and $[Ni_2trien_3](PtCl_4)_2$ were determined on a modified Curie–Cheneveau balance.[16]

The measurements were made at 25° using ferrous ammonium sulfate (μeff = 5.25)[17] as a calibrating agent. From the mass susceptibilities measured at 25° the molecular susceptibility (χ_M) was determined. The effective Bohr magneton numbers were calculated from the formula

$$\mu\text{eff} = 2.83\sqrt{\chi_M T}$$ [18]

The average effective moments per Ni(II) ion were:

$[Ni_2\ trien_3]Cl_4 = 2.93$ eff. Bohr magneton numbers
$[Ni_2\ trien_3](NO_3)_4 = 2.91$ eff. Bohr magneton numbers
$[Ni_2\ trien_3][PtCl_4]_2 = 2.87$ eff. Bohr magneton numbers

This is in good agreement with the values expected for two unpaired electrons in the nickel(II) ion with octahedral valence bond direction.

Acknowledgments.—Mr. N. L. Cull prepared the $[Ni_2\ trien_3][PtCl_4]_2$ complex compound. The C, H and N analysis were performed by the Clark Micro Analytical Laboratories, Urbana, Illinois.

Summary

1. Spectrophotometric investigation of the nickel(II) ion–triethylenetetramine system indicates the existence of the colored $[Ni\ trien]^{+2}$ and $[Ni_2\ trien_3]^{+4}$ ions in solution.

2. The following compounds of the $[Ni_2\ trien_3]^{+4}$ ion were prepared: $[Ni_2\ trien_3]Cl_4 \cdot 2H_2O$, $[Ni_2\ trien_3](NO_3)_4 \cdot H_2O$ and $[Ni_2\ trien_3][PtCl_4]_2$.

3. It was not possible to isolate any compounds containing the $[Ni\ trien]^{+2}$ ion.

4. No optically active isomers could be isolated, possibly because of the ionic-metal-to-donor-atom link.

5. Magnetic studies of the compounds of the $[Ni_2\ trien_3]^{+4}$ ion indicate the existence of two unpaired electrons in the octahedral complex compounds.

NEW ORLEANS, LOUISIANA RECEIVED APRIL 18, 1949

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[16] F. W. Grey and Farquarson, *J. Sci. Insti.*, **9**, 1 (1932).

[17] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 155.

[18] Ref. 17, p. 79.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. III. Platinum(II) and Palladium(II) Complexes with Triethylenetetramine[1,2]

BY HANS B. JONASSEN AND N. L. CULL

Elements showing a coördination number of four may form complex compounds with linkages of either the tetrahedral sp^3 or the planar dsp^2 type. The most abundant and satisfactory evidence for the planar structure may be found among the compounds of bivalent platinum and palladium.[3] The alleged resolution of optically active complex compounds of these ions by Reihlen[4] is the only evidence for a possible tetrahedral structure. However, the optical isomer was never obtained free from the resolving agent. Other workers[5,6] were unable to effect any resolution of platinum(II) and palladium(II) complex compounds. Mills and Quibell[7] and Lidstone and Mills[8] successfully resolved bis-chelate complexes of platinum(II) and palladium(II) which would be optically active if the central ion directed its valence forces toward the corners of a planar square or square pyramid. Dipole moment studies, however, completely eliminate the latter possibility.[9] Magnetic susceptibility measurements of the complexes of bivalent platinum and palladium have shown them to be diamagnetic,[10,11] which constitutes further evidence for planar dsp^2 linkage.[12]

In this investigation triethylenetetramine ($H_2NC_2H_4NHC_2H_4NHC_2H_4NH_2$) (abbrev. trien) was used as a coördinating agent for platinum(II) and palladium(II) complex compounds. Since trien acts as a quadridentate group,[13,14] its use offers interesting possibilities because the amine with little difference in strain may assume either a planar or a tetrahedral configuration around the central ion.

In the tetrahedral complex the presence of two unpaired electrons in the sp^3 linkage should produce paramagnetism.[12] Furthermore, if the linkage in the tetrahedral complex were mainly covalent[12] the complex should be capable of resolution since its structure is unsymmetrical.

A planar complex on the other hand would show diamagnetism due to dsp^2 type linkage,[12] and would be non-resolvable.

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[1] Based on a portion of the M.S. thesis of N. L. Cull.

[2] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the 115th National Meeting at San Francisco, March, 1949.

[3] D. P. Mellor, *Chem. Rev.*, **33**, 137 (1943).

[4] H. Reihlen and K. Nestle, *Ann.*, **447**, 211 (1926).

[5] K. A. Jensen, *Z. anorg. allgem. Chem.*, **241**, 115 (1939).

[6] H. D. K. Drew, F. S. H. Read and H. J. Tress, *J. Chem. Soc.*, 1549 (1937).

[7] W. H. Mills and T. H. Quibell, *ibid.*, 839 (1935).

[8] A. G. Lidstone and W. H. Mills, *ibid.*, 1754 (1939).

[9] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 225 (1936).

[10] W. Z. Biltz, *Z. anorg. allgem. Chem.*, **170**, 161 (1928).

[11] R. B. Janes, THIS JOURNAL, **57**, 471 (1935).

[12] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1944, p. 118.

[13] H. B. Jonassen and B. E. Douglas, THIS JOURNAL, **71**, 4094 (1949).

