(7) M. Goehring, "Ergebnisse and Probleme der Chemie der Schwefelstickstoffverbindungen", Akademie-Verlag, Berlin, 1957, p 155.
(8) H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, **15**, 385 (1972).
(9) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1767 (1966).
(10) L. Zborilova, J. Touzin, D. Navratilova, and J. Mrkosova, *Z. Chem.*, **12**, 27 (1972).
(11) J. Weiss, *Angew. Chem.*, **74**, 216 (1962).
(12) R. D. Smith and G. B. Street, *Inorg. Chem.*, **17**, 938 (1978).
(13) *Methoden Org. Chem. (Houben-Weyl), 9th Ed.*, 825, 849 (1965).
(14) H. W. Roesky, E. Wehner, E.-J. Zehnder, H.-J. Deiseroth, and A. Simon, *Chem. Ber.*, in press.
(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, 1970, p 324.
(16) R. J. Gillespie, D. R. Slim, and J. D. Tyrer, *J. Chem. Soc., Chem. Commun.*, 253 (1977).

Contribution from the Chemical Engineering Division,
Argonne National Laboratory, Argonne, Illinois 60439

Vapor Complexes of Samarium(III) and Samarium(II) Chlorides with Aluminum(III) Chloride

G. N. PAPATHEODOROU* and G. H. KUCERA

Received June 8, 1978

The electronic absorption spectra of vapor-phase compounds formed by reacting SmCl$_3$(s) and SmCl$_2$(s) with gaseous Al$_2$Cl$_6$ have been measured at temperatures up to 800 K and total pressures up to 13 atm. The spectra of the pale yellow Sm^{III}–Al–Cl gaseous complex(es) were characteristic of the f → f electronic transitions of Sm(III). The spectra of the red-brown Sm^{II}–Al–Cl gaseous complex(es) showed high-intensity, broad bands which are attributed to 4f → 5d transitions of Sm(II). Spectrophotometric measurements have been used to investigate the partial pressures of the vapor complexes at different Al$_2$Cl$_6$ pressures. Thermodynamic considerations suggest that the SmAl$_3$Cl$_{12}$ is the predominant vapor species formed by the trivalent samarium. For the reaction SmCl$_3$(s) + $^3/_2$Al$_2$Cl$_6$(g) → SmAl$_3$Cl$_{12}$(g) the values of $\Delta H = 6.7$ kcal/mol and $\Delta S = -1.0$ eu have been derived. At 650 K the volatility enhancement of Sm(II) has been estimated to be $\sim 10^{10}$. Rare earth oxides have been halogenated and vapor transported using Al$_2$Cl$_6$ or Al$_2$Br$_6$. A new method for the preparation of anhydrous rare earth halide crystals is suggested. The data are discussed in terms of the systematics of formation and structure of gaseous lanthanide chloride complexes.

Introduction

In recent years the formation of vapor complexes of transition metal halides with "acidic" halide vapors (e.g., Al$_2$Cl$_6$, Fe$_2$Cl$_6$) has been widely investigated by different research groups.[1-6] Spectrophotometric,[2-5] mass spectrometric,[1] and transpiration techniques[1,4,6] have been used to obtain thermodynamic information for these complexes. Very little work, however, has been done for the vapor complexes involving lanthanide or actinide halides. Exceptions are the investigations of Gruen et al.,[7] of Zvarova et al.,[8] and the recent work of Sørlie and Øye.[9] From a practical point of view, the interest in the rare earth–acidic vapor complexes arises from their potential use both as agents for chemical separations of the elements[8] and as gain media in the construction of high-power vapor lasers.[10]

Our present work is a part of a general study of the thermodynamics,[5,11-13] electronic absorption,[11-13] and Raman spectroscopy[14-16] of vapor complexes. The investigation concerns the vapor complexes of Sm(II) and Sm(III) chlorides with aluminum chloride. Spectrophotometric studies have been used to establish the formation of yellow Sm(III) and ceramic-red Sm(II) vapor complexes formed according to the reactions

$$m\mathrm{SmCl_3(s)} + n\mathrm{Al_2Cl_6(g)} \rightarrow m\mathrm{SmCl_3}\cdot n\mathrm{Al_2Cl_6(g)} \quad (1)$$

$$m'\mathrm{SmCl_2(s)} + n'\mathrm{Al_2Cl_6(g)} \rightarrow m'\mathrm{SmCl_2}\cdot n'\mathrm{Al_2Cl_6(g)} \quad (2)$$

From the measurements, the thermodynamics and stoichiometry of reaction 1 are derived. The data are discussed in terms of the electronic spectral properties and possible structure of the vapor complexes. The thermodynamic and structural properties of the Sm(III) complex are compared with the corresponding properties of the Nd(III)[7a] and Ho(III)[17] complexes.

Experimental Section

Anhydrous aluminum chloride was prepared from the corresponding Cerac/Pure Inc. reagent by repeated slow sublimations in fused silica tubes under vacuum.

