

Figure 8. Electronic spectrum of **1a** in nitrobenzene at room temperature in the near-IR and visible regions (—) along with their Gaussian analyses (---).

anodic wave is observed if the potential is scanned in such a manner as to cycle only the first reductive response (Figure 7), and also the anodic current (i_{pa}) is found to be decreased. However, the separation between the two cathodic peaks is 330 mV, which reflects the reduction of two different metal centers in the same molecular entity. The other possibility of stepwise reduction of the same metal center is thus nullified. This separation is a characteristic feature⁶ of many dinuclear transition metal complexes. Thus, the proposition of the dimeric structure for **1e** is supported by electrochemical investigations.

Electronic Structures and Spectral Properties. Compounds **1a–e** produce intense purple colors in solutions, which exhibit highly rich optical spectra (Figure 8). The spectra of compounds **1a**, **1b**, and **1e** are found to be very similar while those for **1c** and **1d** are similar to each other, and the overall spectral features for all these complexes are comparable. The typical feature of the electronic spectrum of any one of these complexes is the occurrence of four weak bands in the red and near-infrared regions followed by intense absorption³¹ in the visible region (Table 4; supplementary material).

Since all four low-energy d–d transitions are observed for **1a–e**, we assume a flattened tetrahedral Au(II) unit in these complexes.

(31) Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168.

As both mononuclear and dinuclear complexes exhibit similar spectral features, it is considered that the major contribution to the optical spectrum is originating from the gold(II) center of Au(pma)X in a flattened tetrahedral environment. We have chosen a coordinate system³¹ in which the tetrahedral t_2 orbital set is (d_{xz} , d_{yz} , $d_{x^2-y^2}$). In this system a tetragonal distortion toward the square-planar configuration would be expected to yield a $^2B_2(d_{x^2-y^2})$ ground state for Au(II). The splitting of the E level (d_{xz} , d_{yz}) is probably due to some additional distortion to C_2 . The relative energies of the gold d and selected ligand σ and π orbitals are based on the electronic spectroscopic results.³¹ The thiolato sulfur and gold bonding is considered to involve one π - and two σ -type interactions.²⁶ The optical spectral band positions and a reasonable but tentative transition assignment picture are presented in Table 4 (supplementary material).

Concluding Remarks

Crucial evidence regarding the nature and structure of the compounds is obtained from the analysis of their EPR spectra. The very small A_{Au} values observed in the EPR spectra are strongly indicative^{24–26} of the low metal character of the highest occupied molecular orbital. No hyperfine structure originating from the interaction with the nitrogen nuclei of the ligand pma is observed in the EPR spectra of complexes **1a–e**. Two pairs of ionizations are observed in the XPS spectrum of **1c**, consistent with the presence of both a Au(II) center and a Au(III) center. All attempts to prepare single crystals of any one of these complexes have failed, so all investigations were confined to powders and solutions of the compounds.

Acknowledgment. We thank the RSIC, IIT, Madras, India, for spectroscopic facilities. Thanks are due to Professor A. Chakravorty of IACS, Calcutta, India for providing electrochemical facilities. A.P.K. thanks Dr. B. Ghosh and Dr. S. Pal for help with the electrochemical studies.

Registry No. **1a**, 139944-30-2; **1b**, 139944-31-3; **1c**, 139944-32-4; **1d**, 139944-33-5; **1e**, 139944-34-6; A, 19257-96-6; NaAuCl₄, 15189-51-2; KAuBr₄, 14323-32-1; pyridine-2-carboxaldehyde, 1121-60-4; *o*-aminobenzenethiol, 137-07-5.

Supplementary Material Available: Table 4, giving electronic spectral band positions of the complexes, textual details of the molecular orbital calculations, and Table 5, giving input parameters for SCF-X α -SW calculations for Au(NH₃)₂(SCH₃)Cl (8 pages). Ordering information is given on any current masthead page.

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Vaporization and Vapor Complexation in the Gold(III) Chloride–Aluminum(III) Chloride System

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The vapors over solid gold(III) chloride and the vapor-phase equilibria of the gold(III) chloride–aluminum(III) chloride binary system have been investigated spectrophotometrically. The thermodynamic functions of the sublimation $2\text{AuCl}_3(\text{s}) = \text{Au}_2\text{Cl}_6(\text{g})$ were determined: $\Delta H_S^\circ = 114.2 \pm 1.8 \text{ kJ mol}^{-1}$ and $\Delta S_S^\circ = 160.5 \pm 3.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ($480 < T < 580 \text{ K}$). One predominant vapor complex found in the binary system formed according to the reaction $\text{AuCl}_3(\text{s}) + \frac{1}{2}\text{Al}_2\text{Cl}_6(\text{g}) = \text{AuAlCl}_6(\text{g})$ with $\Delta H_R^\circ = 59.9 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta S_R^\circ = 91.5 \pm 1.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ($470 < T < 550 \text{ K}$). At 470 K and 1 atm $\text{Al}_2\text{Cl}_6(\text{g})$ pressure the volatility enhancement of AuCl_3 is ~ 300 . The electronic absorption spectra of the $\text{Au}_2\text{Cl}_6(\text{g})$ and $\text{AuAlCl}_6(\text{g})$ molecules were interpreted in terms of a distorted square planar geometry of Au(III). "Bridged" and "terminal" ligand-to-metal charge-transfer bands were identified in the spectra.

