contained dried CsF and about 7 ml of diglyme. After heating the bomb at 80° for 4 days, the volatile portion was fractionated (−98°) and then further purified by gas chromatography by using an 8-ft column packed with 20% Kel-F oil on Chromosorb P. The pentafluoroethylsulfuryl fluoride[16] (30%) was further characterized by ^{19}F nmr spectra (Table I) and by its infrared spectrum which has bands at 1476 (vs), 1336 (m), 1255 (vs), 1240 (sh, vs), 1208 (m), 1152 (s), 999 (m), 817 (s), 754 (w), 644 (sh, w), and 610 (sh, w) cm^{-1}. Its experimental molecular weight was 203 (202).

Preparation of C_2F_5SCl. A mixture of $(C_2F_5S)_2$ (4.75 mmol) and Cl_2 (6.0 mmol) was heated at 90-100° for 6 hr in a Pyrex vessel. Separation of the mixture by fractional condensation gave unreacted disulfide (−78°), C_2F_5SCl (−108°), and a mixture of Cl_2 and C_2F_5SCl at −196°. The infrared spectrum consists of bands at 1330 (m), 1230 (vs), 1168 (m), 1122 (s), 980 (s), 965 (sh), 753 (m), and 550 (w) cm^{-1}.

Reaction of C_2F_5SCl and $(CF_3S(O)O)_2Zn$. Approximately 1 mmol of C_2F_5SCl was condensed onto $(CF_3S(O)O)_2Zn$ in a Pyrex vessel and the volatile products were monitored every 6 hr over a 36-hr period. The major products identified were CF_3Cl, $(C_2F_5S)_2$, $C_2F_5SCF_3$,[10] and some unreacted C_2F_5SCl. No $CF_3SO_2SC_2F_5$ was detected during this period.

Preparation of $CF_3SO_2SC_2F_5$ and $C_2F_5SO_2SCF_3$. A mixture of 5 mmol each of $CF_3S(O)Cl$ and $C_2F_5S(O)Cl$ was condensed at −183° into a 500-ml Pyrex flask equipped with a Teflon stopcock and then warmed to 25°. Over a period of 1.5 hr approximately 3.5 ml of mercury was added with shaking. The mixture was fractionated through traps cooled to −63, −78, and −196°. Further purification of the materials retained in the traps at −63 and −78° was accomplished with gas chromatography using an 8-ft column packed with Kel-F No. 3 oil on Chromosorb P. This resulted in the isolation of 0.4 mmol of a mixture of the thiosulfonates. Additional attempts to separate the mixture by gas chromatography were unsuccessful and attempts to reproduce or alter this reaction resulted in no isolation of the two products.

Registry No. $HNF_2 \cdot KF$, 13841-05-9; SOF_2, 7783-42-8; $FS(O)NF_2$, 39937-04-7; $CF_3S(O)F$, 812-12-4; $CF_3SO_2SCF_3$, 358-15-6; $C_2F_5S(O)F$, 20621-31-2; HCl, 7647-01-0; $C_2F_5S(O)Cl$, 39937-08-1; C_2F_4, 116-14-3; SO_2F_2, 2699-79-8; $C_2F_5SO_2F$, 354-87-0; $(C_2F_5S)_2$, 679-77-6; Cl_2, 7782-50-5; C_2F_5SCl, 39937-11-6; $[CF_3S(O)O]_2Zn$, 39971-65-8; $CF_3S(O)Cl$, 20621-29-8; $CF_3SO_2SC_2F_5$, 39937-13-8; $C_2F_5SO_2SCF_3$, 39937-14-9; Hg, 7439-97-6; $C_2F_5SO_2SC_2F_5$, 39937-15-0.

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[16] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 2640 (1957).

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Spectrophotometric Study of the Platinum(II) Chloride-Aluminum Chloride Vapor Complex

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The reaction of solid *cluster* platinum(II) chloride (Pt_6Cl_{12}) with gaseous aluminum chloride to form a purple gaseous complex has been studied spectrophotometrically. Thermodynamic considerations suggest the stoichiometry for the reaction: $^1/_6Pt_6Cl_{12}(s) + Al_2Cl_6(g) \rightarrow PtAl_2Cl_8(g)$ (ΔH^R = 7.8 kcal/mol, ΔS^R = 6.4 eu). The visible electronic absorption spectrum of the gaseous complex was compared with the spectrum of Pt(II) centers in liquid LiCl and interpreted in terms of a square-planar $PtCl_4$ group sharing edges with two tetrachloroaluminates.

