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

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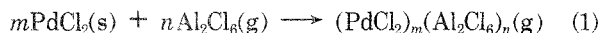
The reaction of solid α -PdCl₂ with gaseous Al₂Cl₆ to form a deep red gaseous complex has been studied spectrophotometrically. Thermodynamic considerations suggested the stoichiometry for the reaction PdCl₂(s) + Al₂Cl₆(g) → PdAl₂Cl₈(g): $\Delta H_R = 7.2$ kcal/mol, $\Delta S_R = 9.45$ eu. The visible and uv electronic absorption spectrum of the PdAl₂Cl₈ complex was interpreted in terms of a square-planar PdCl₄ sharing edges with two tetrachloroaluminates. The data for the above reaction were compared with the data available in the literature for the corresponding reaction of NiCl₂. The electronic absorption spectrum of NiAl₂Cl₈(g) is reported and interpreted as a NiCl₆ octahedron sharing faces with two tetrachloroaluminates.

I. Introduction

In recent years the existence of vapor complexes of metal chlorides, with highly volatile chlorides of aluminum and iron(III), has attracted the interest of different investigators. These gaseous complexes are widely distributed throughout the periodic table, including metal monochlorides to metal pentachlorides.

The first complexes to be investigated were the NaAlCl₄¹ and NaFeCl₄.²⁻⁴ Later the alkaline earth chlorides (Mg and Ca),^{5,6} divalent 3d metal (Mn, Fe, Co, Ni, and Zn)⁵ chlorides, and the chlorides of Cd⁵ and Pb⁵ with either Al₂Cl₆ or Fe₂Cl₆ have been studied by vapor pressure equilibrium methods. Representative chlorides from the lanthanides (NdCl₃) and from the actinides (UCl₄ and UCl₅) have been investigated spectroscopically by Gruen and coworkers.^{7,8} Zvarova and Zvara⁹ have shown the formation and separation, by means of gas chromatography, of gaseous complexes of the lanthanide (Ce, Pr, Pm, Gd, Tb, Dy, Tm, Yb, and Lu) chlorides with Al₂Cl₆. The general formula for the gaseous complexes with aluminum chlorides is (MCl_k)_m·(Al₂Cl₆)_n. In all cases studied, the value of *m* is 1, while the value of *n* varies between 0.5 and 2.

In the present report the existence of a dark red vapor complex of palladium chloride with aluminum chloride is established. Furthermore, the equilibrium



has been studied by measuring spectrophotometrically the absorbance of the gaseous complexes over α -PdCl₂(s). The thermodynamic quantities for the above equilibrium and the spectroscopic properties of the Pd-Al-Cl gaseous complexes are discussed in terms of the stoichiometry and structure of the gaseous molecules.

II. Experimental and Results

Chemicals and Equipment. The anhydrous aluminum chloride was prepared from high-purity aluminum metal and gaseous HCl.¹⁰

The γ -palladium(II) chloride was purchased from Matthey Bishop, Inc.¹¹ The salt was dried at 150° for several hours under vacuum of less than 1 μ . The anhydrous ma-

terials were handled under vacuum in tight containers or in a drybox with water vapor level less than 2 ppm.

The spectrophotometric measurements were performed on a Cary Model 14H spectrophotometer equipped with a high-temperature cell compartment¹² (1-cm maximum path length). The spectra were digitally recorded on paper tape, and the calculation and plotting of molar absorptivities were carried out by a digital computer. The quartz optical cells were the uv type rectangular 1-cm cells purchased from Pyrocell.

Method. Each optical cell was connected with a 10 cm long, 3-mm i.d., side quartz tube. A calibrated 10-cm³ buret and water were then used for measuring the volume of the cell. The side tube was calibrated in cm³ of the total volume (cell plus tube). These procedures permitted the determination of the cell volume with an error of less than 0.5%. The height of each cell did not exceed 9 cm and the total volume varied between 8 and 24 cm³.

In a typical experiment amounts of AlCl₃ and PdCl₂, preweighed on a microbalance, were transferred into the dry and degassed cell. The cell was evacuated and sealed on a premarked point of the side tube. The amounts of AlCl₃ were adjusted so that all the AlCl₃ in the cell was in the vapor phase at temperatures between 500 and 600°K. The cell was then heated for 15–30 min at 700°K and finally transferred into the furnace of the spectrophotometer. The vertical and horizontal temperature gradients of the high-temperature compartment of the spectrophotometer were less than 2°. In most cases the spectra were re-

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TABLE I: Determination of Molar Absorptivity