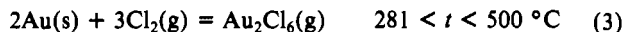
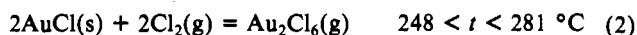
Introduction

The different solid and gaseous species formed during chlorination of gold have been the subject of investigation of some early publications.^{1–4} It has been pointed out¹ that two solids AuCl_3

and AuCl are formed at different temperatures and chlorine pressures. At temperatures below 500 °C three distinct equilibria have been reported to occur^{2,3} at a chlorine pressure of ~ 1 atm:

(1) Fischer, W.; Biltz, W. *Z. Anorg. Allg. Chem.* **1928**, *176*, 81.
(2) Biltz, W.; Fischer, W.; Juza, R. *Z. Anorg. Allg. Chem.* **1928**, *176*, 121.

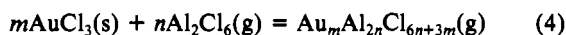
(3) (a) Hager, J. P.; Hill, R. B. *Metall. Trans.* **1970**, *1*, 2723. (b) James, S. E.; Hager, J. P. *Metall. Trans.* **1978**, *9B*, 501.
(4) Landsberg, A.; Hoatson, C. L. *J. Less-Common Met.* **1970**, *22*, 327.



At higher temperatures Au_xCl_y ($x = 1-2$) vapor molecules have been shown to exist in equilibrium with Au^0 and $\text{Cl}_2(\text{g})$. The low-temperature $\text{Au}_2\text{Cl}_6(\text{g})$ species has been definitely identified by transpiration experiments,²⁻⁴ and the thermodynamic functions of reaction 1 have been reported.

The possibility of enhancing the volatility of AuCl_3 through vapor complexation was first examined by a transpiration-mass spectrometric technique.³ Two well-known⁵ complexing agents, $\text{Al}_2\text{Cl}_6(\text{g})$ and $\text{Fe}_2\text{Cl}_6(\text{g})$, were tested. It was pointed out that considerable enhancement of the transport rates of gold occurred in the presence of $\text{Fe}_2\text{Cl}_6(\text{g})$ but no similar results were obtained with $\text{Al}_2\text{Cl}_6(\text{g})$. The vapor "complex" molecule responsible for the enhancement was $\text{AuFeCl}_6(\text{g})$, which is similar in composition to other vapor complex metal halide molecules formed by a variety of elements. Vapor complexation and the resulting volatility enhancement have been investigated thoroughly in recent years, and comprehensive reviews are available.⁵⁻⁷

The present study reports the existence of a red vapor complex of gold(III) chloride with aluminum chloride (Au-Al-Cl). The gas-solid equilibrium



has been investigated by measuring spectrophotometrically the partial pressures of the vapor complex, and both the stoichiometry and the thermodynamics of the reaction have been established. Furthermore spectrophotometric measurements have been used to reevaluate the thermodynamic functions of gold(III) chloride vaporization according to eq 1. The electronic absorption spectra and molar absorptivities of the vapor complex and of $\text{Au}_2\text{Cl}_6(\text{g})$ have been measured and discussed in terms of possible structure in the vapor phase. The data would be of importance in connection with the development of commercial processes for the extraction of gold from ores and concentrates through chloride vaporization.^{3,8} After submission of the present paper for publication, a new work appeared in the literature⁹ where the thermodynamics of vaporization of the Au-Cl_2 system (reactions 1-3) have been determined spectrophotometrically and the electronic absorption spectra of $\text{Au}_2\text{Cl}_6(\text{g})$ have been measured. The part of our data reported here on $\text{Au}_2\text{Cl}_6(\text{g})$ is in agreement with this recent work.

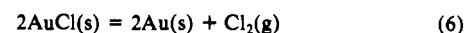
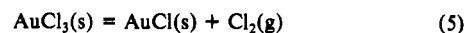
Experimental Section

All chemicals used in this work are very hygroscopic, and thus all experimental preparations were carried out in sealed Pyrex tubes and/or in an inert atmosphere of a glovebox, having water vapor content less than 1 ppm.

Anhydrous aluminum chloride was purchased from Cerac Pure/Inc. (Milwaukee, WI) and was purified by repeated sublimations in Pyrex tubes under vacuum.