Introduction

It has been shown[2-6] that gaseous aluminum chloride reacts with many MCl_k metal chlorides to form gaseous complexes with the general formula $(MCl_k)_m(Al_2Cl_6)_n$. In most cases studied $m = 1$ while the value of n varies between $^1/_2$ and 2.

Among the different metal chlorides investigated by vapor pressure equilibrium measurements were some alkali and alkaline earth chlorides (M = Na, K, Mg, Ca)[2,3] and some chlorides of 3d metal cations (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)).[3] The chlorides of Nd(III),[4a] U(III), U(V),[4b] and Pd(II)[5] have been studied spectrophotometrically.

In the present report the existence of a purple vapor complex of platinum chloride with aluminum chloride has been established. Furthermore, the equilibrium

$$(m/6)Pt_6Cl_{12}(s) + nAl_2Cl_6(g) \rightarrow (PtCl_2)_m(Al_2Cl_6)_n(g) \qquad (1)$$

has been studied by measuring spectrophotometrically the partial pressures of the gaseous complex(es) over the "cluster" platinum chloride (Pt_6Cl_{12}). The thermodynamic quantities of the above equilibrium and the electronic absorption spectrum of the gaseous complex are discussed in terms of the stoichiometry and possible structure of the gaseous molecule.

Experimental Section

Chemicals and Equipment. High-purity anhydrous aluminum chloride was prepared from Baker Analytical reagent $AlCl_3$ by slow sublimation in silica tubes under vacuum. The sublimation was repeated six times.

The platinum(II) chloride was prepared as previously described.[7a] Large quantities of the cluster platinum chloride Pt_6Cl_{12} were prepared by recrystallization of $PtCl_2$ from its dilute solutions in liquid Al_2Cl_6.[7b] The spectrophotometric measurements were performed on a Cary Model 14 spectrophotometer equipped with a high-temperature cell compartment[8] (15-cm maximum path length). The quartz cells were the uv-type cylindrical cells, purchased from Pyrocell. The

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[2] (a) E. W. Dewing, *Nature (London)*, 214, 483 (1967); (b) *Met. Trans.*, 1, 2169 (1970).

[3] K. N. Semenenko, T. N. Naumova, L. N. Gorokhov, and A. V. Bovoseloca, *Dokl. Akad. Nauk SSSR*, 154, 649 (1964).

[4] (a) H. A. Oye and D. M. Gruen, *J. Amer. Chem. Soc.*, 91, 2229 (1969); (b) D. M. Gruen and R. L. McBeth, *Inorg. Chem.*, 8, 2625 (1969).

[5] G. N. Papatheodorou, *J. Phys. Chem.*, 77, 472 (1973).

[6] K. Lascelles and H. Schafer, *Z. Anorg. Allg. Chem.*, 383, 249 (1971).

[7] (a) G. N. Papatheodorou and G. P. Smith, *J. Inorg. Nucl. Chem.*, 35, 799 (1973); (b) G. N. Papatheodorou, unpublished work.

[8] R. A. Lynde and J. D. Corbett, *Inorg. Chem.*, **10**, 1746 (1971).

Table I. Determination of Molar Absorptivity

E-1 $P_0 = 3.21 \times 10^{-3}T$, atm $n_{Pt} = 1.54 \times 10^{-5}$, mol $V = 28.5$ cm^3 $h = 10$ cm		E-2 $P_0 = 3.12 \times 10^{-3}T$, atm $n_{Pt} = 0.969 \times 10^{-5}$, mol $V = 29.0$ cm^3 $h = 10$ cm		E-3[a] $P_0 = 5.28 \times 10^{-3}T$, atm $n_{Pt} = 1.415 \times 10^{-5}$, mol $V = 26.8$ cm^3 $h = 10$ cm		Average absorptivity		
T, K	ϵ_{max}	T, K	ϵ_{max}	T, K	ϵ_{max}	T, K	λ_{max},[b] Å	ϵ_{max}
		500	113.7	500	112.1	500	368.0	112
550	113.0	550	116.6	550	115.5	550	369.5	115
600	117.0	600	119.6	600	117.4	600	371.2	118
650	121.8	650	123.2	650	122.1	650	372.5	122

[a] The data for experiment E-3 are given in Figure 1. [b] The values of ν_{max} (the frequency at which the maximum absorptivity occurs) were found to be the same for all three experiments.