E-97 ^a			E-101 ^b		E-107 ^c		E-109 ^d	
<i>T</i> , °K	ν_{\max} , μ^e	ϵ_{\max}	<i>T</i> , °K	ϵ_{\max}	<i>T</i> , °K	ϵ_{\max}	<i>T</i> , °K	ϵ_{\max}
500	485.5	174	600	217	575	206	550	197
550	488	189	650	227	600	212	600	205
600	490.5	194	700	236	650	218	650	212
650	493	204	750	244	700	227	700	218
700	496	211			750	235	750	226
750	499	216			800	241		
800	502	223						

^a $P_0 = 4.65 \times 10^{-3}$ atm; $n_{\text{Pd}} = 1.024 \times 10^{-5}$ mol; $V = 9.95$ cm³.
^b $P_0 = 4.326 \times 10^{-3}$ atm; $n_{\text{Pd}} = 7.038 \times 10^{-5}$ mol; $V = 15.25$ cm³.
^c $P_0 = 4.468 \times 10^{-3}$ atm; $n_{\text{Pd}} = 5.906 \times 10^{-5}$ mol; $V = 8.95$ cm³.
^d $P_0 = 2.407 \times 10^{-3}$ atm; $n_{\text{Pd}} = 5.532 \times 10^{-5}$ mol; $V = 15.95$ cm³.
^e The values of ν_{\max} (the frequency at which the maximum absorptivity occurs) were found to be the same for all four experiments.

corded in the range between 600 and 800°K and in intervals of 50°K. The pressure P' of $\text{Al}_2\text{Cl}_6(\text{g})$, without correction for consumption due to reaction 1, was calculated from the difference $P' = P_0 - P_D$. Here P_0 is the "ideal gas" pressure of Al_2Cl_6 , and P_D is the correction⁷ due to the dissociation¹³ of the dimer Al_2Cl_6 .

Determination of Molar Absorptivity. The cells were filled with small amounts of PdCl_2 to ensure that all of the PdCl_2 was in the gaseous complex state in the range of temperatures studied. The "apparent" molar absorptivity $\epsilon(\lambda)$ for the gaseous complex(es) of wavelength λ was then determined from the relation

$$\epsilon = AV/n_{\text{Pd}}h \quad (2)$$

where V is the volume of the optical cell, h is the 1-cm optical path length, A is the absorbance at wavelength λ , and n_{Pd} the total number of Pd moles placed into the cell.

Four different spectrophotometric experiments were carried out for this determination of $\epsilon(\lambda)$. The characteristics of each of these experiments are shown in Table I. The spectra were recorded from 4 to 30 kK. No bands were found in the 4–12 kK range. A strong absorption band close to 20 kK and a very weak band close to 15 kK were observed (Figure 1). From the listed values in Table I, it appears that ϵ_{\max} varies almost linearly with temperature. A plot of ϵ_{\max} vs. T for all four experiments gives a set of straight lines with slopes very close to $0.15 \text{ M}^{-1} \text{ cm}^{-1} \text{ deg}^{-1}$. However, the absolute magnitude of ϵ_{\max} is subject to a nonsystematic variation from one experiment to another. Averaging all four experiments, we can express ϵ_{\max} as a function of T

$$\epsilon_{\max} \approx 117.5 + 0.15T \text{ M}^{-1} \text{ cm}^{-1} \quad 500^\circ\text{K} \leq T \leq 800^\circ\text{K} \quad (3)$$

The constant term (117.5) is calculated with a 5% variation, which we attribute to errors associated with the weighing of the small amounts of PdCl_2 . On the other hand, the second term of the equation (i.e., the relative change of absorptivity with temperature) is well established with an error of less than 1%. A comparison of the last experiment (E-109 in Table I) with the other three experiments indicates that, within experimental error, the absorptivity ϵ is independent of the Al_2Cl_6 pressure. This implies that either only one gaseous species is present or that two or more species with equal "atomic absorptivi-

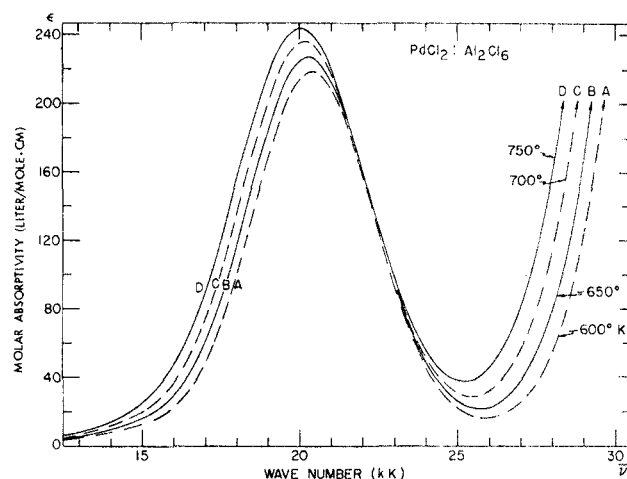


Figure 1. Absorption spectra of the palladium chloride-aluminum chloride vapor complex as a function of temperature.