The gold(III) chloride was prepared by reacting Au metal with chlorine gas (Matheson, Oevel, Belgium), at 250 °C in sealed evacuated fused silica tubes. The gold(III) chloride produced was further purified by slow sublimation in Pyrex tubes under a chlorine pressure of ~2 atm. The sublimation was performed in long furnaces with a temperature gradient between 250 and 280 °C. Pure AuCl_3 was obtained by this procedure in the form of long (~1 cm) purple-red needle crystals.

At temperatures above 160 °C the red solid AuCl_3 was stable only in the presence of chlorine gas. The stability of AuCl_3 versus temperature was a function of the chlorine pressure. Under $P_{\text{Cl}_2} = 1$ atm, the red gold(III) chloride crystals dissociated to a yellow solid at 280 °C. The above behavior is due to the reduction of gold(III) to gold(I) and metallic gold according to the reactions



Rectangular fused silica cells of 1- or 0.5-cm path length (Hellma GmbH & Co., Müllheim, Baden, Germany) were used for the UV-vis measurements. The cells were degassed and filled with preweighed amounts of AuCl_3 and AlCl_3 in the glovebox. Gaseous chlorine was added in the cells at a vacuum-gas line system and trapped with liquid nitrogen. The cells were then sealed with a butane flame under vacuum.

The absorption measurements were performed with a Hitachi 220S spectrophotometer. A high-temperature optical furnace was constructed and inserted in the sample compartment of the spectrophotometer. Two independent heaters were used for heating and adjusting the temperature gradient along the optical cell. A detailed description of the furnace is given elsewhere.¹⁰ During the experiments the portion of the cell interrupting the optical path was at temperature 2-3 °C higher than the rest of the cell. This kept the solids away from the optical path and permitted absorption measurement of vapors in equilibrium with volatile solids.

The methods for investigating spectrophotometrically equilibria of reactions of the type (1) and (4) have been described previously.^{11,12} The apparent molar absorptivity, ϵ_x , and the apparent partial pressure P_x of the absorbing vapors of Au_2Cl_6 or the Au-Al-Cl complex were determined by different sets of experiments using Beer's law

$$\epsilon_x = \frac{AV}{Nl} \quad P_x = \frac{ART}{\epsilon_x l} \quad (7)$$

where A is the optical density, V the cell volume, N the moles of the species containing Au(III) in the gas phase, and l the path length.

For both Au_2Cl_6 and the Au-Al-Cl complex the molar absorptivity experiments were carried out in cells containing no solid $\text{AuCl}_3(\text{s})$ over a certain temperature range. Due to the extremely small quantities (typically less than 1 mg) of $\text{AuCl}_3(\text{s})$ required for these measurements the following method was used for filling up the cells. A small chunk of $\text{AuCl}_3(\text{s})$ and preweighed amounts of $\text{AlCl}_3(\text{s})$ were placed into the cell. After addition of the appropriate chlorine pressure the cell was sealed on the side filling tube, approximately 10 cm away from the main rectangular body. The AuCl_3 chunk was placed in the side tube and the cell was equilibrated at a given temperature, so as to obtain the desired gold(III) chloride pressure in the vapor phase. The cell was then removed from the furnace and the rectangular part was quenched in cold water in order to solidify the gases away from the excess AuCl_3 solid. Finally, the remaining AuCl_3 chunk was removed from the cell by sealing off the side tube. The amount of AuCl_3 thus transported in the optical cell was determined after the end of the spectrophotometric measurements by atomic absorption of Au^{3+} in aqueous solutions. Following the procedures of ref 9, we have also measured the molar absorptivity of the vapor complex and of $\text{Au}_2\text{Cl}_6(\text{g})$ by reacting small amounts of Au metal (0.1-1 mg weighed on a Cahn-2000 electrobalance) with chlorine in sealed optical cells with or without aluminum chloride present.

The partial pressures P' of the Al_2Cl_6 dimer were calculated from the amounts of the salt placed in the cell and the relation $P' = P_0 - P_D$. Here P_0 is the "hypothetical" undissociated Al_2Cl_6 ideal gas pressure calculated from the amounts of aluminum chloride added in the cell and P_D is the correction for dissociation to AlCl_3 monomer.¹¹

The chlorine gas of ~1 atm, added in all spectrophotometric cells, has an absorption band at ~330 nm which partially overlaps with the UV bands of the Au_2Cl_6 and Au-Al-Cl vapor molecules. In separate experiments we have measured the temperature/pressure dependence of the molar absorptivity of $\text{Cl}_2(\text{g})$, and then we have used the data to correct our absorption spectra for the chlorine contribution.

