻¹ and down to ~5000 cm⁻¹ while the corresponding to the octahedral transitions are above 13000 cm⁻¹ and up to 30000 cm⁻¹. Thus, it is more likely that the measured spectra for the Li-Cr-Cl complex are related to the tetrahedral energies with the assumption that the high energy bands at ~24000 and 31000 cm⁻¹ are components of a charge transfer (CT) band. This view is also supported from the Cs-Cr-Cl vapor spectra (Fig. 2b) where the substitution of Li⁺ in the second coordination sphere of Cr³⁺ by the more polarizable Cs⁺ affects the position of the CT band but does not influence the lower energy d→d band (s). Similar appears to be the situation with the CT spectra of the Cr₂Cl₆ dimmer (Figure 2a).
Due to the presence of Li a distortion is imposed on the \( \text{CrCl}_4^- \) tetrahedral. Assuming \( \text{LiCrCl}_4 \) stoichiometry the Li is expected to be edge bridged to the tetrahedral imposing a \( C_{2v} \) symmetry. Such a geometry splits all the degenerate energy states of the tetrahedral \( (T_1 \rightarrow A_2, B_1, B_2 ; T_2 \rightarrow A_1, B_1, B_2) \) including the ground state \( [^4T_1 (F)] \) and this alters the calculated tetrahedral energies.

| Table III. Estimated \(^{(a)}\) Energies of Electronic Transition of Cr(III) in Octahedral \( \text{CrCl}_6^2^- \) and Tetrahedral \( \text{CrCl}_4^- \) Fields. |
|---------------------------------------------------------------|
| **CrCl\(_6^2^- \) (O\(_6\) symmetry)** | **CrCl\(_4^- \) (T\(_d\) symmetry)** |
| Transition \( [\leftarrow^4A_2 (F)] \) | Energy \( (\text{cm}^{-1}) \) | Transition \( [\leftarrow^4T_1 (F)] \) | Energy \( (\text{cm}^{-1}) \) |
| \( ^2T_{1g} (G) \), \( ^2E_g (G) \)\(^{(b)} \) | 11220 | \( ^2T_2 (F) \) | 5300 |
| \( ^4T_{2g} (F) \) | 13670 | \( ^2E (G) \)\(^{(b)} \) | 7500 |
| \( ^2T_{1g} (G) \)\(^{(b)} \) | 16300 | \( ^4A_2 (F) \) | 11500 |
| \( ^4T_{1g} (F) \) | 19125 | \( ^2T_1 (G) \), \( ^2T_{2g} (G) \)\(^{(b)} \) | 12500 |
| \( ^4T_{1g} (P) \)\(^{(c)} \) | 29580 | \( ^4T_1 (P) \)\(^{(c)} \) | 13650 |

\(^{(a)}\) The estimation was based on the Tanabe-Sugano diagrams \(^{(9)}\); \(^{(b)}\) Combinatory (spin forbidden) bands; \(^{(c)}\) An F to P transition

Most octahedral spectra of Cr\(^{3+} \) show also weak spin forbidden transitions to the \( ^2E_g (G) \), \( ^2T_{1g} (G) \) and \( ^2T_{2g} (G) \) states. These states are rather insensitive to the ligand field strength and appear at about the same energy for all octahedral species (see e.g. the Tanabe-Sugano diagrams). Similar is the situations in tetrahedral fields for the \( ^2T_1 (G) \) and \( ^2T_2 (G) \) states and for \( D_0/B \) values less than 2 while the energy of the \( ^2E (G) \) band changes drastically with ligand field strength. The spectra in Figs. 1-3 and the values listed in Table II show two bands marked as \( \alpha \) and \( \beta \) which appear to be at the same position in all four spectra of \( \text{LiCrCl}_4, \text{CsCrCl}_4, \text{Cr}_{2} \text{Cl}_6 \) and \( \text{CrCl}_3 \). In the first three molecules the Cr\(^{3+} \) is presumably four coordinated and the assignment of the \( \alpha \) and \( \beta \) bands to the spin forbidden transition might be reasonable. On the other hand, the appearance of the same bands in the \( \text{CrCl}_3(g) \) spectra where the Cr\(^{3+} \) is in a different geometry and ligand field strength makes this assignment questionable.

**CONCLUSIONS**

In conclusion, the vapor spectra behavior over the A-Cr-Cl (A=Li,Cs) systems indicate that most of the electronic transition can be associated to tetrahedral states in distorted \( (C_{2v}) \) field and thus, support the stoichiometry of the ACrCl\(_4 \) (A=Li,Cs) vapor complexes. On the other hand, no definite assignments can be made. Additional electronic absorption measurements including the near IR region as well as Raman spectroscopic data are needed in order to elucidate the structure and have a better understanding of the vapor complexation in this system. Such measurements are presently in progress.
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