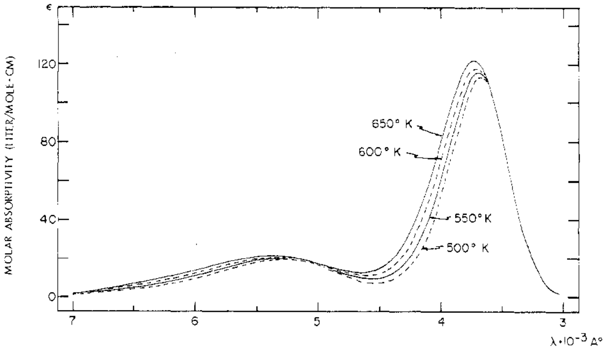

Figure 1. Absorption spectra of the platinum chloride–aluminum chloride vapor complex as a function of temperature.

anhydrous materials were handled under vacuum, in tight containers or in a drybox.

Method. In a typical experiment, amounts of $AlCl_3$ or Pt_6Cl_{12}, preweighed on a microbalance, were transferred into a dry and degassed quartz cell with a known volume and path length (5 or 10 cm). The cell was then sealed under vacuum and heated for 8–12 hr at 600 K. Finally it was transferred into the furnace of the spectrophotometer. In most cases the spectra were recorded at four different temperatures (500, 550, 600, 650 K). The amounts of $AlCl_3$ were adjusted so that all $AlCl_3$ in the cell was in the vapor phase at temperatures between 500 and 600 K. The pressure of the Al_2Cl_6 gas was estimated from the ideal gas equation of state and from the literature data for the dissociation of Al_2Cl_6.[4]

Determination of Molar Absorptivity. Three experiments were designed in order to determine the molar absorptivity $\epsilon(\lambda)$ of the gaseous platinum complexes. The 10-cm cells were filled with small known amounts of Pt_6Cl_{12} (~3.0 mg) to ensure that all the solid was in the gaseous phase. The absorbance, $A(\lambda)$, of the complexes as a function of λ was then recorded between 4 to 33 kK. The characteristics of each experiment are shown in Table I. The molar absorptivity was then evaluated from the equation $\epsilon(\lambda) = A(\lambda)(V/n_{Pt})h$, where V and h are the volume and path length of the cell, respectively, and n_{Pt} is the number of moles of $PtCl_2$ placed in the cell. Only a strong absorption band close to 27 kK (3700 Å) and a weak band close to 19 kK (5200 Å) were observed in the range of 4–33 kK. The data at four different temperatures are shown in Figure 1.

Solid Pt_6Cl_{12} in Equilibrium with Al_2Cl_6 Gas. In a series of experiments we have determined the nature of the solid phase(s) of $PtCl_2$ in equilibrium with Al_2Cl_6 gas and we have excluded the formation of the $PtCl_2$–Al_2Cl_6 solid complex compound. These experiments were performed in sealed and evacuated fused-silica tubes containing small quantities of Pt_6Cl_{12} and $AlCl_3$. The silica tubes were placed in furnaces and kept at different temperatures (500, 550, 600, 650 K) for a period of 2–5 days. At these temperatures all the $AlCl_3$ was in the gaseous phase and reacted with the (excess) Pt_6Cl_{12} according to eq 1. After cooling and solidifying the Al_2Cl_6(g) away from the solid phase(s), the silica tube was opened in a drybox and the solid phases were identified by X-ray powder diffraction patterns. It was found that in the temperature range 500–650 K, the only solid phase present was the Pt_6Cl_{12}[9] solid. Furthermore, in the same experiments we observed that the Pt_6Cl_{12} solid could be transported from a hotter to a cooler zone of the silica tube forming small single crystals in a dendrite arrangement. This last observation indicated that the decomposition of the $PtCl_2$–Al_2Cl_6 gaseous complex yields the Pt_6Cl_{12} solid.