Results and Discussion

The absorption spectra of vapors obtained from cells containing Au_2Cl_6 or $\text{Au}_2\text{Cl}_6\text{-Al}_2\text{Cl}_6$ show a visible band with a maximum between 450 and 480 nm as well as UV bands below 300 nm. Due to the overlapping bands of the pure Au_2Cl_6 and the $\text{Au}_2\text{Cl}_6\text{-Al}_2\text{Cl}_6$ mixture, careful measurements are needed in order to determine and distinguish the molar absorptivities and absorbances (i.e. partial pressures) of the two different systems.

Molar Absorptivity of Au_2Cl_6 . Six experiments were performed for the determination of the molar absorptivity of the dimeric gold(III) chloride in the temperature range 515-600 K. The optical cells were filled by vapor transporting Au_2Cl_6 or by adding

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 (12) Kucera, G. H.; Papatheodorou, G. N. *J. Phys. Chem.* 1979, 83, 3213.

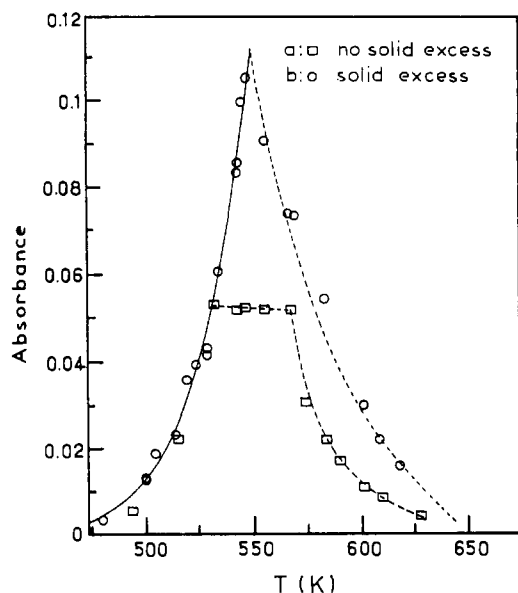


Figure 1. Absorbance of $\text{Au}_2\text{Cl}_6(\text{g})$ at 460 nm vs temperature from cells having excess and no excess solid AuCl_3 .

known amounts of Au metal as described above, and the cell was placed in the furnace of the spectrophotometer. The maximum absorbance of the visible band at ~ 460 nm was then measured at different temperatures. Typical results obtained from experiment E-3 are shown in Figure 1 (curve a). Up to ~ 250 °C the absorbance increases due to the vaporization of $\text{Au}_2\text{Cl}_6(\text{s})$ added in the cell. At ~ 250 °C all Au_2Cl_6 is in the vapor phase, and the absorbance remains constant up to ~ 300 °C where the decomposition of the vapor starts according to eqs 2 and 3. When excess solid is added in the cell, the decomposition starts before obtaining a constant value for the absorbance (line b in Figure 1). It is thus obvious that the molar absorptivity of Au_2Cl_6 , ϵ_{460} , can be measured only in the limited temperature range where the absorbance remains constant and all the salt is in the vapor phase.

The characteristics of the six experiments used for determining ϵ_{460} are shown in Table A (supplementary material), and the overall spectrum at 550 K is in Figure 2. The data indicate a small systematic variation of ϵ_{460} with temperature which can be represented within $\pm 2.1\%$ by the equation

$$\epsilon_{460} = 2239 - 0.92T \quad (\text{L mol}^{-1} \text{cm}^{-1})$$

in the temperature range $515 < T < 600$ K.

The band positions and relative intensities of the spectra shown in Figure 2 are in good agreement with the recently published data of Rustad and Gregory.⁹ There is however a difference of $\sim 10\%$ between the values of molar absorptivity in Figure 2 and those reported in ref 9. This difference is attributed to errors in determining the small amounts of AuCl_3 or Au^0 added in the cell and the small absorbances measured in the visible region of the spectra.

Apparent Molar Absorptivity of the Au–Al–Cl Vapor Complex.

The number of Au atoms participating in the vapor complex(es) (i.e. the value of m in eq 4) is not known, and only apparent values of ϵ/mol of Au(III) in the gas phase can be calculated according to eq 7. Six different spectrophotometric cells were used to determine the apparent molar absorptivity of the vapor complex, and their characteristics are shown in Table B (supplementary material). On the basis of these experiments, the molar absorptivity of the visible band at 466 nm, ϵ_{466} (see Figure 2), was determined. Due to dissociation of the vapor complex to $\text{Al}_2\text{Cl}_6(\text{g})$ and $\text{Au}_2\text{Cl}_6(\text{g})$, the measured absorbance in the 466-nm region has in principle contributions from both the Au–Al–Cl complex and the $\text{Au}_2\text{Cl}_6(\text{g})$ dimer. However, as will be discussed later, at temperatures below 585 K and Al_2Cl_6 pressures between 0.5 and 1.5 atm the dissociation of the complex (Table I) is rather small and the contribution of $\text{Au}_2\text{Cl}_6(\text{g})$ to the overall absorbance is less than 1%. Thus, it was not necessary to correct the vapor