A new method has been employed for the preparation and purification of samarium(III) chloride. Anhydrous and degassed Sm$_2$O$_3$ ($\sim$2 g) was placed in fused silica tubes ($\sim$1 cm i.d. × 20 cm long) containing an excess of aluminum cloride ($\sim$2 g). The evacuated and sealed tube was then placed in a furnace and the temperature was raised slowly (3–4 h) to 300 °C. Near 200 °C the following reaction began:

$$\mathrm{Sm_2O_3(s)} + \mathrm{Al_2Cl_6(g,l)} \rightarrow \mathrm{Al_2O_3(s)} + 2\mathrm{SmCl_3(s)} \quad (3)$$

The chlorination was completed within a few hours and the remaining excess of Al$_2$Cl$_6$(g) created a pressure of $\sim$2 atm in the tube. The tube was then placed in a tilted furnace where the lower part of the tube, containing the solids (Al$_2$O$_3$ + SmCl$_3$), was at 350 °C and the upper part was near the melting point of aluminum chloride (180 °C). With this thermal gradient, SmCl$_3$ was vapor transported according to reaction 1 and was deposited in the form of small yellow crystals ($\sim$0.1 mm × 1 mm) at the middle of the tube. Within 2 days the vapor transport yielded $\sim$1 g of SmCl$_3$. Reaction 3 appears to be very general for the preparation of lanthanide and actinide halides using aluminum halides. To date, we have prepared and vapor transported NdCl$_3$, NdBr$_3$, PrCl$_3$, ErCl$_3$, YCl$_3$, ThCl$_4$, UCl$_3$, and UCl$_4$ by reacting the corresponding oxide with Al$_2$Cl$_6$ or Al$_2$Br$_6$. The yields are high and by controlling the rate of vapor transport small single crystals of the halides can be obtained.

Initially the red-brown samarium(II) chloride was prepared[18] by fusing together a 1:2 mixture of samarium metal and samarium(III) chloride at $\sim$750 °C. It was later found, however, that SmCl$_3$ could be reduced at $\sim$250 °C by either Sm or Al metal in fused silica tubes containing an excess of Al$_2$Cl$_6$ liquid or gas. The reduction yielded a dark red binary liquid which contained large amounts of Al$_2$Cl$_6$. This liquid solidified at $\sim$220 °C and was very stable up to 500 °C; at this temperature, the aluminum chloride began to react with the fused silica tubes. By heating the liquid under vacuum at 300 °C, all Al$_2$Cl$_6$ was removed, leaving a red-brown powder whose X-ray patterns showed the presence of SmCl$_2$ plus other unidentifiable samarium chloride compounds. In the presence of excess Al$_2$Cl$_6$ vapors, the red-brown liquid was vapor transported to a colder part of the tube. A similar binary liquid was also formed by mixing SmCl$_2$ with Al$_2$Cl$_6$. Vapors over these liquids were red-brown giving identical electronic absorption spectra.

The anhydrous materials were handled in evacuated fused-silica tubes or in a helium-atmosphere drybox with a water vapor level <20 ppm.

0020-1669/79/1318-0385$01.00/0 © 1979 American Chemical Society

The method for investigating equilibria of type (1) spectrophotometrically has been described elsewhere.[5] A Cary Model 17H spectrophotometer equipped with a high-temperature cell compartment has been used. The optical cells were cylindrical cells of 5–10-cm path length and 22 mm o.d. The wall thickness of the low-pressure cells (4 atm or less) was 1 mm, whereas that for the high-pressure cells (up to 13 atm) was 3 mm. The temperature gradient along the optical cell was adjusted so that the cell windows were 2–3 °C hotter than the center of the cell where the solid samarium salts were maintained at temperature T.

The apparent molar absorptivity, ϵ, and the partial pressure, P_c, of the vapor complex were determined by two different sets of experiments,[11] using Beer's law: $\epsilon = AV/n{\cdot}l$ and $P_c = ART/\epsilon{\cdot}l$, where A is the optical density; V, the cell volume; n, the moles of samarium in the gas phase; and l, the path length. The pressure P_0, of the "hypothetically" undissociated Al_2Cl_6 and the partial pressure P' of the Al_2Cl_6 dimer present were calculated from the moles of Al_2Cl_6 added to the cell and the monomer–dimer equilibrium as described in ref 11–13.

The spectrophotometric experiments were successfully employed for the study of the Sm^{III}–Al–Cl vapor complex. At temperatures below 600 K, a yellowish, $SmCl_3$–xAl_2Cl_6 liquid was found, but at higher temperatures the only condensed phase present in the cell was $SmCl_3$. Measurements of A (or P_c) as a function of time showed that the gas–solid equilibrium was reached in less than 45 min.