At temperatures above 700 K, the black-red Pt_6Cl_{12} crystals in the presence or absence of Al_2Cl_6(g) started forming a yellowish powder which was either another $PtCl_2$ form or different oxidation state of platinum chloride. This new solid, however, was not observed by visual means and/or by X-ray diffraction at temperatures below 650 K where all of the equilibrium experiments were performed.

Partial Pressure(s) of the Gaseous Complex(es). The optical cells were filled with excess quantities of Pt_6Cl_{12}. The pressure of the gaseous complex(es) over the solid Pt_6Cl_{12} was determined from the relation $P_c = (A_{max}/\epsilon_{max})RT$, where A_{max} is the measured absorbance[10] at V_{max} of the high-intensity band and ϵ_{max} is the average absorptivity of the complex(es) as given in Table I. Measurements of P_c as a function of time showed that equilibrium was reached in a period of 3–4 hr. In general, the cells were equilibrated for 5 hr before making the spectral measurements at that temperature. Eleven separate experiments with different pressures P' of Al_2Cl_6(g) were performed, yielding the values of A_{max}, P_c, and P' given in Table II.

The main source of error lies in the determination of the absorbance and is associated with the uncertainties in the background of the spectra and the values of ϵ_{max}. The overall uncertainty in the determination of P_c in this experiment is estimated to be less than ±3%.

Discussion

Thermodynamic Treatment of the Data. A comparison of experiment E-3 with experiments E-1 and E-2 (Table I) indicates that, within experimental error, the absorptivity ϵ is independent of the Al_2Cl_6 gas pressure. This implies either that one gaseous species is present or that two or more species with equal "atomic absorptivities" are present. Thus in a mixture of l gaseous complexes $(PtCl_2)_m(Al_2Cl_6)_n$ ($m = m_1, m_2, \ldots, m_l$; $n = n_1, n_2, \ldots, n_l$), the molar absorptivity ϵ_i of the ith complex is related to the molar absorptivity

$$\epsilon_i = m\epsilon$$

and the K_i equilibrium constant according to reaction 1 is

$$K_i = P_i/[P']^{n_i}$$

with P_i being the partial pressure of the ith complex.

Figure 2 shows that the vapor pressure of the gaseous complexes ($P_c = \Sigma_j{}^l m_j P_j$) is proportional to the pressure of Al_2Cl_6. This indicates[5] that each gaseous species was formed with *one* Al_2Cl_6 molecule per mole. The equilibrium constants K_i of these complexes are expected to vary with temperature according to the second law (*i.e.*, $\ln K_i$ varies linearly with $1/T$). However, Figure 3 shows that $\ln K - \ln (P_c/P')$ varies also linearly with $1/T$. Since $K = \Sigma_i m_i K_i$

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(9) K. Brodersen, G. Thiele, and H. G. Schnering, *Z. Anorg. Allg. Chem.*, **337**, 120 (1965).

(10) In the temperature of the measurements 500–650 K, the vapor pressure of Pt_6Cl_{12} is very low (less than ~10^{-10} atm) [A. Landsberg and J. L. Shaller, *J. Less-Common Metals*, **23**, 195 (1971)] and Pt_6Cl_{12}(g) or Pt_3Cl_6(g) does not contribute to the absorption of light. Preliminary experiments[7b] have also shown that in the absence of Al_2Cl_6 and at temperatures below 900 K, no gaseous platinum chlorides can be detected spectrophotometrically. Therefore the measured optical densities in the presence of Al_2Cl_6 are due only to Pt gaseous complexes.