ties" are present. Thus in a mixture of l gaseous complexes $(\text{PdCl}_2)_m(\text{Al}_2\text{Cl}_6)_n$ ($m = m_1, m_2, \dots, m_l$ and $n = n_1, n_2, \dots, n_l$) the molar absorptivities $\epsilon_1, \epsilon_2, \dots, \epsilon_l$ of the absorbing complexes are related to the apparent molar absorptivity ϵ

$$\epsilon_i = m_i \epsilon, \quad i = 1, 2, \dots, l \quad (4)$$

The uv spectrum of the gaseous complexes was recorded in a somewhat different way. Due to the high absorptivity of the uv bands, the number of moles of PdCl_2 to be complexed in the gaseous phase (in order to give absorbances in the range permitted by the instrument) is very small and cannot be weighed accurately. However, we were able to determine the absorptivity in the uv region by preparing a very dilute, but unknown, concentration of the gas and by measuring the relative intensities of the uv and visible bands. For wavenumbers below 50 kK, there is only one uv band present at ~ 41 kK. The absorbance of this band was measured with the 0 to 2 slidewire while for the same cell the absorbance of the visible band (at ~ 20 kK) was measured with the 0.0 to 0.1 slidewire. It was found that at 600°K $\epsilon_{\max}(41 \text{ kK})/\epsilon_{\max}(20 \text{ kK}) \approx 80$. From this relation and the value of $\epsilon_{\max}(20 \text{ kK})$ of 210 (at $T = 600^\circ\text{K}$) we were able to approximate the absorptivity scale in the uv region.

Solid PdCl_2 in Equilibrium with Al_2Cl_6 Gas. In order to determine the nature of the solid phase(s) in equilibrium with gaseous Al_2Cl_6 and to exclude the possibility of a $\text{PdCl}_2\text{-Al}_2\text{Cl}_6$ solid compound above 500°K, we performed the following experiments.

Excess quantities of $\gamma\text{-PdCl}_2$ ¹⁴ and small quantities of Al_2Cl_6 were sealed in an evacuated 10-cm long quartz tube whose volume was about 20 cm³. The quartz tube was then placed in a vertical windowed furnace and the temperature of the furnace was raised slowly to 650°K. The sample was kept at that temperature for 3 hr to ensure equilibrium. The upper end of the tube was then quenched in water, and all the aluminum chloride, with some gaseous complex, was solidified. After reaching room temperature, the tube was opened and the X-ray diffraction pattern of the solid in the lower end of the tube was

(13) JANAF Thermochemical Data, The Dow Chemical Co., Midland, Mich.

(14) J. R. Soulen and W. H. Chappell, *J. Phys. Chem.*, **69**, 3669 (1965).

taken. The pattern showed that α -PdCl₂^{15,16} was the only solid phase present. No additional lines, indicating either the β ¹⁷ and γ forms or possible solid compound formation with Al₂Cl₆, were present. We have repeated the same type of experiment at two different equilibration temperatures, 550 and 750°K. In all cases the only solid found (after breaking the tube) was the α -PdCl₂.

Finally, in a fourth experiment, the quartz tube containing the α -PdCl₂ and Al₂Cl₆ was placed in a vertical windowed furnace in such a way that the excess α -PdCl₂ was maintained in the bottom of the tube at 550°K, while the other end of the sample tube was in a cooler zone at about 520°K. The tube was maintained in this way for several days. Daily visual observations indicated the formation of small red single crystals in the middle of the sample tube. These crystals were identified by X-ray diffraction as α -PdCl₂. This last experiment eliminated any possibility of solid complex compound formation and shows that the decomposition of the gaseous complex yields the α -PdCl₂ form.

Partial Pressures of the Gaseous Complex(es). The optical cells were filled with excess quantities of PdCl₂. The apparent partial pressure of the gaseous complex(es) over the solid α -PdCl₂ was determined from the relation

$$P_c = (A_{\max}/\epsilon_{\max})RT \quad (5)$$

where A_{\max} is the measured absorbance at ν_{\max} and ϵ_{\max} is the apparent absorptivity of the complex(es) as given in eq 3. Measurements of P_c as a function of time and at constant temperature showed that the equilibrium was reached very fast. An equilibration time of less than 10 min was sufficient before making spectral measurements. Seven separate experiments with different pressures (P') of Al₂Cl₆ were performed and the values of A_{\max} , P_c , and P' are given in Table II.

