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# Vapor Complexes of Erbium(III) Chloride with Aluminum(III), Gallium(III) and Indium(III) Chlorides

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The formation of vapor complexes of lanthanide chlorides with aluminum chloride are well established [1, 2]. Thermodynamic considerations have shown that the gas–solid reactions:

$$LCl_3(s) + nACl_3(g) \rightarrow LCl_3 \cdot nACl_3(g) \qquad (1)$$

where L = Nd [2, 3], Eu [2], Sm [4], Gd [5] or Ho [6] and A = Al [2, 4–6] or Ga [3], gives a variety of vapor complexes with n = 1, 3, 4. At temperatures between 600–800 K the predominant vapor species appears to be the n = 3 with a formula $L(ACl_4)_3$. From a practical point of view the interest in the lanthanide halide–'acidic' vapor halide complexes arises from their potential use both as agents for chemical separations [1] and as gain media in the construction of high-power vapor lasers [7, 8].

Recently we have been concerned with the formation and spectroscopic properties of vapor complexes of $ErCl_3$ with $AlCl_3$, $GaCl_3$ and $InCl_3$ as 'carrier' gases. The purposes of the investigation are: (1) to study spectrophotometrically the thermodynamic quantities and stoichiometries of reaction 1 (L = Er; A = Al, Ga, In), (2) to establish their systematics on going from Al to In and (3) to use Raman spectroscopic methods to measure the vibrational frequencies of the complexes and thus obtain structural information as in the case of transition metal halide complexes [9, 10]. The thermodynamic investigations and our endeavors to obtain the Raman spectra will be reported elsewhere [11]. In the present note the formation and absorption spectra of the Er–Cl–In, Er–Cl–Ga and Er–Cl–Al vapor complexes are reported. The observed f ← f intensities of the lanthanide hypersensitive transitions are discussed in terms of the possible structures of the predominant vapor complexes present.

The source and purification of the $AlCl_3$, $GaCl_3$ and $InCl_3$ salts were the same as before [4, 10]. 'Anhydrous' $ErCl_3$ was purchased from Cerac/Pure Inc. and was further purified by heating under vacuum and finally by vapor transport in an atmosphere of $Al_2Cl_6$ (g) [4, 10]. The anhydrous materials were handled in evacuated fused-silica tubes or in a helium atmosphere dry box with a water vapor level <20 ppm. The method and equipment for measuring the absorption spectra and apparent molar absorptivity has been described before [4]. Cylindrical optical cells were used (5–10 cm path length) containing 3–5 atm. of carrier gas and having no excess of $ErCl_3(s)$ at the temperatures at which the spectra were recorded. The $ErCl_3$ was introduced into the cell by vapor transport and its amounts were determined by chemical analysis [11].

The absorption spectra of the $ErCl_3$ complexes with the three different 'carrier' gases are shown in Fig. 1. For each system the spectra show two relatively intense absorption bands at ~19 100 cm$^{-1}$ and ~26 300 cm$^{-1}$ which are characteristic of the two $Er^{+3}$ hypersensitive transitions $^2H_{11/2} \leftarrow {}^4I_{15/2}$ and $^4G_{11/2} \leftarrow {}^4I_{15/2}$ respectively. Weaker non-hypersensitive transitions are also present in the spectra at the expected energy regions [12]. The value of the molar absorptivity at 19 100 cm$^{-1}$ for the Er–Cl–Al complex is in agreement with that reported previously for the same vapor [8].