Table II. Partial Pressures of the Platinum Gaseous Complex

Expt no. and characteristics	T, K	$A_{\max}$[a]	10^2P_c, atm	P', atm	10^2K
E-4	550	0.29	1.14	0.598	1.94
$V = 27.8$ cm^3	600	0.54	2.25	0.652	3.57
$h = 10$ cm	650	0.85	3.75	0.690	5.74
$P_0 = 1.09 \times 10^{-3}T$, atm					
E-5	500	0.565	2.07	2.26	0.92
$V = 27.3$ cm^3	550	1.140	4.47	2.48	1.84
$h = 10$ cm	600	2.05	8.55	2.70	3.14
$P_0 = 4.52 \times 10^{-3}T$, atm					
E-6	500	0.290	1.06	1.16	0.92
$V = 27.9$ cm^3	550	0.625	2.45	1.28	1.94
$h = 10$ cm	600	1.090	4.55	1.39	3.39
$P_0 = 2.33 \times 10^{-3}T$, atm					
E-7	600	1.35	5.63	1.57	3.70
$V = 27.35$ cm^3					
$h = 10$ cm					
$P_0 = 2.63 \times 10^{-3}T$, atm					
E-8	500	0.115	0.42	0.43	0.98
$V = 28.6$	550	0.225	0.88	0.47	1.91
$h = 10$ cm	600	0.425	1.77	0.51	3.56
$P_0 = 0.86 \times 10^{-3}T$, atm	650	0.720	3.17	0.54	6.25
E-9	500	0.32	1.18	1.15	1.03
$V = 29.0$ cm^3	550	0.66	2.59	1.26	2.10
$h = 10$ cm	600	1.20	5.00	1.38	3.76
$P_0 = 2.30 \times 10^{-3}T$, atm	650	1.97	8.68	1.46	6.32
E-10	500	0.38	1.39	1.49	0.94
$V = 14.3$ cm^3	550	0.79	3.10	1.64	1.92
$h = 5$ cm	600	1.46	6.09	1.79	3.52
$P_0 = 2.98 \times 10^{-3}T$, atm	650	2.56	11.28	1.90	6.30
E-11	500	0.48	1.76	1.99	0.90
$V = 14.3$ cm^3	550	1.12	4.39	2.19	2.04
$h = 5$ cm	600	2.11	8.80	2.37	3.86
$P_0 = 3.97 \times 10^{-3}T$, atm	650	3.28	14.46	2.54	6.02
E-12	550	2.14	8.40	4.72	1.81
$V = 14.2$ cm^3	600	4.08	17.02	5.16	3.41
$h = 5$ cm					
$P_0 = 8.61 \times 10^{-3}T$, atm					
E-13	550	1.44	5.65	2.79	2.06
$V = 14.35$ cm^3	600	2.56	10.68	3.04	3.64
$h = 5$ cm					
$P_0 = 5.07 \times 10^{-3}T$, atm					
E-14	500	0.97	3.55	3.90	0.92
$V = 14.7$ cm^3	550	2.26	8.87	4.29	2.91
$h = 5$ cm	600	4.12	17.19	4.66	3.82
$P_0 = 7.80 \times 10^{-3}T$, atm	650	6.60	29.09	5.00	6.35

[a] Values for a 10-cm path length.

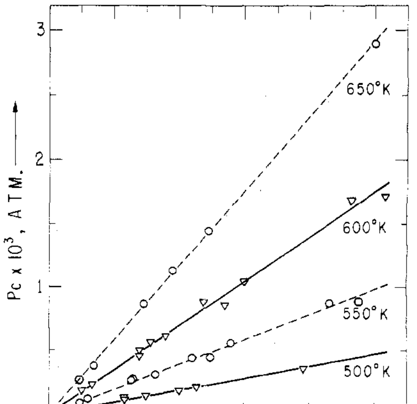

Figure 2. Plots of the pressure (P_c) of the gaseous complex(es) *vs.* the pressure (P') of gaseous aluminum chloride.

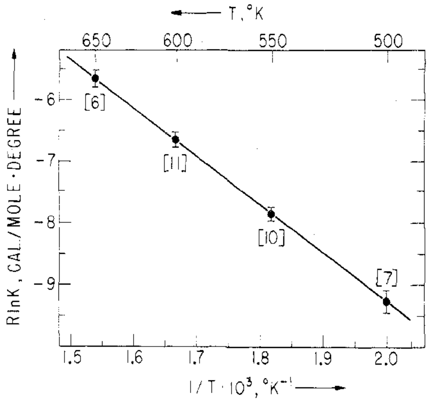

Figure 3. Plot of $R \ln K$ *vs.* $1/T$ for reaction 2 with the value of $m_j = 1$.