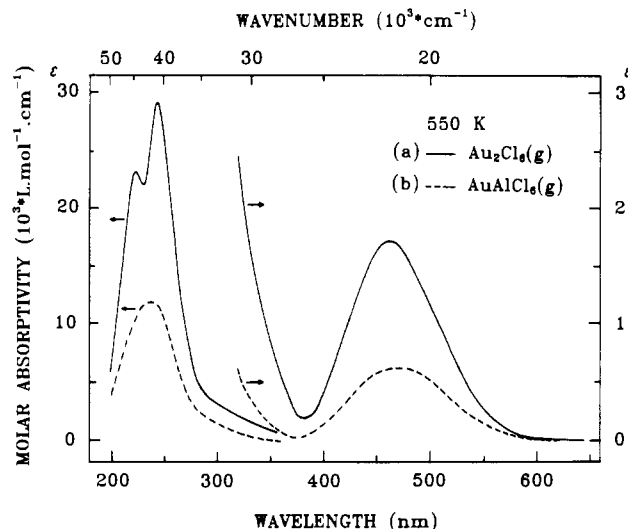


Figure 2. Molar absorptivities of $\text{Au}_2\text{Cl}_6(\text{g})$ and $\text{AuAlCl}_6(\text{g})$.

complex spectra for the presence of $\text{Au}_2\text{Cl}_6(\text{g})$. A small variation of ϵ_{466} with temperature was observed, and from the measurements in the six cells it was found that ϵ_{466} could be represented within $\pm 2.6\%$ by the relation

$$\epsilon_{466} = 846 - 0.4T \quad (\text{L mol}^{-1} \text{cm}^{-1}) \quad (8)$$

with $460 < T < 590$ K.

The overall experimental uncertainty of $\sim 2.5\%$ arises mainly from the errors in determining the small amounts of AuCl_3 or Au^0 added in the cell.

The data (Table B) indicate that within experimental error the apparent molar absorptivity is independent of Al_2Cl_6 pressure. As in previous cases of other vapor complexes,^{11,12} this implies that either one gaseous species is present or that two or more species with equal "atomic" (in Au(III)) absorptivities are formed.

Due to the high intensity of the UV band at 235 nm, direct measurement of the molar absorptivity was not possible. By measuring however the absorbances of the visible and UV bands at ~ 150 °C where the intensities of both bands were within the measuring limit of our spectrophotometer, we found that $A_{235}/A_{466} \approx 18$, which was used to determine the absorptivity scale in the UV region (Figure 2).

Thermodynamics of the $\text{AuCl}_3(\text{s})$ Vaporization. The partial pressure $P_{\text{Au}_2\text{Cl}_6}$ of $\text{Au}_2\text{Cl}_6(\text{g})$ over excess of $\text{AuCl}_3(\text{s})$ in optical cells containing $\text{Cl}_2(\text{g})$ was determined by measuring the absorbance at 460 nm (A_{460}) and using eq 7. Four such experiments were performed, and their characteristics are given in Table C (supplementary material). The temperature dependence of the absorbance A_{460} is shown for experiment E-13 in Figure 1b. The occurrence of the maximum absorbance (i.e. the maximum $\text{Au}_2\text{Cl}_6(\text{g})$ concentration) at a certain temperature is associated with the reduction of Au(III) to Au(I) and Au^0 , which takes place beyond that temperature according to reactions 2 and 3. Measurements of A_{460} as a function of time at constant temperature showed that equilibrium was reached in a period of 3–4 h. In general before measurement of A_{460} , the cells were equilibrated for ~ 5 h at a given temperature.

The equilibrium constant of reaction 1 is $K_1 = P_{\text{Au}_2\text{Cl}_6}$ and the deduction of the enthalpy and entropy according to the "second law" is presented in Figure 3 (lower part). A least-squares treatment of the data obtained from all four cells yielded the thermodynamic functions of vaporization listed in Table I. Our data are compared in the table with the data obtained by the earlier investigations. Within experimental error our enthalpy and entropy values agree with the previously reported values in ref 2–4 and 9.

Stoichiometry and Thermodynamics of the Vapor Complex(es).