III. Discussion

Thermodynamic Treatment of the Data. According to reaction 1, the equilibrium constant of the i th gaseous complex ($n = n_i$, $m = m_i$) with partial pressure P_i is

$$K_i = P_i / (P' - \sum_{j=1}^l N_j P_j)^{n_i} \quad (6)$$

In the absence of information (e.g., mass spectrometric studies) regarding the principal gaseous complexes present, a thermodynamic treatment of the data for all possible reactions leading to different complex species is futile. However, the treatment can be significantly simplified from the experimental fact that the measured apparent pressure P_c is proportional to P' .

$$P_c = (1/b)P' \quad (7)$$

The validity of this proportionality is illustrated in Figure 2. Relation 7 implies¹⁸ that (a) each gaseous complex contains one Al₂Al₆ molecule per mole and that (b) there is only one predominant complex species present. The general formula of this complex is (PdCl₂)_mAl₂Cl₆ with $m = 1, 2, 3, \dots$

The, thus far, investigated gaseous¹⁻⁹ or solid¹⁹ complexes of Al₂Cl₆ with transition metal chlorides contain always one transition metal atom per mole of complex, while the number of Al atoms varies from 1 to 4. Thus, we consider it reasonable to make the assumption that in the

TABLE II: Partial Pressures of the Palladium Gaseous Complex

Experiment no. and characteristics	T, °K	A _{max}	P _c , atm	P', atm	10K
E-102	602.5	1.895	0.450	1.980	2.95
V = 12.2 cm ³	648	2.500	0.619	2.107	4.16
P ₀ = 3.31 × 10 ⁻³ T	702	3.280	0.848	2.137	6.59
E-103	549	0.5025	0.113	0.761	1.75
V = 21.5 cm ³	601	0.7425	0.176	0.826	2.71
P ₀ = 1.39 × 10 ⁻³ T	650	1.000	0.248	0.878	3.94
	699.5	1.280	0.330	0.914	5.66
	747.5	1.600	0.427	0.928	8.54
	801.0	1.815	0.501	0.905	12.45
E-104	601	3.02	0.717	3.110	2.99
V = 9.5 cm ³	624.2	3.60	0.873	3.220	3.72
P ₀ = 5.21 × 10 ⁻³ T	651.5	4.225	1.049	3.340	4.57
	699.5	5.125	1.311	3.530	5.90
E-105 ^a	651	4.545	1.128	3.587	4.59
V = 8.5 cm ³	676.7	5.165	1.310	3.700	5.48
P ₀ = 5.59 × 10 ⁻³ T	701.5	5.885	1.521	3.801	6.67
E-106	601.5	0.455	0.108	0.447	3.19
V = 24.55 cm ³	651.5	0.590	0.147	0.472	4.50
P ₀ = 0.756 × 10 ⁻³ T	700.0	0.735	0.190	0.485	6.40
	749.5	0.875	0.234	0.482	9.45
	800.5	0.980	0.271	0.455	14.69
E-111	550.5	0.385	0.087	0.588	1.74
V = 24.3 cm ³	600.5	0.575	0.136	0.635	2.73
P ₀ = 1.073 × 10 ⁻³ T	650.0	0.795	0.197	0.674	4.14
	699.5	1.055	0.272	0.701	6.35
	749	1.24	0.331	0.702	8.96
	799	1.397	0.386	0.676	13.38
E-112	600	2.040	0.484	2.196	2.83
V = 11.6 cm ³	649.5	2.830	0.702	2.351	4.25
P ₀ = 3.688 × 10 ⁻³ T	699.5	3.760	0.962	2.482	6.32
	750.5	4.775	1.278	2.570	9.89
	800.0	5.70	1.570	2.590	15.3

^a A 0.5-cm path length cell was used but the absorbance is referred to 1-cm path length.

PdCl₂(s)-Al₂Cl₆(g) system the predominant gaseous complex is a mononuclear ($m = 1$) palladium species and that the equilibria leading to complexes with $m \geq 2$ occur only to a slight extent. This view is also supported by the recent²⁰ isolation of a diamagnetic palladium aluminate compound with an 1:1 PdCl₂:Al₂Cl₆ stoichiometry.

(15) H. Schäfer, U. Wiese, K. Rinke, and K. Brendet, *Angew. Chem.*, **79**, 244 (1966).

(16) A. F. Wells, *Z. Kristallogr. Mineralogr. Petrogr., Abt. A*, **100**, 189 (1938).

