[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Chloro Complexes of Palladium(II) in Solution

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Spectrophotometric measurements in palladium(II) perchlorate solutions containing varying amounts of chloride ion demonstrate the formation of at least six chloro complexes of palladium, namely, $PdCl^+$, $PdCl_2$, $PdCl_3^-$, $PdCl_4^=$ and two higher complexes, probably $PdCl_5^=$ and $PdCl_6^=$. The latter two are much more strongly dissociated than the first four. Palladium(II) ion is also complexed by nitrate ion, with formation of highly dissociated species.

The assumption is generally made that palladium(II) forms a single complex ion with chloride, namely, $PdCl_4^=$. The dissociation constant of this complex has been reported[1] as $[Pd^{++}][Cl^-]^4/[PdCl_4^=] = 6 \times 10^{-14}$ at 25°, a value obtained by e.m.f. measurements. Actually no less than six chloro complexes are formed by divalent palladium in aqueous solution, as can be readily demonstrated spectrophotometrically. The present study deals with the evidence for the existence of these complexes; equilibrium constants have not been determined.

Experimental

Palladium(II) Perchlorate Solution.—A weighed amount of palladium metal (Eastern Smelting and Refining Corporation) was dissolved in fuming nitric acid and the solution was evaporated to a small volume. Perchloric acid (60%) was added in excess and the solution was evaporated to fumes to expel nitric acid. Dilution to volume was made with water; the final acidity was 1 *M* in perchloric acid. The palladium content was verified by dimethylglyoxime precipitation. The solution was tested for palladium(IV) by adding excess potassium iodide and shaking with carbon tetrachloride. No coloration of iodine was visible in the extract.

In some experiments a palladium solution was used which was obtained by adding nitric acid to palladous dimethylglyoximate and evaporating to dryness several times, followed by fuming with perchloric acid. The same results were obtained with this solution as with that prepared directly from palladium metal, thus demonstrating the adequate purity of the metal for the present purpose.

Method.—Absorption measurements were made with a Beckman Model B spectrophotometer having 1-cm. cells.

The general absorption characteristics of the palladium(II)-chloride system were obtained in a series of experiments in which the hydrochloric acid concentration was varied from zero to 1.0 *M* at constant palladium concentration (Fig. 1). All solutions were 0.1 *M* in perchloric acid.

In a second set of experiments, a 0.0044 *M* palladium perchlorate solution in 1.0 *M* perchloric acid (final concentrations) was treated with increasing increments of hydrochloric acid so that the molar ratio Cl/Pd varied from zero to 4. The absorbance of each mixture was measured at various wave lengths. The results for 410 and 430 mμ are shown in Fig. 2. In a third series, the absorbance measurements at suitable wave lengths were extended to solutions in which Cl/Pd ratios ranged up to 50 (Fig. 3). Similar results, not shown, were obtained with 0.0018 and 0.0092 *M* palladium solutions. Moreover, identical results were obtained when sodium chloride was used in place of hydrochloric acid.

In a final series of experiments, absorption curves were obtained for relatively high Cl/Pd ratios at a constant ionic strength of 1.00 *M* (Fig. 4). The purpose of these measurements was to find whether or not an isosbestic point exists under these conditions.

Discussion

Perchlorate ion does not appreciably complex palladium(II) ion. Solutions of palladium(II) in 0.1 and 1.0 *M* perchloric acid have virtually identical absorption curves, with maximum absorption at 380 mμ (molar extinction coefficient = 84).

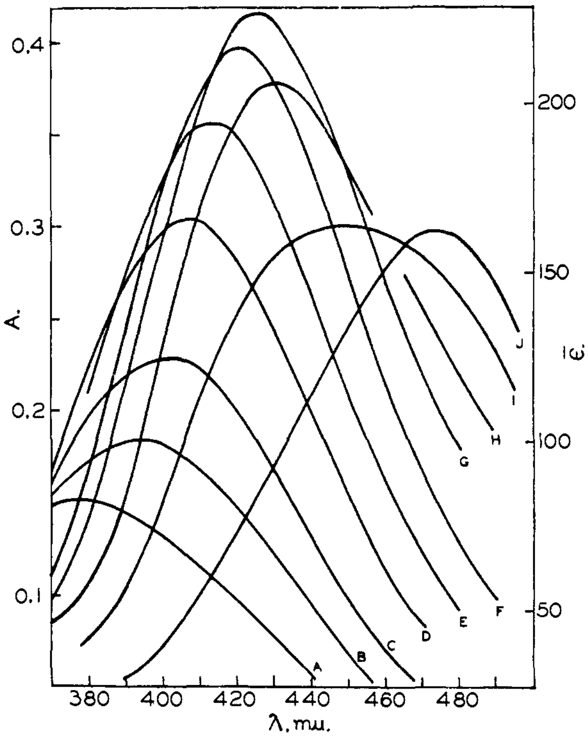

Fig. 1.—Absorbance (log I_0/I) and average molar extinction coefficient of Pd(II)-chloride system *vs.* wave length as a function of chloride concentration: total Pd concentration 0.00184 *M*. Chloride concentrations (*M*): A, 0; B, 0.0005; C, 0.0010; D, 0.00184; E, 0.0030; F, 0.0050; G, 0.010; H, 0.025; I, 0.10; J, 1.0; all solutions 0.10 *M* in perchloric acid.