The apparent partial pressure of the vapor complex $P_{\text{Au–Al–Cl}}$ was determined in three experiments with cells having an excess of $\text{AuCl}_3(\text{s})$ at different aluminum chloride pressures. "In situ"

Table I. Thermodynamic Functions of Gold(III) Chloride Dimer and Vapor Complexes

| | reacn | ΔH° , kJ/mol | ΔS° , J/(mol K) | T range, K | ref |
|----------------|---|------------------------------|---------------------------------|------------|------------------------|
| R ₁ | 2AuCl ₃ (s) = Au ₂ Cl ₆ (g) | 114.3 ± 1.1 | 173.2 ± 2.2 | 432–515 | 9 |
| | | 113.2 | 168.0 | 470–520 | 3 |
| | | 110.9 | 167.1 | 340–515 | 4 |
| | | 112 ± 4.2 | 168 ± 8 | | 1 |
| | | 114.2 ± 1.8 | 160.5 ± 3.3 | 475–575 | this work ^a |
| R ₂ | AuCl ₃ (s) + 1/2Al ₂ Cl ₆ (g) = AuAlCl ₆ (g) | 59.9 ± 0.8 | 91.5 ± 1.6 | 470–550 | this work ^a |
| R ₃ | 1/2Au ₂ Cl ₆ (g) + 1/2Al ₂ Cl ₆ (g) = AuAlCl ₆ (g) | 2.8 ± 1.25 | 11.2 ± 2.4 | 470–550 | this work |

^aDetermined from the relation $RT \ln K = T\Delta S^\circ - \Delta H^\circ$ and assuming ΔS° and ΔH° constant over the temperature range studied.

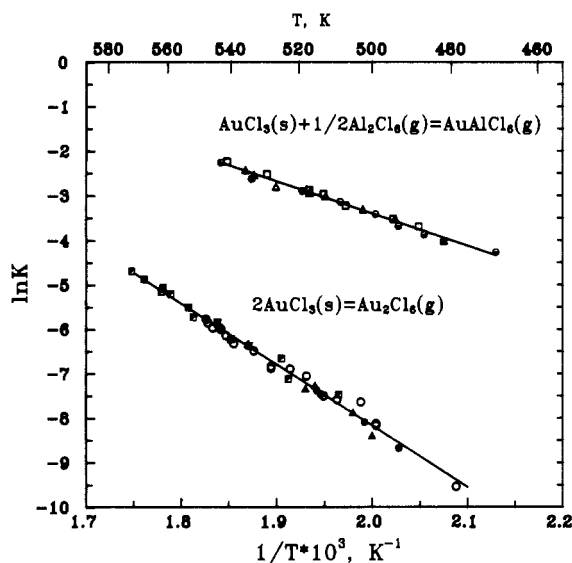


Figure 3. Plots of $\ln K$ vs $1/T$ for reactions R₁ (lower part) and R₂ (upper part) in Table I. Symbols indicate measurements from the different experiments as follows: ○, E-13; □, E-14; ●, E-15; ▲, E-16; △, E-17, $P_0 = 9.87 \times 10^{-4}T$; ⊙, E-18, $P_0 = 5.39 \times 10^{-4}T$; □, E-19, $P_0 = 21.53 \times 10^{-4}T$.

high-temperature Raman experiments using a Kr⁺ ion laser¹³ showed that at temperatures between 470 and 550 K the AuCl₃ solid phase remained unchanged during 4–5 h equilibration under Al₂Cl₆/Cl₂ gas atmosphere. No changes in the Raman spectra due to solid solution or compound formation between AuCl₃ and AlCl₃ were observed. The characteristics of the partial pressure experiments are shown in Table D (supplementary material). The absorbance at 466 nm was measured after equilibrating the cell for ~4 h at a given temperature. Apart from Cl₂(g), the dimer Au₂Cl₆(g) also contributes to the total absorbance at this wavelength. Thus, after the correction due to Cl₂(g) was made, the Au₂Cl₆(g) contribution was taken into account by calculating at each temperature the expected absorbance due to Au₂Cl₆(g). The vapor complex apparent vapor pressure was then calculated from the relation

$$P_{\text{Au-Al-Cl}} = \frac{A_{466}RT}{\epsilon_{\text{Au-Al-Cl}}l} - \frac{\epsilon_{\text{Au}_2\text{Cl}_6}K_1}{\epsilon_{\text{Au-Al-Cl}}}$$

and the values of $P_{\text{Au-Al-Cl}}$ were used for the determination of the equilibrium constant K_4 for reaction 4

$$K_4 = P_{\text{Au-Al-Cl}}/P_{\text{Al}_2\text{Cl}_6}^n$$

where $P_{\text{Al}_2\text{Cl}_6}$ is the equilibrium partial pressure of Al₂Cl₆ in the cell ($P_{\text{Al}_2\text{Cl}_6} = P' - nP_{\text{Au-Al-Cl}}$).