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

(18) From eq 4-7 it follows that

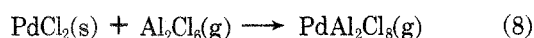
$$P_c = \sum_{j=1}^l m_j P_j, P' = (P_i/K_i)^{n_i} + \sum_{j=1}^l n_j P_j = b \sum_{j=1}^l m_j P_j, i = 1, 2, \dots, l$$

This last equation, based on the experimentally determined relation 8, is an identity; thus $n = n_1 = n_2 = \dots = 1$ and $P_j = 0$ ($j \neq i$). For the only nonvanishing partial pressure (e.g., P_i) we have $(1/K_i) + 1 = b$ which determine the equilibrium constant of reaction 1.

(19) (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).

(20) G. N. Papatheodorou, to be submitted for publication.

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



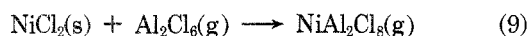
and the equilibrium constant is

$$K = P_c / (P' - P_c)$$

The values of K are listed in the last column of Table II. A deduction of the enthalpy and entropy of this equilibrium, according to the second law, is shown in Figure 3. Thirty-two experimentally determined values of $R \ln K$ are plotted vs. $1/T$. The least-squares treatment of the data shown yields a value of $\Delta H_R = 7.2 \pm 0.16$ kcal/mol for the enthalpy of reaction 8 over the range of temperature studied. For the same temperature range a value for the entropy of reaction $\Delta S_R = 9.45 \pm 0.75$ is obtained.

A comparison between the angles and distances of the PdCl_4 square in solid PdCl_2 ¹⁶ and of the AlCl_4 in gaseous¹³ Al_2Cl_6 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 square-planar PdCl_4 . In view of this consideration we propose in Figure 4 a structural model for the PdAl_2Cl_8 gaseous complex. The angle ω was introduced in order to determine the position of Al atom (and the AlCl_4 units) with respect to the PdCl_4 plane. Using this model ($\omega = 0$) and the structural parameters of the Al_2Cl_6 dimers¹³ we calculated a statistical²¹ third law translational and rotational entropy for reaction 8: $\Delta S_{\text{TR}} = 3.8 \pm 0.3$, $500^\circ\text{K} < T < 800^\circ\text{K}$. This value, and the experimentally determined entropy, suggest a small vibrational entropy contribution of ~ 5 eu.

We shall now compare the thermodynamic functions of reaction 8 with the available in the literature^{5b} corresponding functions for the $\text{NiCl}_2\text{-Al}_2\text{Cl}_6$ reaction.



$$\Delta H = 7.5 \text{ kcal/mol} \quad \Delta S = 9 \text{ eu}$$

It appears that the stabilities of the PdAl_2Cl_8 and NiAl_2Cl_8 gaseous complexes are very similar. In his work, Dewing^{5b} concluded that the similarities of the stabilities of the MAl_2Cl_8 ($\text{M} = \text{Ca}, \text{Mn}, \text{Co}, \text{and Ni}$) complex can be best interpreted as implying that the bonding of the divalent ions in the complex is very similar to that in the solid. All MCl_2 solids have similar structures with the divalent metal in octahedral coordination while the PdCl_2 solid is a completely different structure with Pd^{2+} in square-planar coordination. These differences, however, do not alter the thermodynamic functions of reactions 8 and 9, which implies that the characteristic structure and coordination in the solid is also present in the gaseous complex. Thus we should expect that local geometry of Ni^{2+} in NiAl_2Cl_8 is very close to O_h while the geometry of Pd^{2+} in PdAl_2Cl_8 is very close to D_{3h} .

Electronic Spectra. In Figure 5 the absorption spectrum of the PdAl_2Cl_8 gaseous complex is shown in the region from 4 to 5 kK. The visible and near-ir spectrum is characterized by one high-intensity band at wave number close to 20 kK. A low-intensity band can be also observed in the 14-15-kK region. The uv spectrum shows a very strong absorption band at 40.2 kK.