Complications, however, arose with the spectrophotometric measurement of the Sm^{II}–Al–Cl vapor complex. When an excess of $SmCl_2$ was used, large amounts of a red-brown, $SmCl_2$–Al_2Cl_6, binary liquid were formed. Volatilization of all Al_2Cl_6 from this liquid required temperatures above 500–600 °C and long equilibration times. At these temperatures, $AlCl_3(g)$ attacked the silica cell, giving rise to large baseline shifts. Furthermore, a thin metallic-red film (probably $SmCl_x$; $x < 2$) was formed on the cell windows, making the absorption measurements impossible. Five experiments designed to measure the absorbance of the Sm^{II}–Al–Cl vapor complex over solid $SmCl_2$ at various pressures (1–3 atm) were unsuccessful. At lower temperatures (250–450 °C), the red-brown liquid phase was always present and absorbance measurements were possible. These measurements were not indicative of equilibrium conditions since the absorbance was found to depend on both the time and the temperature pretreatment of the cell. It was possible, however, by obtaining spectra at different time intervals and from cells previously preheated at different temperatures, to approximate a range of the partial pressures of the Sm^{II}–Al–Cl complex over the red liquid.

In the molar absorptivity measurements, similar difficulties were also encountered. Due to the high optical density of the Sm^{II}–Al–Cl complex, small amounts (~10^{-6} mol) of $SmCl_2$ were used; the $SmCl_2$ was either placed or vapor transported into the cell. Upon initial heating of the cell, the red-brown liquid was formed. Increasing the temperature to 300 °C volatilized all condensed phases; a white deposit was observed on the cell walls and the absorption spectra were indicative of Sm(III) rather than Sm(II) vapor complexes. Four experiments for measuring the molar absorptivity of Sm^{II}–Al–Cl were unsuccessful. Stabilization of the divalent samarium vapor complex was possible, however, by adding to the cell small amounts of aluminum metal, permitting the measurement of the molar absorptivity of Sm^{II}–Al–Cl to be made as a function of temperature.

Finally, for an independent approximation of the partial pressures of Sm^{II}–Al–Cl over the red-brown binary liquid formed by $SmCl_2$ and Al_2Cl_6, two simple "vapor density" experiments were designed. For these experiments, the red-brown liquid was first equilibrated, at temperature T, with aluminum chloride vapors in a large fused-silica tube (~50 mm i.d. × 50 mm long) having a small side-arm tube (~6 mm i.d. × 30 mm long). The temperature of the small tube was kept ~5 °C higher than that of the large tube so as to avoid transport of condensed material in the side tube. The fused silica container was then removed quickly from the furnace and all vapors present were condensed by cooling the side arm in liquid N_2. The number of moles of vapor complex and of aluminum chloride condensed into the side tube were measured by chemical analysis and their partial pressures were calculated from the equilibration temperature and the cell volume.

Results and Discussion

Molar Absorptivity and Spectra. Three experiments were successfully conducted to determine the molar absorptivity of the Sm(III) gaseous complex(es) at different temperatures. The absorption spectrum at 750 K is shown in Figure 1. All bands observed are characteristic of the f → f transitions of Sm(III)[19] and the relative band intensities are similar to those observed in acidic water solutions.

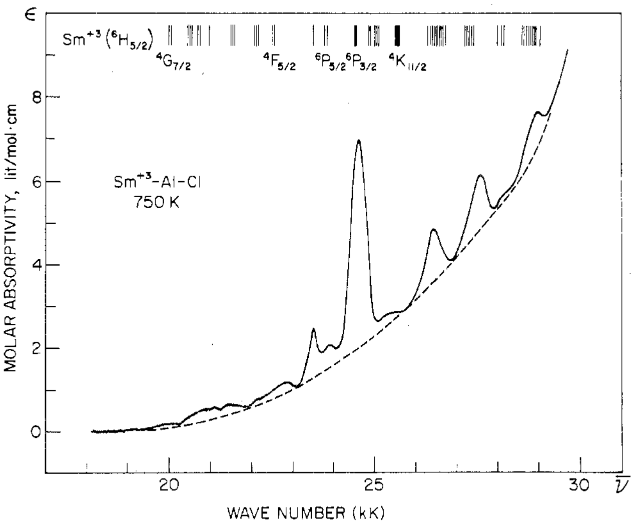

Figure 1. Absorption spectrum of the samarium(III) chloride–aluminum chloride vapor complex. Energy states at the top of the figure were taken from ref 19. A dashed line was used as baseline for measuring the molar absorptivity of the 406 nm (2.46 μm^{-1}) band due to the $^6P_{3/2} \rightarrow {}^6H_{5/2}$ transition.

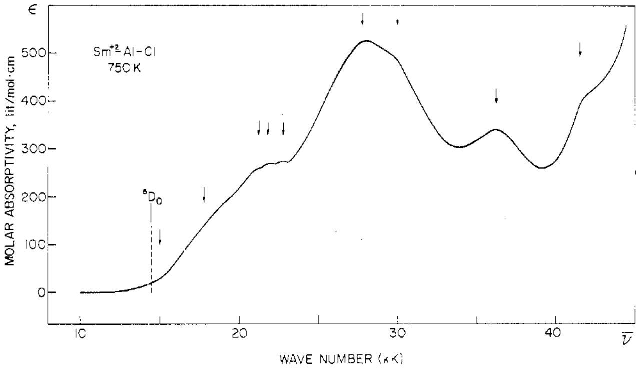

Figure 2. Absorption spectrum of the samarium(II) chloride–aluminum chloride vapor complex(es). Arrows indicate bands listed in Table II. A dashed vertical line shows the position of the $^5D_0$(4f).