Table III. Thermodynamic Quantities for Solid-Gas Reactions

Reaction	ΔH^R,[a] kcal/mol	ΔS^R,[a] eu
$^1/_6\mathrm{Pt_6Cl_{12}(s)} + \mathrm{Al_2Cl_6(g)} \rightarrow \mathrm{PtAl_2Cl_6(g)}$	7.8 ± 0.13	6.4 ± 0.7
$\mathrm{PdCl_2(s)} + \mathrm{Al_2Cl_6(g)} \rightarrow \mathrm{PdAl_2Cl_6(g)}$	7.2 ± 0.16[b]	9.45 ± 0.75[b]

[a] Determined from the relation $RT \ln K = T\Delta S - \Delta H$, assuming ΔS and ΔH are constants over the entire temperature range. [b] Reference 5.

at all temperatures, then the expected linearity for $\ln K_i$ on $1/T$ and the experimentally found relation in Figure 3 suggest that there is only one predominant complex species present.

With the values of $n = 1$ equilibrium 1 becomes

$$(m_j/6)\mathrm{Pt_6Cl_{12}(s)} + \mathrm{Al_2Cl_6(g)} \rightarrow \mathrm{Pt}_{m_j}\mathrm{Al_2Cl}_{2m_j+6}\mathrm{(g)} \qquad (2)$$

$$K_j = P_c/m_jP' \quad (m_j = 1, 2, 3, \ldots)$$

A deduction of the enthalpy and entropy of this equilibrium for the different values of m_j can be derived from Figure 3. The least-squares treatment of the data shown yields

$$R \ln K = 6.36 - 7.82(1/T)$$

Thus

$$\Delta H_j^\circ = 7.8 \pm 0.13 \text{ kcal/mol}$$
$$\Delta S_j^\circ = (6.4 \pm 0.7) + R \ln m_j \text{ eu}$$

In the absence of information (*e.g.*, mass spectrometric studies, measurements of the total pressure) we have no way to establish the value of m_j. However, since the gaseous[2-6] and solid[11] complexes of the transition metal halides with $\mathrm{Al_2Cl_6}$ presently known always contain *one* $\mathrm{M^{2+}}$ cation per mole of complex, we considered it reasonable to make the assumption that in the $\mathrm{PtCl_2\text{-}Al_2Cl_6}$ system the predominant complex is also mononuclear ($m_j = 1$) and that equilibria leading to complexes with $m_j \geqslant 2$ occur only to a slight extent.

Using this assumption we have listed in Table III the thermodynamic quantities of eq 1 ($m = 1$, $n = 1$). These values are compared with the corresponding thermodynamic quantities of the $\mathrm{PdCl_2\text{-}Al_2Cl_6}$ reaction.[5] It appears that the stabilities of these complexes, containing different $n\mathrm{d}^8$ cations, are very similar. This implies[5] that the bonding and local coordination of the $n\mathrm{d}^8$ cations in the gaseous phase are similar to those in the solid.

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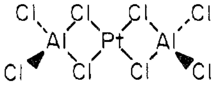
(11) (a) J. A. Ibers, *Acta Crystallogr.*, **15**, 967 (1962); (b) R. F. Belt and H. Scott, *Inorg. Chem.*, **3**, 1785 (1964); (c) J. Brynestad, S. von Winbush, H. L. Yakel, and G. P. Smith, *Inorg. Nucl. Chem. Lett.*, **6**, 889 (1970); (d) J. Brynestad, H. L. Yakel, and G. P. Smith, *Inorg. Chem.*, **9**, 686 (1970).

A comparison of the angles and distances of the $PtCl_4$ square in solid Pt_6Cl_{12} (or K_2PtCl_4)[9] with those of the $AlCl_4$ tetrahedron in gaseous Al_2Cl_6[12] shows that changes of bond lengths and bond angles by less than 3% make the Cl-Cl edge of the $AlCl_4$ tetrahedron equal with the Cl-Cl side of the $PtCl_4$ square. Thus, as in the case of $Pd(AlCl_4)_2$,[5] a possible model for the $PtAl_2Cl_6$ complex is



with an anticipated D_{2h} molecular symmetry (see also the following section). Using this model[13] and the structural parameters for the Al_2Cl_6(g) dimer, we have calculated a statistical third-law translational and rotational entropy for reaction 1 (Table III)

$$\Delta S^{\mathrm{T,R}} = 4.3 \text{ eu} \quad 600 < T < 700 \ K$$

This value and the experimentally determined overall entropy suggest small vibrational contributions of ~2 eu.