The only known all-chloride Pd(II) complex is PdCl_4^{2-} which is a typical example of a well-known square-planar

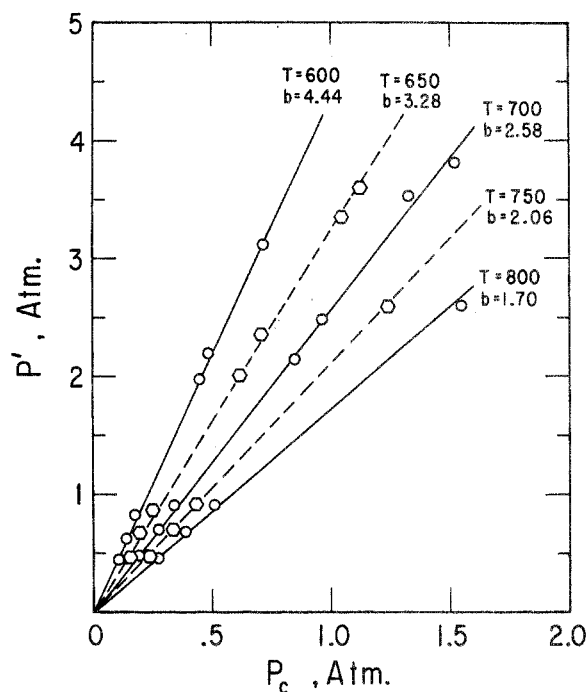


Figure 2. Plots of P' vs. P_c at different temperatures. The slopes b were determined from a least-squares treatment of the data.

diamagnetic complex. In Table III we give the absorption data of PdCl_4^{2-} in the solid state and in solution. The assignments of the $d \rightarrow d$ transitions are based on the data of Day, *et al.*,²² on K_2PdCl_4 and on the data and ligand field calculations of Martin and coworkers²³ on solid K_2PtCl_4 . The assignments of the uv band are based on MO calculations.²⁴ These high-intensity absorptions are attributed to ligand-to-metal charge transfer transitions ($L \rightarrow M$).

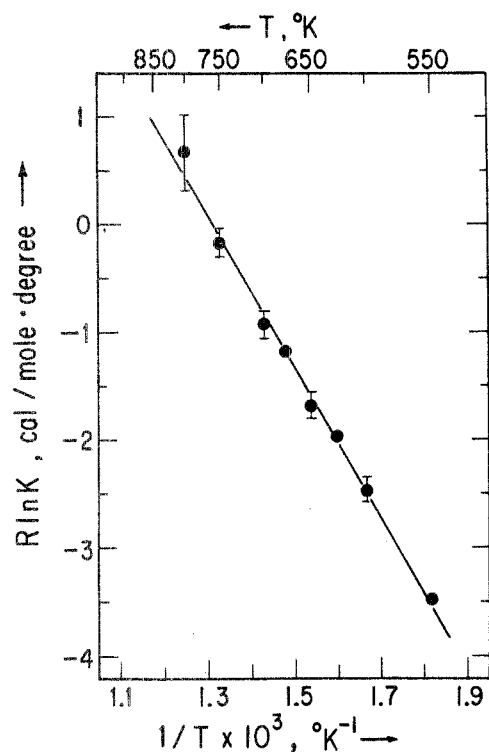
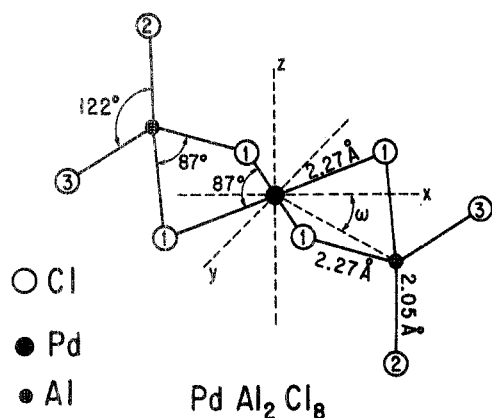
A comparison of the visible spectrum of the solid K_2PdCl_4 and of PdCl_4^{2-} in solution indicates that the two first spin-allowed bands of the K_2PdCl_4 are not separable in the solution, while the third spin allowed band of the solid seems to disappear under the first charge transfer band in the solution. In the last column of Table III we have listed for comparison the absorption data for the gaseous PdAl_2Cl_8 complex. It appears that in the visible region the same band(s) is(are) present for both the gaseous and solution spectrum. Their main differences are a substantial enhancement of intensity, a slight red shift, and some broadening in going from the aqueous HCl solution to the gas. All these differences are reasonably attributed to temperature differences. As Figure 1 shows, the broadening of the band and the red shift increases with increasing temperature. In fact, an extrapolation of the spectrum in Figure 1 to room temperature, where the PdCl_4^{2-} solution spectrum was taken, gives $\epsilon_{\text{max}} (300^\circ\text{K}) \approx 160$ and $\nu_{\text{max}} (300^\circ\text{K}) \approx 21$ kK.

(21) A calculation of the moment of inertia of the gaseous complex, as a function of ω , shows that the entropy contribution of the moment of inertia increases by only 0.7 eu for changes of ω between 0 and 45° .