The molar absorptivity of the most intense band at 406 nm, ϵ^*_{406}, measured from the dashed baseline shown in the figure, has been used for calculating the partial pressures of the vapor complex in the equilibrium experiments to be discussed below. Temperature-dependence studies (Table I)[20] show that ϵ^*_{406} decreases with increasing temperature from an average value of 6.45 ± 0.2 L/(mol cm) at 650 K to a value of 5.65 ± 0.3 L/(mol cm) at 750 K. The baseline (dashed line in Figure 1), on which the f → f spectrum is superimposed, increased in intensity with increasing temperature and the overall spectra were reproducible and independent of the thermal history of the cell. Cells previously used for spectral measurements up to 750 K showed a flat baseline when cooled to room temperature. This behavior indicates that the "background" seen in Figure 1 is probably due to the tail of a high-energy charge-transfer band of either the Sm^{III}–Al–Cl molecule or an unknown impurity [e.g., Sm^{II}–Al–Cl]. The spectrophotometric equilibrium experiments (with excess $SmCl_3$ in the cell) have shown that the location of the 406-nm maximum did not change with temperature and/or pressure of Al_2Cl_6.

The molar absorptivity data for the Sm(II) gaseous complex are given in Figure 2 and Table I.[20] No temperature effect

Table II. Broad Absorption Bands of Sm(II) in Different Environments (in $cm^{-1} \times 10^3$)[a]

Sm^{II}-Al-Cl 700 K	Sm^{II}; water[24] 300 K	Sm^{II}; KCl[23] 300 K
(15.5)[b] w		
		16.83 s
	17.9 s	
		18.62 s
(19) m		
		(19.82)
(21.5) m		
(22) w	23.4	(23.25) m
(22.7) w		
		24.66 s
27.4[c] s	30.20 s	29.45 s
29.46[c] s	32.6 s	30.26 s
36.6 s	38.0 s	40.24 s
43.8 s	41.9 m	44.3 s

[a] Band intensities are marked as w = weak; m = medium; s = strong. [b] Shoulder band. [c] In going from 725 to 800 K, a red shift of ~300 cm^{-1} was observed for this band.

on the molar absorptivity was observed. In going from 723 to 799 K, the value of ϵ at 365 nm did not change but a red shift of approximately 4 nm was observed. Spectra of Sm(II) have been previously obtained by stabilizing the divalent ions in different host crystals[21-24] and in solutions.[24,25] The spectra consist of a set of sharp bands with energies below 2.0 μm^{-1} and a set of broad bands which extend to the UV region. The former are attributed to 4f → 4f transitions which are not present in the solution spectra[24,25] or in our vapor spectra. The broad bands are attributed to transitions between 4f and 5d, 6s, 6p... levels. A comparison of the broad-band spectra of Sm^{II}–Al–Cl with those of Sm(II) in KCl[23] and in aqueous solution[24] is given in Table II.

The temperature-dependence studies[21,23] and the substitution of the host lattice from KCl to KI[23] or from CaF_2 to BaF_2[22] show that the bands below ~2.5 μm^{-1} shift to the blue, while the bands above 2.5 μm^{-1} shift to the red, with increasing temperature and/or decreasing ionic strength of the anions. Furthermore, the number of bands below 2.5 μm^{-1}, their intensities, and their positions change drastically with the crystal field environment, while the bands between ~2.7 and ~3.2 μm^{-1} and the higher energy UV bands appear in all spectra. For high or low symmetry fields, the d orbitals are sensitive and split to different levels; the s orbitals, however, remain unchanged, while the p orbitals split only in low symmetry fields. It is thus possible that the broad bands below 2.5 μm^{-1} are due to 4f ← 5d transition and that the changes observed in going from the Sm^{II}–Al–Cl to the Sm(II)/KCl spectra (Table II) arise from different ligand field splittings of the d orbitals. On the other hand, the higher energy bands arise from s orbitals and from the less sensitive to environmental symmetry p orbitals.

It is noteworthy that the lower energy bands of the Sm^{II}–Al–Cl complex overlap with the $^5D_0(4f)$ state at ~1.45 μm^{-1} (Figure 2) from which stimulated emission to the $^7F_1$ state has been found to occur in different host crystals.[21-23,26] For this reason the Sm^{II}–Al–Cl complex has potential as a gain medium in vapor-phase lasers, and further investigation of the complex is warranted. In this respect, studies similar to those used for investigating trivalent rare earth vapor lasers[10,17,27] will be useful.