From Fig. 1 it is evident that a number of species other than Pd^{++} must exist in palladium-chloride solutions. As the chloride concentration is increased while the palladium concentration is maintained constant, the wave length of maximum absorption rises from 380 mμ to about 470 mμ in 1 *M* hydrochloric acid. The average molar extinction coefficient, $\bar{\epsilon}$, increases to a maximum of about 250 at Cl/Pd = 4 or 5 and then decreases. The existence of one or more complexes higher than $PdCl_4^=$ is thus indicated. The increase in absorbance at 380 mμ as Cl/Pd rises from 0 to 1, and the decrease of absorbance as this ratio rises above 1 clearly shows the formation of $PdCl^+$.

The existence of $PdCl^+$, $PdCl_2$ and $PdCl_3^-$

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(1) D. H. Templeton, G. W. Watt and C. S. Garner, THIS JOURNAL, 65, 1608 (1943).

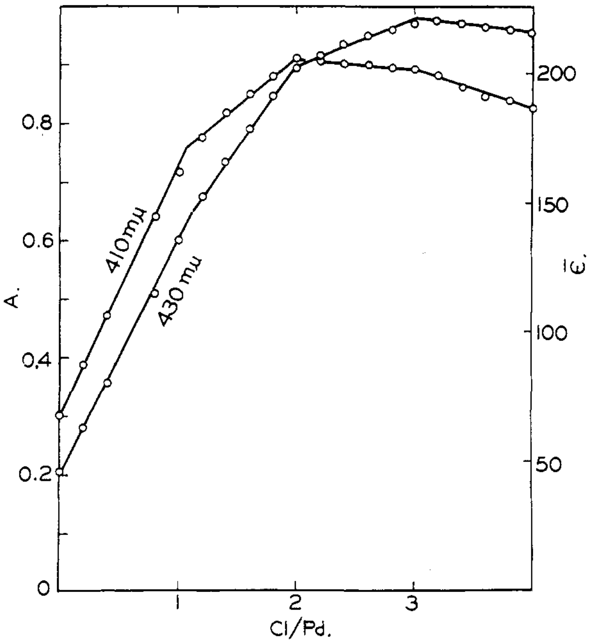

Fig. 2.—Absorbance and average molar extinction coefficient at 410 and 430 mμ of Pd(II)-chloride system as a function of the ratio Cl/Pd; total palladium concentration 0.0044 *M*; all solutions 1.0 *M* in perchloric acid.

is proved by plotting absorbance at suitable wave lengths against Cl/Pd at constant total palladium concentration (Fig. 2). Sharp breaks in absorbance are obtained at Cl/Pd = 1.05, 2.0 and 3.0. The existence of $PdCl_4^=$ is already well known.[2] Evidently these complexes are but slightly ionized into the next lower species and chloride ion.

Of particular interest is the formation of complexes higher than $PdCl_4^=$, which is demonstrated by the gradual decrease in absorbance when Cl/Pd is made larger than 4 (Fig. 3). That at least two higher complexes are formed is proved by the failure to obtain an isosbestic point with increasing chloride concentration at constant ionic strength and acidity (Fig. 4). At the chloride concentrations existing in this series, complexes lower than $PdCl_4^=$ cannot be present in significant amounts, so that $PdCl_4^=$ must be in equilibrium with more

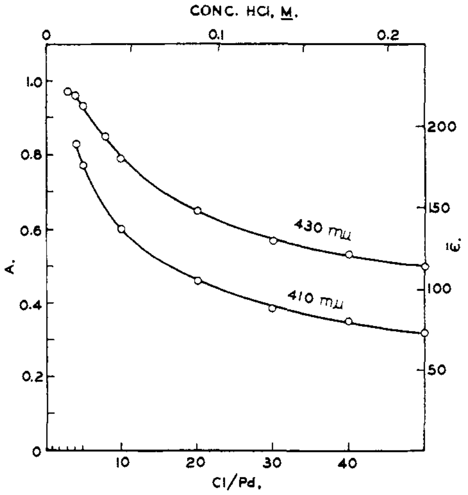

Fig. 3.—Absorbance and average molar extinction coefficient at 410 and 430 mμ of Pd(II)-chloride system at higher chloride concentrations.