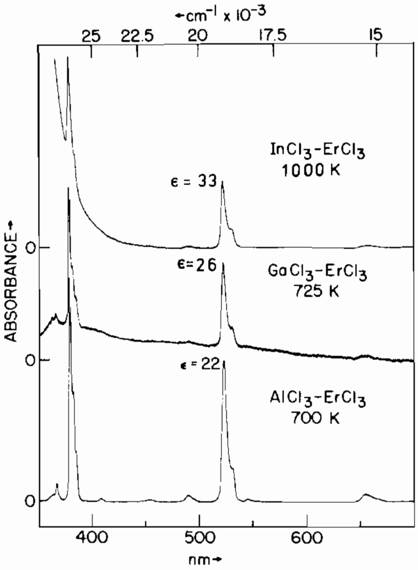

Fig. 1. Absorption spectra of erbium chloride vapor complexes with aluminum, gallium and indium chlorides. The molar absorptivity $\epsilon$ of the $^2H_{11/2} \leftarrow {}^4I_{15/2}$ band is given in L/(mol cm).

Temperature and pressure dependence studies of the Er–Cl–Al and Er–Cl–Ga spectra indicated that no drastic changes occur in the peak or integrated intensities as well as in the position of the $^2H_{11/2}$ and

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TABLE I. Integrated ($\sigma$) and Peak ($\epsilon$) Intensities of the $^2H_{11/2} \leftarrow {}^4I_{15/2}$ Transition for the Er–Cl–A Vapor Complexes (A = Al, Ga, In).

| T<br>K | Al |  | Ga |  | In |  |
|---|---|---|---|---|---|---|
|  | $\sigma^a$ | $\epsilon^b$ | $\sigma^a$ | $\epsilon^b$ | $\sigma^{a,c}$ | $\epsilon^{b,c}$ |
| 575 |  |  | 155(5) | 25(1) |  |  |
| 675 |  |  | 165(5) | 26(1) |  |  |
| 775 | 155(3)$^d$ | 22(1) | 172(5) | 26.5(1) |  |  |
| 900 | 160(3) | 23(1) |  |  | 210(10) | 29(1) |
| 1000 |  |  |  |  | 235(15) | 33(2) |
| 1100 |  |  |  |  | 260(20) | 36(2) |

$^a$Average values in L nm/mol cm; the oscillator strength of this band is ~1.6 × $10^{-7}$ × $\sigma$. $^b$Average values in L/mol cm. $^c$In this temperature range $\sigma$ and $\epsilon$ for the indium system depend slightly on 'carrier' gas pressures; the values given are averages from cells at different pressures. $^d$Numbers in parenthesis indicate the spread of the values from the average.

$^4G_{11/2}$ bands. Table I gives the temperature variation of the $^2H_{11/2}$ band intensities for these two systems. For the Er–Cl–In complexes however a temperature (Table I) and pressure [11] dependence of the peak and integrated intensities of the $^2H_{11/2}$ band has been observed. For the same system the $^4G_{11/2}$ band is supperimposed on a temperature dependent tail of a U.V. band (probably due $InCl_3$ dissociation products) and no conclusions could be drawn about its relative intensity changes. At temperatures above 800 K for the gallium complex(es) and above 1100 K for the indium complex(es) the molar absorptivity was found to decrease rapidly.

As indicated in Fig. 1 and Table I the band intensities ($\epsilon$,$\sigma$) decrease with decreasing size of the metal atom in the carrier gas, *i.e.* in the sequence In > Ga > Al. This decrease in intensity is similar to that observed for the hypersensitive transitions of $Er^{+3}$ and other trivalent lanthanides in different environments and is attributed to the decreasing electron donating ability (basicity) [13] of the ligand. This effect and the hypersensitivity of the lanthanide electronic transitions have been discussed in recent review articles [13–15].