For two cells i and j at the same temperature having different Al₂Cl₆ pressures, we can write

$$\frac{P_{\text{Au-Al-Cl}}^{(i)}}{[P^{(i)} - nP_{\text{Al}_2\text{Cl}_6}^{(i)}]^n} = \frac{P_{\text{Au-Al-Cl}}^{(j)}}{[P^{(j)} - nP_{\text{Al}_2\text{Cl}_6}^{(j)}]^n}$$

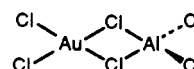
(13) Nalbandian, L.; Papatheodorou, G. N. Raman spectra and molecular vibrations of Au₂Cl₆(g) and AuAlCl₆(g). *Vib. Spectrosc.*, in press.

This last equation was used to evaluate the stoichiometric coefficient n at different temperatures by combining the set of experimental values listed in Table D. The average value of n was found to be

$$\bar{n} = 0.53 \pm 0.07$$

without any systematic variation with temperature or Al₂Cl₆(g) pressure. Thus, the predominant vapor complex(es) has (have) the formula (AuCl₃)_mAlCl₃, with a value of m which cannot be calculated from our experiments. It is noteworthy, however, that the thus far investigated gaseous complexes of Al₂Cl₆ with transition metals^{5,14} contain always one transition metal atom per molecule while the number of Al atoms varies from 1 to 4 (e.g. FeAlCl₆,^{15,16} ZrAl₂Cl₁₀,¹⁴ SmAl₃Cl₁₂,⁵ ErAl₄Cl₁₅⁵). Thus, it is reasonable to assume that the AlCl₃ is bound to one AuCl₃ (i.e. $m = 1$). With the values of $m = 1$ and $n = 0.5$, the equilibrium constant of reaction 4 can be calculated from our data at different temperatures. The enthalpy and entropy of reaction according to the "second law" can be deduced by least-squares fitting the data in Figure 3 (upper part). The results are given in Table I.

By combination of the data of reactions R₁ and R₂ listed in Table I, the thermodynamics of the all gas reaction R₃ can be calculated. For the latter reaction both the enthalpy and entropy values are close to zero, indicating that the coordination number⁶ and geometry⁵ of Au(III) and Al(III) do not change during the reaction. Thus, the square planar coordination of Au(III) in Au₂Cl₆(g)¹³ and the tetrahedral coordination of Al(III) in Al₂Cl₆(g)¹⁷ are preserved in AuAlCl₆(g), and the most probable configuration is



having a tetrahedral AlCl₄ bound by an edge with a square planar AuCl₄. This structure has been further confirmed by vibrational spectroscopy and normal coordinate analysis.¹³

Finally, the thermodynamic data in Table I permit the calculation of the volatility enhancement ρ of AuCl₃(s) in the presence of Al₂Cl₆(g)

$$\rho = \left[\frac{P_{\text{Au-Al-Cl}}}{P_{\text{Au}_2\text{Cl}_6}} \right] = \frac{K_4}{K_1} P_{\text{Al}_2\text{Cl}_6}^{1/2}$$

and the enhancement per unit pressure of Al₂Cl₆(g) is

$$\ln \rho = \frac{6530}{T} - 8.3$$

which gives that at temperatures between 470 K (i.e. the boiling point of AlCl₃) and 570 K the volatility enhancement varies between 300 and 20.

Electronic Spectra. Gold(III) with a [Xe]d⁸ configuration and chlorides as ligands has a tendency, like the other second- and third-row d⁸ transition metal ions, to form square planar complexes [AuCl₄] in acidic aqueous solutions,¹⁸ in a variety of organometallic

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Table II. Assignment of the Spin-Allowed Transition in "Square Planar" Gold(III) Chloride Compounds

| assgnt $^1A_{1g} \leftarrow$ | AuCl ₄ ^{-a} (soln 1 M HClO ₄) | | [AuCl ₄][(n-C ₄ H ₉) ₄ N] ^b (in solns (T = 77–300 K)) | | Au ₂ Cl ₆ (g) (T = 550 K) | | AuAlCl ₆ (g) (T = 550 K) | |
|---------------------------------|--|-------------------------------|---|---------------------------------|--|----------------------------------|--|-------------------------------|
| | 10 ⁻³ ν, cm ⁻¹ | ε _{max} ^c | 10 ⁻³ ν, cm ⁻¹ ^d | ε _{max} ^{c,d} | 10 ⁻³ ν, cm ⁻¹ | 1/2ε _{max} ^c | 10 ⁻³ ν, cm ⁻¹ | ε _{max} ^c |
| $^1A_{2g}$ | | | 21.8 | 16 | | | | |
| 1E_g | 25.8 | 450 | 26.4 | 300 ^e | 21.7 ^f | 870 | 21.5 | 630 |
| $^1B_{1g}$ | | | | | | | | |
| $^1A_{2u} + ^1E_u(\pi)$ | 32.0 (M ← L) | 5300 | 30.5 (M ← L) | 6500 | (~32) | | (~32) | |
| $^1E_u(\sigma)$ | 44.5 (M ← L) | 27500 | 44.2 | 42500 | 41.1 ^f (M ← L _b) 45.8 ^f (M ← L _t) | 14600 11590 | 42.5 (M ← L _b) (M ← L _t) | 12000 |