Thermodynamics and Stoichiometry. Six spectrophotometric experiments were performed with different pressures P' of Al_2Cl_6 over excess solid $SmCl_3$. The apparent partial pressures P_c of the Sm^{III}–Al–Cl complex were calculated from the absorbance A^*_{408} of the 408-nm band and the previously measured values ϵ^*_{408} of the molar absorptivity. The values of P', A^*_{406}, and P_c are listed in Table III.[20] The pressures P' for four experiments were between 1.5 and 3.5 atm and for the remaining two experiments, between 8 and 12 atm. Temperature-dependence studies were made in intervals of 50 K from 600 to 800 K. At 600 K the formation of yellow $SmCl_3 \cdot xAl_2Cl_6$ liquid was observed in the high-pressure cells. The presence of liquid in the low-pressure cells at 600 K could not be definitely excluded. For all cells, however, no liquid was observed at temperatures of 650 K or higher.

Table IV. Calculated n for reaction 1

temp, K	$\Delta P = P'(i) - P'(j)$, atm	no. of combinations	av n and std deviation
650	$\Delta P > 4$	8	1.51 (0.02)
700	$\Delta P > 4$	8	1.48 (0.02)
750	$\Delta P > 4$	8	1.49 (0.02)
a	$\Delta P > 4$	24	1.495 (0.02)
a	$\Delta P > 2$	27	1.49 (0.03)
a	$\Delta P > 1$	36	1.51 (0.06)

[a] All temperatures.

Table V. Thermodynamic Quantities for Solid-Gas Reactions

	reaction	ΔH,[a] kcal/mol	ΔS,[a] eu	temp range, °C	ref
A	$SmCl_3(s) + 1.5Al_2Cl_6(g) \rightarrow SmAl_3Cl_{12}(g)$	6.7 ± 0.2	−1.0 ± 0.2	600–800	this work
B	$NdCl_3(s) + 1.5Al_2Cl_6(g) \rightarrow NdAl_3Cl_{12}(g)$	10.8 ± 0.3	2.5 ± 0.3	600–800	7a[b]

[a] Determined from the relation $RT \ln k = T\Delta S - \Delta H$ assuming ΔS and ΔH are constant over the entire temperature range. [b] The data in ref 7a support the view that two mononuclear Nd complexes are present and the thermodynamics of formation for both $NdAl_3Cl_{12}$ and $NdAl_4Cl_{15}$ have been derived.

Since $P_c << P_{Al_2Cl_6}$, the equilibrium constant of reaction 1 is $K = P_c/P'^n$. From measurements at the same temperature but in two cells, i and j, having different Al_2Cl_6 pressures we have

$$n = \frac{\ln [P_c(i)/P_c(j)]}{\ln [P'(i)/P'(j)]} = \frac{\ln [A^*_{406}(i)/A^*_{406}(j)]}{\ln [P'(i)/P'(j)]} \quad (4)$$

Equation 4 was used to evaluate n at different temperatures by combining the data from the sets of experiments listed in Table IV. The uncertainties involved in calculating n depend on the differences between the Al_2Cl_6 pressures in the two cells considered. When $P'(j)$ is close to $P'(i)$, 3% uncertainties in P' and P_c give rise to a 24% error in n. However, when a high-pressure and low-pressure cell are combined, $\Delta P' = P'(j) - P'(i) > 4$ atm, 3% uncertainties in the pressures give ~4.5% error in n. Table IV gives the average values of n and the standard deviations calculated at different temperatures using different sets of experiments. Combinations of the two high-pressure and the four low-pressure experiments show that $n = 1.5$ and is independent of temperature. This implies that the predominant vapor complex is $(SmCl_3)_m \cdot {}^3/_2Al_2Cl_6$. The value of m cannot be calculated from our data, but we shall assume that the complex is mononuclear in samarium ($m = 1$). This assumption has been used previously for the transition-metal chloroaluminate complexes and is supported by mass spectrometric studies.[1] Thus the stoichiometry of the predominant vapor complex is believed to be $SmAl_3Cl_{12}$. With the values of $n = 1.5$ and $m = 1$ the equilibrium constants, K, of eq 1 have been calculated and are listed in Table III.[20] A deduction of the enthalpy and entropy of this equilibrium is derived from Figure 3. A least-squares treatment of the data yields the thermodynamic quantities listed in Table V. The large experimental uncertainties for the 600 K data are due to the small absorbances measured and/or the possible formation of liquid at this temperature.