(22) P. Day, A. F. Orchard, A. J. Thompson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

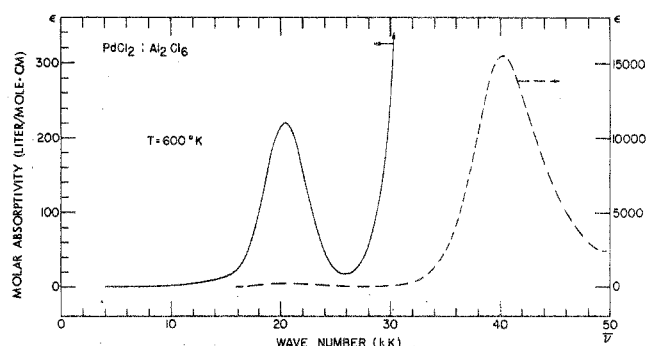
(23) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4**, 1682 (1965); as amended, **5**, 1298 (1966).

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Figure 3. Plot of $R \ln K$ vs. $1/T$ for reaction 8.Figure 4. Molecular model of the PdAl_2Cl_8 gas.

Although the effect of temperature has not been measured for PdCl_4^{2-} in solution, it has been measured in the case of K_2PtCl_4 crystals²³ between 15 and 300°K, and in the case of PtCl_4^{2-} centers in liquid alkali chloride solvents between 600 and 1100°K.²⁵ Here, also, an increase in temperature greatly enhances the intensity, shifts the peak to the red, and broadens the band. These effects are plausibly accounted for by vibronic interactions in which asymmetric vibrational states, which destroy the center of symmetry of MCl_4^{2-} anion, become increasingly populated with increasing temperature.²³ Therefore, it is more likely that the broad band, occupying the visible spectrum of PdAl_2Cl_8 , covers at least two spin-allowed $d \rightarrow d$ transitions of the palladium atom in a ligand field with approximately D_{4h} local symmetry.

In contrast with the agreement observed in the visible region, a comparison of the uv spectra of PdCl_4^{2-} and PdAl_2Cl_8 indicates definite differences. The three charge

Figure 5. Absorption spectrum of $\text{Pd}(\text{AlCl}_4)_2(\text{g})$ from 4 to 50 kK.TABLE III: Assignments of the K_2PdCl_4 Solid and PdCl_4^{2-} Solution Spectra

Assignment $^1A_{1g} \rightarrow$	$\text{K}_2\text{PdCl}_4^a$ solid, 300°K		$\text{PdCl}_4^{2-}{}^b$ soln, 2 M HCl		PdAl_2Cl_8 gas, 300°K	
	ν , kK	ϵ_{max}	ν , kK	ϵ_{max}	ν , kK	ϵ_{max}
$^3E_g, ^3B_{1g}^a$	17 (18) ^c	7 (19)	(16)		(~15)	
$^1A_{2g}^a$	(20)	(67)	21	152	20	220
1E_g or $^1B_{1g}^a$	22.6 23.0	128 80				
$^1B_{1g}$ or $^1E_g^a$	(29.5)	(67)				
d			(30.2) ^d	(540)		
$^1A_{2u} +$ $^1E_u(\pi)^{b,c}$			35.8	10,400		
					40.2	15,800
$^1E_u(\sigma)^{b,c}$			44.9	28,300		

^a From ref 22. ^b From ref 24. ^c Shoulder. ^d Orbital forbidden charge transfer band.^{24b}

transfer bands in aqueous HCl have been replaced in PdAl_2Cl_8 by one band of intermediate energy. Since the charge transfer transitions originate essentially from ligand-based molecular orbital levels, their energies should be very sensitive to the electronic environment of the chloride ligand. Environments pulling away the electronic density of the ligand are expected to give rise to charge transfer transitions at higher energy.²⁶ In the case of the PdAl_2Cl_8 molecule the bridged chloride is strongly polarized by the aluminum atom, and the Cl electronic density is substantially different from that of Cl in PdCl_4^{2-} (aqueous HCl). Thus the $L \rightarrow M$ charge transfer is hindered by the aluminum, and the energies of the charge transfer bands occur at higher energies. From these considerations, we suggest that the only uv band in the PdAl_2Cl_8 spectrum is the $^1A_{1g} \rightarrow ^1A_{2u} + ^1E_u(\pi)$ charge transfer transition. A further support for this assignment is the similarity of the relative intensities of the uv and visible bands for the PdAl_2Cl_8 , with the relative intensities of the $^1A_{1g} \rightarrow ^1A_{2u} + ^1E_u(\pi)$ and $^1A_{1g} \rightarrow ^1A_{2g}$ bands in the PdCl_4^{2-} (in 2 M HCl) molecule.