So far there is no structural information available for the lanthanide halide vapor complexes. However, on the basis of the limited structural studies on transition metal halide vapor complexes [9, 10] it is reasonable to assume that the $LX_3 \cdot nAX_3$ (X = halide) structures have $AX_4^-$ tetrahedra bound to the lanthanide by a face, an edge or a corner. This is illustrated in Fig. 2 where possible sets of structures for different n values are presented. In the 'ring' type structures $R_n$(n = 1, 2, 3...) the lanthanide is four coordinated with two terminal and two bridged halides and is bound to the $AX_4^-$ 'tetrahedral' by either an edge (n = 1) or corners (n ⩾ 2). This bonding arrangement and coordination, within the ligand fraction of the molecule, is similar to that found in dimeric $L_2X_6$ vapors. In the 'cluster' type structures $K_n$, $K'_n$ the lanthanide ion preserves the coordination found in the solid halides (*i.e.* six-folds for end lanthanides and nine-fold for early lanthanides) and is bound to $AX_4^-$ by an edge (*e.g.* $K_3$ structure) or a face (*e.g.* $K'_3$) and/or involves bidentate $Al_2Cl_7^-$ bridging (*e.g.* $K_4$). The $K_n$ and $K'_n$ structures contain no L–X terminal halide and cannot be formed with lower than n = 3 values.

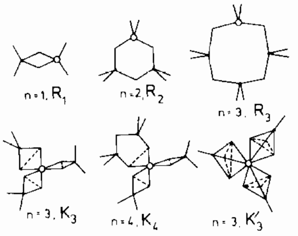

Fig. 2. Structural models for the lanthanide vapor complexes $LX_3 \cdot nAX_3$; ○ = L, ● = A.

'Ring' type structures can be easily extended to higher than n = 3 values and may include more than one four coordinated lanthanide atom per molecule. For example, a $2LX_3 \cdot 2AX_3$ molecule could have a structure similar to $R_3$. The six coordinated $K_n$ structures can be also extended for n > 4 by the inclusion of $A_2X_7^-$ bidentate units in the molecule. However, because of charge distribution and steric requirement the nine coordinated $K'_3$ structure cannot be extended to higher n values.

Independent of the structures (*i.e.* $R_n$ or $K_n$ or $K'_3$) adopted by the Er–Cl–A complexes, the A–Cl interaction will decrease the basicity of the chlorides coordinated to Er in the sequence In > Ga > Al, and thus the intensity of the hypersensitive transitions are expected to follow the same sequence. The data presented in Fig. 1 support this view. Furthermore a comparison of the band intensities for Nd–Cl–Ga [3] and Nd–Cl–Al [2] or for $CsNdI_4$ and $LiNdI_4$ [3] vapor complexes shows the same trends on going from Ga to Al or from Cs to Li.

The spectral changes with temperature and 'carrier' gas reported here, cannot give any information with respect to the number of possible species present and/or conclusions about their structure. In relation, however, to the proposed structures in Fig. 2 the following observation could be made which might be helpful in choosing certain molecular structures for the lanthanide vapors:

*1.* If the lanthanide vapor complex equilibria contain species only from one of the proposed structure series $R_n$(n = 1, 2, 3, 4 ...) or $K_n$(n = 3, 4, ...) or $K'_3$ then the ligand basicity and coordination number will *not* change along the series, and the band intensity of the hypersensitive transitions will be rather insensitive to the relative concentrations of the different species. In such a case no intensity changes of the hypersensitive bands are expected with increasing temperature and/or pressure.

*II.* If, on the other hand the equilibria involve crossings from one structure series to another (*e.g.* dissociation of $K_3'$ to form $R_1$), then the coordination number and (most likely) the average basicity of the ligands change and the intensities of the hypersensitive transitions will be, in contrast to the above case I, more sensitive to the relative concentrations of the species present. In other words temperature and/or pressure dependences of the hypersensitive band intensities are expected when both $R_n$ and $K_n$ (or $K_3'$) type structures are present in the vapor.

For the data presented here (Table I), case I is probably applicable for the *predominant* vapor complex components of the Er–Cl–Al and Er–Cl–Ga systems, while case II is more likely to describe the Er–Cl–In system. However, a more specific identification of the species for all Er–Cl–A vapor systems requires additional thermodynamic and/or structural (*e.g.* Raman spectroscopic) information [11].

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