Electronic Spectra. The only known platinum(II)-chloro complex is the square-planar diamagnetic $PtCl_4^{2-}$.[14] As shown in Table IV, the near-ir and visible spectra of this complex (Pt^{2+} in aqueous HCl) are characterized by three absorption maxima. However, recent studies on the electronic absorption spectra of Pt(II) centers in liquid alkali chloride solvents[7a] have shown that the spectrum of the $PtCl_4^{2-}$ anion can be substantially modified by the influence of its next-nearest-neighbor alkali metal cations. Polarization of the coordinated chlorides by the outer shell of highly polarizing cations (*e.g.*, Li^+) leads to a drawing together of the two spin-allowed, ${}^1A_{2g} \rightarrow {}^1A_{1g}$ and ${}^1E_g \rightarrow {}^1A_{1g}$, bands. The resulting absorption spectrum is then characterized by two (instead of three) absorption maxima.

In Table IV we compare the band coordinates of the spectrum of the gaseous platinum aluminum chloride complex with those for $PtCl_4^{2-}$ in liquid LiCl at 923 K. The same two bands with the same relative intensities are clearly present in both the melt and the gaseous spectra.

There are two conspicuous differences between the two spectra (Figures 1 and 3 of ref 7a): (a) a substantial enhancement of intensity, a slight red shift, and some broadening in going from the gaseous complex spectrum to the molten solution spectrum; (b) the absence of the tail of the charge-transfer band in the gaseous complex spectrum. The first effect (a) can be reasonably attributed to the temperature differences. In fact, from the temperature dependence of the melt spectrum we can extrapolate a spectrum at 650 K for the $PtCl_4^{2-}$ in supercooled LiCl, with absorption maxima and intensities quite similar to those of the gaseous complex.

Table IV. Coordinates of Absorption Bands for $PtCl_4^{2-}$

	Temp, K	${}^3A_{2g}$ + ${}^3E_g \leftarrow {}^1A_{1g}$	${}^1A_{2g} \leftarrow {}^1A_{1g}$	${}^1E_g \leftarrow {}^1A_{1g}$
$PtCl_4^{2-}$ (in 2 *M* HCl)[a]	300	21.0[c] (15)[d]	25.4 (57)	30.3 (62)
$PtCl_4^{2-}$ (in LiCl(l))[b]	923	18	26.2 (205)	
$PtAl_2Cl_8$(g)	650	18.8 (20)	26.6 (121)	

[a] Reference 14. [b] Reference 7a. [c] Wavenumber in kK (1 kK = 1000 cm^{-1}). [d] Molar absorptivity in parentheses.

The second effect (b) can be possibly accounted for, as in the case of the $PdAl_2Cl_8$[5] gaseous complex, by the Cl→Pt charge-transfer hindrance, which is due to the strong polarization of the bridged Cl(Pt-Cl-Al) by the aluminum atom.

In view of the above considerations, we conclude that the platinum ions in the gaseous complex are in an approximate D_{4h} local geometry with energy states perturbed by the polarizing power of the aluminum ions. The band assignments of the spectrum are the same as in the spectrum of the Pt(II) in liquid LiCl and are given in Table IV.

The effect of temperature on the spectrum of the gaseous complex (Figure 1) is characteristic[14b] for centrosymmetric complexes and is attributed to vibronic interactions which destroy the center of symmetry of the $PtCl_4^{2-}$ anion and become increasingly populated with increasing temperature. The association of the electronic absorption spectrum of the gaseous complex with the spectrum of $PtCl_4^{2-}$ in a close to square-planar coordination is in agreement with that proposed in the molecular model of the previous section. A close to D_{2h} molecular symmetry for the $Pt(AlCl_4)_2$ gas is compatible with the interpretation of the absorption spectrum and explains the similarities in the magnitude of the thermodynamic quantities of the reaction in Table III.

Registry No. Pt_6Cl_{12}, 12200-23-6; Al_2Cl_6, 13845-12-0; $PtAl_2Cl_8$, 40354-82-3.

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(12) "JANAF Thermochemical Data," Dow Chemical Co., Midland, Mich.

(13) The bond angles and bond distances used were approximated, within 3%, from the corresponding distances in $PtCl_4$[9] and $AlCl_4$.[12] See also proposed model in ref 5.

(14) (a) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 4, 1682 (1965); (b) *ibid.*, 5, 1298 (1966); (c) references cited in ref 14a and 14b.