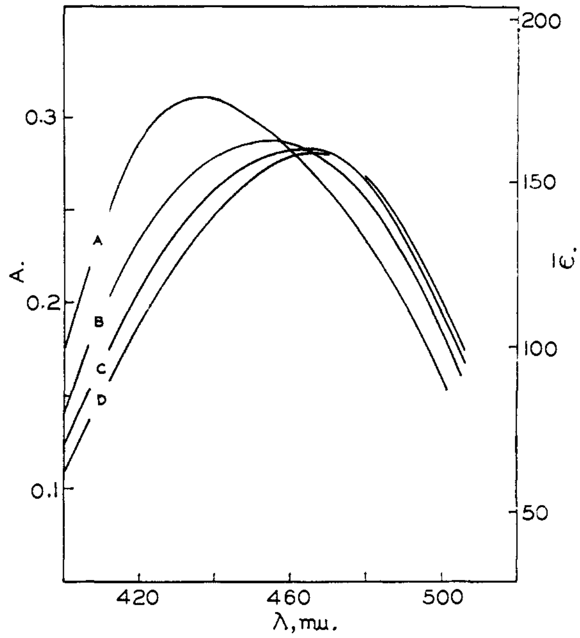

Fig. 4.—Absorbance and average molar extinction coefficient of Pd(II)-chloride system as a function of wave length at various chloride concentrations and constant ionic strength ($HClO_4$ + HCl) of 1.00 *M*. Total palladium concentration 0.0176 *M*. Chloride concentrations (*M*): A, 0.0353; B, 0.070; C, 0.106; D, 0.141. Corresponding Cl/Pd ratios are 20, 40, 60 and 80.

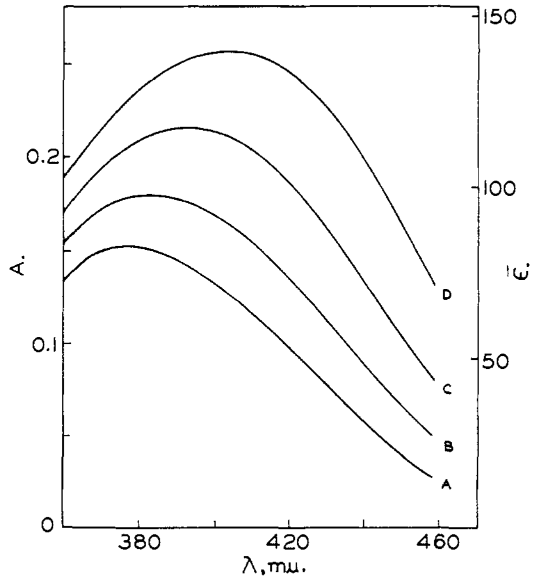

Fig. 5.—Absorbance–wave length curves for Pd(II)-nitrate solutions. Palladium concentration 0.0184 *M*. Concentration of nitric acid (*M*): A, 0; B, 0.20; C, 1.00; D, 3.1. All solutions 0.1 *M* in perchloric acid.

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(2) For example, the application of the method of continuous variations shows the formation of this complex (G. H. Ayres, *Anal. Chem.*, **25**, 1622 (1953)).

than one higher complex. Our data do not show what the composition of these species is, but there seems little reason not to infer the formation of $PdCl_5^{=}$ and $PdCl_6^{\equiv}$. Hexacovalency of palladium (II) is thus indicated. It may be noted that nickel, the vertical neighbor of palladium in the periodic system, appears to give a complex chloride of the hexacovalent type, namely, $Li_4NiCl_6 \cdot 10H_2O$.[3] Tricovalent nickel chloride complexes (M^INiCl_3) are well known in the solid state.

The rather rapid decline in absorbance for $Cl/Pd > 4 < \sim 10$ points to a moderate stability of $PdCl_5^{=}$, but not comparable to the stability of the lower complexes. From Fig. 3 it may be seen that in a 0.0044 *M* palladium solution the absorbance at 410 mμ decreases from 0.82 at $Cl/Pd = 4$ to 0.60 at $Cl/Pd = 10$ ($[Cl^-] = 0.04$ *M*). This means that at least 25% of $PdCl_4^{=}$ has been converted into higher complexes under the latter conditions. In 0.1 *M* chloride solution probably less than half of the palladium is present as $PdCl_4^{=}$ when the total palladium concentration is small compared to the chloride concentration.

Complexing with Nitrate.—Addition of chloride-free nitric acid to a palladium(II) perchlorate solution alters the absorption curve of palladium(II) ion (Fig. 5). The absorbance increases (in the 360–500 mμ range investigated) and the absorption maximum is shifted to longer wave lengths with increasing nitrate ion concentration. The species formed are markedly dissociated at low nitrate concentrations.