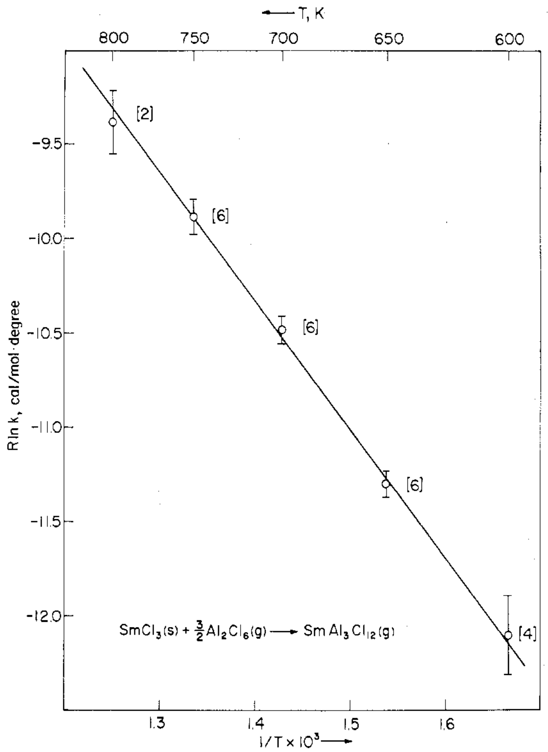

Figure 3. Plot of $R \ln K$ vs. $1/T$ for reaction A in Table V. Numbers in brackets indicate the number of experimental points used at each temperature.

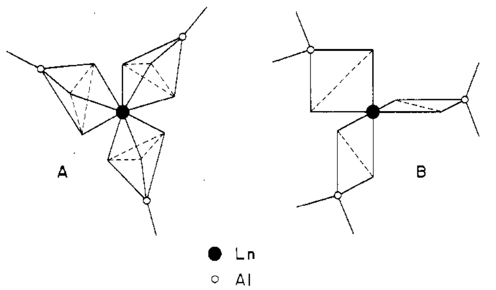

Figure 4. Molecular models for the $LnAl_3Cl_{12}$ vapors. For model A, the lanthanide is ninefold coordinated (early lanthanides); for model B, the lanthanide is in near octahedral coordination (end lanthanides).

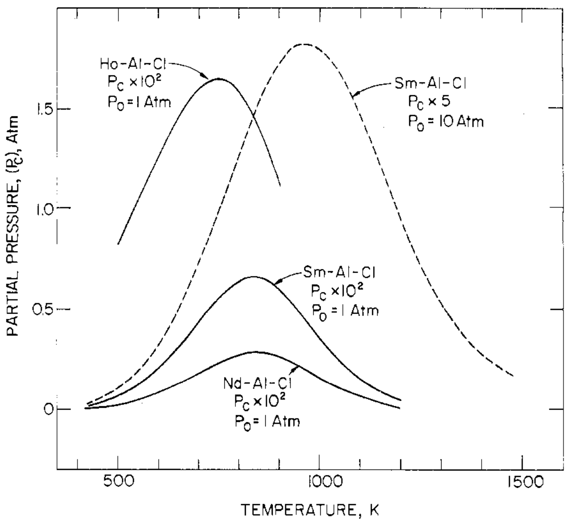

Figure 5. Apparent partial pressures of $NdCl_3$,[7a] $SmCl_3$, and $HoCl_3$[17] in Al_2Cl_6 atmosphere. For the Nd–Al–Cl the average thermodynamic quantities with $\bar{n} = 1.73$ have been used. For the other systems $n = 1.5$.

The values of ΔH and ΔS for the $SmAl_3Cl_{12}$ and $NdAl_3Cl_{12}$ complexes are compared in Table V. The entropies appear to be very close, but a difference of 2–3 kcal/mol is observed for the enthalpy values. This difference might be attributed to the experimental uncertainties of the methods used. It is possible, however, that the bonding and structures of the vapor complexes are not the same. Schäfer[1] has suggested a structure for the $CrAl_3Cl_{12}$ vapor complex where octahedral coordination is maintained by bonding the edges of three $AlCl_4$ tetrahedra to Cr(III). This structure is shown in Figure 4 as molecule B. It has been argued and shown by both thermodynamic[5,6,11–13] and structural[14–16] studies that the divalent transition metal haloaluminate complexes, MAl_2X_8, have M in a coordination similar to that of the corresponding MX_2 solid. Furthermore, the "AlX_4" tetrahedra fulfill the preference (ligand field) coordination of M by sharing with it an edge (i.e., $PdAl_2Cl_8$, $PtAl_2Cl_8$) or a face (i.e., $NiAl_2Cl_8$, VAl_2Cl_8). Both $NdCl_3$ and $SmCl_3$ solids have a UCl_3 ($P6_3/m$, $C_{6h}{}^2$) structure where the lanthanide is nine-coordinated. Thus, in order to maintain a similar coordination in the vapor phase, the three "$AlCl_4$" tetrahedra should be bound by a face to the lanthanide (molecule A, Figure 4).