The association of the electronic absorption spectrum of the gaseous complex, with the spectrum of PdCl_4^{2-} in a

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(26) The substitution of Br in PdBr_4^{2-} by the less polarizable Cl shifts the charge transfer band toward the blue. The energy of the $^1A_{1g} \rightarrow ^1A_{2u} + ^1E_u(\pi)$ band, for example, shifts to higher energies by ~6 kK as we go from Br to Cl.²⁴

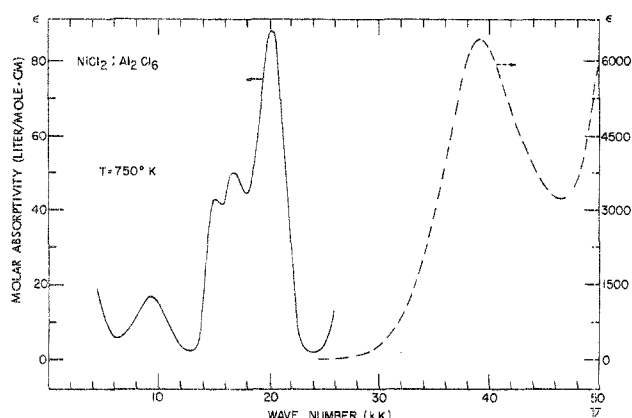


Figure 6. Absorption spectrum of $\text{Ni}(\text{AlCl}_4)_2(\text{g})$ from 4 to 50 kK.

close to square-planar coordination, is compatible with the proposed molecular model. A D_{2h} or C_{2h} (with ω small) molecular symmetry for the PdAl_2Cl_8 gas is anticipated.

Finally, before we close the present section we should like to compare once more the spectrum of the palladium aluminate gaseous complex with that of nickel aluminate. In Figure 6 we give the absorption spectrum of the NiAl_2Cl_8 gaseous complex.²⁷ From the works of Smith and coworkers²⁸ we have identified this spectrum as either a spectrum of Ni^{2+} partitioned between an octahe-

dral and a tetrahedral coordination, the octahedral coordination being the predominant species, or as a Ni^{2+} in a distorted octahedral coordination. Both assignments suggest that the proposed molecular model for PdAl_2Cl_8 (Figure 4) is also valid for the nickel chloroaluminate with the angles ω close to 45° . A D_{3h} molecular symmetry for the NiAl_2Cl_8 molecule is anticipated. With such a symmetry no drastic changes in the coordination of Ni occur as the gaseous complex is formed from the solid NiCl_2 ($\sim O_h$ local symmetry) according to reaction 9. Thus the spectroscopic data for the PdAl_2Cl_8 and NiAl_2Cl_8 gases show that the AlCl_4 tetrahedra of Al_2Cl_6 gas can be bound to the transition metal chloride by either an edge (*i.e.*, $\omega = 0^\circ$ for Pd) or a plane (*i.e.*, $\omega = 45^\circ$ for Ni). This is in agreement with the thermodynamic data and explains the similarities in the magnitudes of the thermodynamic quantities of reactions 8 and 9.

Acknowledgment. The author is deeply indebted to Dr. G. Pedro Smith for allowing him to use his laboratory facilities at the O. R. N. L. The kind help and advice of Drs. J. Brynestad, C. R. Boston, and G. P. Smith during the course of this investigation is also acknowledged.

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Dimeric Structure of a Copper Phthalocyanine Polymorph

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Publication costs assisted by Xerox Corporation

The preparation and characterization of a polymorph of copper phthalocyanine (CuPc) having a dimeric structure is described. The infrared, X-ray, electronic, and esr spectra of the new polymorph, designated x-CuPc, are compared to those of the well-known α - and β -CuPc polymorphs. Distinct differences among the three polymorphs are observed in their infrared and X-ray spectra and these differences are useful in the general characterization of the polymorphs. The electronic spectrum of x-CuPc can be interpreted in terms of a dimer structure which is analogous to that reported for the metal-free phthalocyanine dimer, x- H_2Pc . Additional support for the dimer model is obtained from a qualitative comparison of the esr envelope line shapes for the α -, β -, and x-CuPc polymorphs.

I. Introduction

The phthalocyanines have been reported to exist in at least three different polymorphic phases and the polymorphic form can greatly influence both the pigment¹ and electrical properties^{2,3} of these materials. The β polymorphs are most easily studied by X-ray methods, since single crystals can be prepared by sublimation at approxi-

mately 550° . Robertson⁴ found that β -copper phthalocyanine (β -CuPc) is a monoclinic crystal having the following

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