^a Reference 16. ^b Reference 17. ^c In L/(mol cm). ^d The values of ν are averages for solutions of the compound in CH₃CN in 2-MeTHF-PN and in 2MeTHF-MeOH at 77 and 300 K. ^e The value of ε increased with increasing temperature. ^f Also observed in ref 9.

compounds¹⁹ and in the solid Au₂Cl₆.²⁰ The gold site symmetry is $\sim D_{4h}$, and the ligand field ground state is a singlet $^1A_{1g}$. The energy of two d ← d transitions ($^1A_{2g}$ and 1E_g) as well as two ligand to metal M ← L charge-transfer transitions have been measured in different media and are given in Table II.

The absorption spectra of Au₂Cl₆(g) and AuAlCl₆(g) (Figure 2 and Table II) possess only a relatively strong and broad band in the visible region having an energy close to the weak $^1A_{2g} \leftarrow ^1A_{1g}$ transition but a molar absorptivity (per Au atom) of the same order of magnitude as for the $^1E_g \leftarrow ^1A_{1g}$ transition of AuCl₄⁻. In both molecules each Au(III) is bound to two bridging and to two terminal chlorine atoms, the ligand field is asymmetric, and the gold "site" symmetry is C_{2v} . Presumably the overall ligand field is weaker relative to the "free" AuCl₄⁻ and the separation of the d states smaller. Thus, a reasonable assignment of the visible band of the vapor molecules is (mainly) to the $^1E_g \leftarrow ^1A_{1g}$ transition. The other two $^1A_{2g}$ and $^1B_{1g}$ bands have probably weaker intensities and, as in the case of the vapor complexes of Pd¹¹ and Pt,²¹ are overlapping with the 1E_g band. The C_{2v} distortions of the square planar structure and the absence of a center of symmetry partially breaks the Au(III) d ← d Laporte forbidden transitions and thus enhances the intensity of the visible band of the vapor molecules relative to that of the centrosymmetric D_{4h} (AuCl₄⁻) species. This probably accounts for the observed increase of the molar absorptivity of the 1E_g band on going from solid AuCl₄⁻ to the vapor spectra (Table II). The decreasing ε₄₆₆ values with increasing temperature measured for the AuAlCl₆ molecule (eq 8) are similar to those found for other vapor complexes not possessing a center of symmetry (e.g. CoAl₂X₆⁵).

In the region between 350 and 300 nm (28 000–33 000 cm⁻¹) the absorption spectra of the vapor molecules show (after subtracting the Cl₂ contribution at 320 nm) a broad weak band which is assigned to the $^1A_{2u} + ^1E_u \leftarrow ^1A_{1g}$ (M ← L) transition of the

complex. The molar absorptivity of this band cannot be measured due to its shoulder character and to uncertainties arising from the subtraction of the Cl₂ band.

The UV part of the dimer Au₂Cl₆(g) spectrum is characterized by two absorption maxima at 243 and 218 nm. The presence of two bands can be possibly associated with the different electron-giving abilities of the bridged and terminal chloride ligands. Mason and Gray¹⁹ have pointed out that the ligand-to-metal charge-transfer transitions from the "bridged" ligands have lower energy than those from the terminal ligands. In view of this consideration we have attributed the 243-nm band to the charge-transfer transition originating from the "bridged" (M ← L_b) chlorine atoms and the 218-nm band to the corresponding transition from the "terminal" (M ← L_t) chloride atoms of the Au₂Cl₆ dimer.

In contrast to the resemblance of the dimer and vapor complex spectra in the visible region, the UV spectra show definite differences (Figure 2). The two charge-transfer M ← L_b and M ← L_t bands of the dimer have been replaced in the complex by one band of intermediate energy. This effect could be possibly attributed to the stronger polarization induced to the chlorine atoms by the aluminum in the Au–Cl–Al bridge. Environments pulling away the electronic density of the ligands are expected to give charge-transfer transitions at higher energies. The M ← L_b charge transfer is hindered by aluminum in the complex, the UV band moves at higher energies relative to the corresponding band of the dimer, and presumably the M ← L_b and M ← L_t energy differences become smaller and the overlapping bands appear as a common band in the spectra of the complex.

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Registry No. AuCl₃, 13453-07-1; AlCl₃, 7446-70-0; AuAlCl₆, 73334-09-5.

Supplementary Material Available: Tables A and B, giving maximum absorptivities of Au₂Cl₆(g) and AuAlCl₆(g), respectively, and Tables C and D, giving maximum absorbances and equilibrium partial pressures of Au₂Cl₆(g) and AuAlCl₆(g), respectively (4 pages). Ordering information is given on any current masthead page.

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