From the lattice parameters of $SmCl_3$,[28] we have calculated all angles and distances of the "$SmCl_9$" nine-coordinated structure in the solid. A comparison of these distances with those of "$AlCl_4$" in gaseous Al_2Cl_6 shows that changes of bond angles and bond lengths by less than 4% make the dimensions of the $AlCl_4$ tetrahedra faces match three sets of chloride (triangle) faces of the "$SmCl_9$". On the other hand, molecule B (Figure 4) requires changes of coordination for Sm(III), in going from the solid to the complex and is in contrast with the findings for the transition metal vapor complexes. In view of these considerations, the structure of $SmAl_3Cl_{12}$ is more likely to be similar to that of molecule A. As in the case of $CrAl_3Cl_{12}$, molecule B is a possible structure for the end lanthanides, which are isostructural to YCl_3,[28] with the lanthanide atom in a close-to-octahedral coordination. The recently investigated Ho^{III}–Al–Cl vapor complex[17] probably falls into this category.

From the thermodynamic quantities of formation for Nd^{III}–Al–Cl, Sm^{III}–Al–Cl, and Ho^{III}–Al–Cl, the thermodynamics of dissociation of Al_2Cl_6, and the procedures described in ref 5, the values of P_c for these three complexes have been calculated and are plotted in Figure 5. A constant pressure, P_0, was used at all temperatures. At a temperature T and $P_0 = 1$, the partial pressure of the complex increases with decreasing size of the lanthanide. This is probably due to the fact that the $AlCl_4$ faces or edges match the "$LnCl_9$" edges of the smaller lanthanides with smaller changes of bond angles and bond distances. The appearance of the maximum at P_c and its shift to higher temperatures with increasing pressure P_0 (Figure 5) can be simply justified from the effects of temperature and pressure on the dissociation of aluminum chloride.

Finally, the results of the spectrophotometric and "vapor density" measurements for the Sm^{II}–Al–Cl complex are given in Tables VI[20] and VII,[20] respectively. Due to the difficulties mentioned in the experimental part, the data do not permit an accurate evaluation of the partial pressures, and thus the thermodynamics and stoichiometry of the complex cannot be determined. The data, however, can be used for approximating, within a factor of 2 or 3, the partial pressures of the complex over the red-brown liquid. Values approximated from the spectrophotometric and the vapor density measurements appear to agree. Thus at ~650 K with an aluminum chloride dimer pressure of ~2.5 atm, the range of partial pressures of the Sm^{II}–Al–Cl complex derived from both Tables VI and VII is $\sim 1.5 \times 10^{-3}$ to $\sim 3.5 \times 10^{-3}$ atm. From these values and the literature vapor pressure data of $SmCl_2$[18] the volatility enhancement has been calculated to be $\sim 10^{10}$ at 650 K.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy, Division of Basic Energy Sciences.

Registry No. $SmCl_3$, 10361-82-7; $SmCl_2$, 13874-75-4; $SmAl_3Cl_{12}$, 68645-74-9; Sm_2O_3, 12060-58-1; Al_2Cl_6, 13845-12-0.

Supplementary Material Available: Table I, determination of molar absorptivity, Table III, absorbances, partial pressures, and equilibrium constants for the Sm^{III}–Al–Cl system, Table VI, absorbances and partial pressures of the Sm^{II}–Al–Cl system, and Table VII, vapor density experiments (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) H. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **15**, 713 (1976).
(2) A. Anundskås and H. A. Øye, *Acta Chem. Scand., Ser. A*, **30**, 193 (1976).
(3) F. P. Emmenegger, *Inorg. Chem.*, **16**, 343 (1977).
(4) N. W. Gregory, *J. Phys. Chem.*, **81**, 1857 (1977).
(5) G. N. Papatheodorou and G. H. Kucera, *Inorg. Chem.*, **16**, 1006 (1977).
(6) E. W. Dewing, *Metall. Trans.*, **1**, 2169 (1970).
(7) (a) H. A. Øye and D. M. Gruen, *J. Am. Chem. Soc.*, **91**, 2229 (1969); (b) D. M. Gruen and R. L. McBeth, *Inorg. Chem.*, **8**, 2625 (1969).
(8) T. S. Zvarova, *Radiochim. Acta*, **15**, 542 (1973).
(9) M. Sørlie and H. A. Øye, *J. Inorg. Nucl. Chem.*, **40**, 493 (1978).
(10) (a) W. F. Krupke, "Proceedings of the 2nd Summer Colloquium on Electronic Transition Lasers", J. I. Steinfeld, Ed., M.I.T. Press, Cambridge, Mass., 1976, p 148. (b) R. R. Jacobs, M. J. Weber and R. K. Pearsons, *Chem. Phys. Lett.*, **34**, 80 (1975).
(11) G. N. Papatheodorou, *J. Phys. Chem.*, **77**, 472 (1973).
(12) G. N. Papatheodorou, *Inorg. Chem.*, **12**, 1899 (1973).
(13) G. N. Papatheodorou, *Z. Anorg. Allg. Chem.*, **411**, 153 (1975).
(14) P. L. Radloff and G. N. Papatheodorou, "Proceedings of the Symposium on High Temperature Metal Halide Chemistry", D. Cubicciotti and D. L. Hildebrand, Ed., Vol. 78-1, The Electrochemical Society, Inc., 1978, p 320.
(15) G. N. Papatheodorou and M. A. Capote, ref 14, p 334.
(16) M. A. Capote, G. H. Kucera, and G. N. Papatheodorou, ref 14, p 367.
(17) H. R. Hoekstra, J. P. Hessler, C. W. Williams, and W. T. Carnall, ref 14, p 123.
(18) D. Brown, "Halides of the Lanthanides and Actinides", Wiley, New York, 1968, p 162.
(19) G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals", Interscience, New York, 1968, p 233.
(20) See supplementary material.
(21) G. H. Dieke and R. Sarup, *J. Chem. Phys.*, **36**, 371 (1962).
(22) D. L. Wood and W. Kaiser, *Phys. Rev.*, **126**, 2079 (1962).
(23) W. E. Bron and W. E. Heller, *Phys. Rev.*, **136**, A1333 (1964).
(24) F. D. S. Butement, *Trans. Faraday Soc.*, **44**, 617 (1948).
(25) K. E. Johnson, J. R. Mackenzie, and J. N. Sandoe, *J. Chem. Soc. A*, 2644 (1968).
(26) P. P. Sorskin, M. J. Stevenson, J. R. Lankard, and G. D. Pettit, *Phys. Rev.*, **127**, 503 (1962).
(27) R. R. Jacobs and W. K. Krupke in Lawrence Livermore Laboratory Annual Report No. UCRL 50021-75, 1976, p 529.
(28) R. W. G. Wykoff, "Crystal Structures", Vol. II, Wiley, New York, 1964.

Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada

Gold(III) Fluorosulfate, Its Solution Behavior in HSO_3F, and the Tetrakis(fluorosulfato)aurate(III) Ion

K. C. LEE and F. AUBKE*

Received July 5, 1978

Gold(III) fluorosulfate is found to be a good fluorosulfate ion acceptor. The tetrakis(fluorosulfato)aurate(III) ion, $[Au(SO_3F)_4]^-$, is found in solid, crystalline materials of the composition $M[Au(SO_3F)_4]$, with M = Cs, K, Li, NO, or ClO_2. Their syntheses and vibrational spectra are discussed. Ionic formulation as $M^+[Au(SO_3F)_4]^-$ is suggested. The ability of $Au(SO_3F)_3$ to accept SO_3F^- ions extends also to the system HSO_3F–$Au(SO_3F)_3$. This system is investigated by electrical conductance measurements and by UV–visible, Raman, and NMR (^{19}F and ^1H) spectroscopy. Gold(III) fluorosulfate is thought to be monosolvated and acts as a moderately strong acid in HSO_3F according to $H[Au(SO_3F)_4] + HSO_3F \rightleftharpoons [Au(SO_3F)_4]^- + H_2SO_3F^+$.

Introduction

The chemistry of gold provides many examples where the metal exhibits a formal oxidation state of +3. As expected for a d^8 electron configuraton, a regular or slightly distorted square-planar stereochemistry around gold is commonly found, resulting in diamagnetic compounds.

The square-planar environment for gold is accomplished either by polymerization, as in AuF_3,[1] or by complex formation. Both anionic complexes of the type AuX_4^-, where X is a uninegative, monodentate ligand, and neutral complexes of the type AuX_3L, where L is an electron pair donor ligand, are commonly found.

Of the binary gold(III) compounds of the type AuX_3, the fluorosulfate $Au(SO_3F)_3$, first reported in 1972 by Johnson, Dev, and Cady[2] appears to be the only well documented oxyacid derivative of gold(III).

We became interested in this compound for two reasons: (a) $Au(SO_3F)_3$ should act as a fluorosulfate ion acceptor, allowing the syntheses of complexes containing the anion $[Au(SO_3F)_4]^-$ with hopefully a wide variety of catons, and (b) $Au(SO_3F)_3$ may remove fluorosulfate ions from the self-ionization equilibrium of fluorosulfuric acid[3] (eq 1) and hence

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad (1)$$

act as an acid in HSO_3F. Such behavior would not be unexpected, because solutions of AuF_3 in HSO_3F have been reported to show acidic behavior.[4]

Experimental Section

Chemicals. Commercially available chemicals of analytical reagent or of reagent grade were generally used without purification. Technical grade HSO_3F (Baker and Adamson) was purified by double distillation at atmospheric pressure as described previously. Gold powder, 100 mesh, 99.995% pure, was obtained from Ventron Corp.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[5] bromine(I) fluorosulfate, $BrSO_3F$,[6] chlorine dioxide, ClO_2,[7] chloryl fluorosulfate, ClO_2SO_3F,[8] and potassium fluorosulfate KSO_3F.[3] $AuBr_3$ was obtained from the reaction of gold with Br_2 at 80 °C.

A direct route to $Au(SO_3F)_3$ will be described below in detail.

Instrumentation. Raman spectra were obtained with either a Cary 81 or a Spex Ramalog spectrophotometer, equipped with a heli-

0020-1669/79/1318-0389$01.00/0 © 1979 American Chemical Society