MINNEAPOLIS, MINN.

[3] H. Benrath, *Z. anorg. Chem.*, **205**, 417 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Methylamine Complexes of the Rare Earth (III) Chlorides[1]

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The addition of methylamine to lanthanum, cerium(III), praseodymium, neodymium, samarium and gadolinium chlorides was followed at 700 mm. pressure from room temperature to 300°. Methylamine readily combines with the rare earth chlorides forming a series of complexes of the type $MCl_3 \cdot nCH_3NH_2$ where n varies from 5 to 1. Fractional compounds with $n = 4.5, 3.25, \ldots$ down to 0.75 were observed in several cases.

Introduction

Methylamine complexes of metallic salts were first mentioned by Simon and Glauner[3] who investigated the reaction of methyl, dimethyl and trimethylamine with the lithium halides. They reported that methylamine forms a series of addition compounds with the halides of the type, $LiX \cdot nMeNH_2$. For lithium chloride, n is 1, 2, 3 and 4; lithium bromide, n is 1, 2, 3, 4 and 5; and lithium iodide, n is 1, 2, 2.5, 3, 3.5, and there was some evidence for n being 0.25, 0.50 and 1.5. In a pressure–composition study, Maillard[4] investigated the reaction between methylamine and calcium chloride. The compounds, $CaCl_2 \cdot nMeNH_2$, where n is 2, 4, 6 and 8 were reported. The above two studies seem to complete all the previous work done on the addition of methylamine to anhydrous inorganic salts.

Since the ammonia complexes of the rare earth chlorides are well known[5] it was of interest to study the corresponding compounds formed between the anhydrous rare-earth chlorides and methylamine. The salts involved in this investigation were lanthanum, cerium(III), praseodymium, neodymium, samarium and gadolinium chlorides. The addition of methylamine was followed by observing the change in composition with temperature at a constant pressure of the gaseous amine. This method was found to be preferable to the isothermal study since in the latter case the equilibrium was obtained considerably more slowly.

Experimental

Reagents.—The methylamine hydrochloride was obtained from Eastman Organic Chemicals Co., Rochester, N. Y. The source and the purity of the rare earth oxides used for this study were described in a previous publication.[6]

Preparation of Methylamine.—Anhydrous methylamine was prepared by the method of Kenner and Felsing[7] by treating the hydrochloride with a 40–50% solution of sodium hydroxide in the presence of mercuric oxide. The evolved gas was dried by passing through a four-foot column, 2 inches in diameter filled with barium oxide, and then condensing over metallic sodium chips at Dry Ice temperatures. Contrary to the observation reported by Kenner and Felsing, no blue color was observed in the sodium–methylamine mixture. The methylamine was distilled into the storage system of the apparatus prior to use.

Preparation of the Anhydrous Rare Earth Chlorides.—The anhydrous rare earth chlorides were prepared by the method of Kleinheksel and Kremers.[8] The hydrogen chloride was prepared and dried as described elsewhere.[9] Commercial tank hydrogen chloride was found unsuitable for the

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[1] Abstracted in part from the Ph.D. thesis of Wesley W. Wendlandt, State University of Iowa, June, 1954.

[2] Du Pont Teaching Fellow 1953–1954.

[3] A. Simon and R. Glauner, *Z. anorg. allgem. Chem.*, **178**, 177 (1929).

[4] A. Maillard, *Compt. rend.*, **203**, 187 (1936).

[5] (a) C. Matignon, *Ann.*, Ser. VIII, **8**, 284, 402, 464 (1906); (b) W. Klemm and J. Rockstroh, *Z. anorg. allgem. Chem.*, **176**, 181 (1928); (c) M. Barre, *Compt. rend.*, **156**, 1017 (1913); (d) F. Ephraim and P. Ray, *Ber.*, **62**, 1639 (1929); (e) G. Beck and A. Gasser, *Anal. Chem. Acta*, **3**, 41 (1949); (f) F. Ephraim and R. Block, *Ber.*, **59**, 2692 (1926); (g) F. W. Bergstrom, *J. Phys. Chem.*, **29**, 160 (1925).

[6] A. I. Popov and G. E. Knudson, THIS JOURNAL, **76**, 3921 (1954).

[7] C. T. Kenner and W. A. Felsing, *ibid.*, **61**, 2457 (1939).

[8] J. H. Kleinheksel and H. C. Kremers, *ibid.*, **50**, 954 (1928).

[9] L. F. Audrieth, "Inorganic Syntheses," McGraw-Hill Book Co., New York, N. Y., Vol. III, p. 14, and Vol. II, p. 72.