[14] F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

Absorption Studies

1. **Special Reagents.**—Some special reagents were used in the preparation and study of the complexes formed between bivalent platinum and palladium and trien: the trien was Technical Grade 70% pure (70% trien, 30% water) purchased from Eastman Kodak Company, Rochester, New York. The trien for the absorption studies was distilled over sodium at reduced pressures, the fraction collected boiled at 139–141° at 10 mm. pressure. The trien was standardized potentiometrically. The C. P. chloroplatinic acid was obtained from the American Platinum Company of Newark, New Jersey, and the C. P. palladous chloride from Eimer and Amend, New York, N. Y. All other chemicals and reagents used were of standard C. P. quality.

Preparation of Potassium Chloroplatinite.—Five grams of chloroplatinic acid was treated with 1.6 g. of potassium chloride and the resulting potassium chloroplatinate was reduced with sulfur dioxide solution in the manner described by Keller.[15]

2. **Experimental.**—Standard solutions of 0.001 *M* potassium chloroplatinite, 0.001 *M* potassium chloropalladite and 0.001 *M* trien were used in the absorption studies. Fixed amounts of the potassium chloroplatinite and potassium chloropalladite were mixed with varying amounts of trien in the molar ratios of 1:0, 1:0.5, 1:1, 1:2, 1:5 and 1:10, respectively. The optical densities of these solutions were determined between the wave lengths of 280 and 800 mμ, using a Beckman spectrophotometer and matched Corex cells one centimeter in depth. The optical density values obtained for the potassium chloroplatinite–trien system are shown graphically in Fig. 1, and for the potassium chloropalladite–trien system in Fig. 2. The 1:10 and the 1:5 solutions in both instances showed practically the same absorption spectrum as the 1:2 solution and are not shown on the graphs. Absorption studies using 0.01 *M* potassium chloroplatinite and 0.01 *M* trien were made but the results were not reproducible because of the formation of a precipitate upon standing.

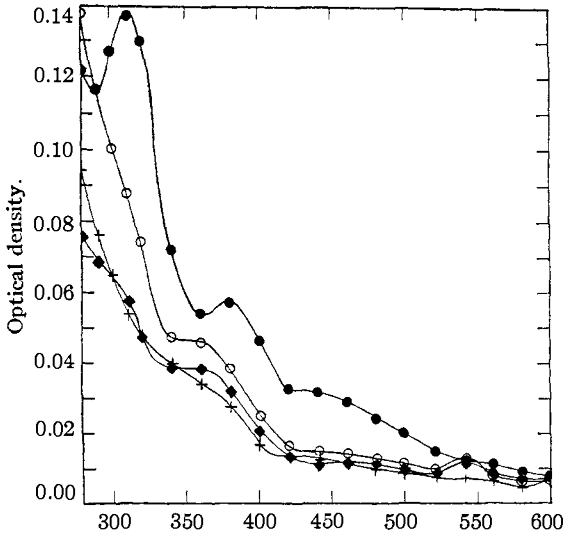

Fig. 1.—Plot of optical density *vs.* wave length for solutions 0.001 *M* in platinum(II) ion with varying concentrations of triethylenetetramine: ●, K_2PtCl_4; ○, 1:0.5; ◆, 1:1; +, 1:2.

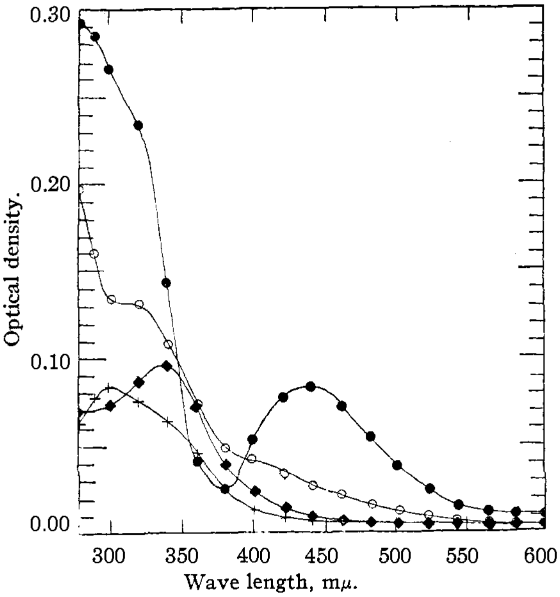

Fig. 2.—Plot of optical density *vs.* wave length for solutions 0.001 *M* in palladium(II) ion with varying concentrations of triethylenetetramine: ●, K_2PdCl_4; ○, 1:0.5; ◆, 1:1; +, 1:2.

3. **Discussion.**—The study of the absorption spectra for the potassium chloroplatinite–trien and the potassium chloropalladite–trien systems clearly indicates the formation of one or more colored complexes in each instance. In the potassium chloroplatinite–trien system a disappearance of the absorption characteristics of the chloroplatinite ion is noted as the mole ratio of trien is increased. A shift of the maxima toward shorter wave lengths is noted for the 1:0.5 and the 1:1 solutions. In the 1:2 solution a disappearance of the characteristic maxima of the chloroplatinite ion occurs. This shifting of the maxima of the absorption curves toward shorter wave lengths is even more marked in the potassium chloropalladite–trien system. It indicates a disappearance of the tetrachloro complexes of bivalent platinum and palladium in solutions of high trien concentration and the formation of one or more trien complexes.

Continuous Variation Studies

Continuous variation studies were also at-

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[15] G. Keller, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 247.

tempted but very little information could be obtained from these. This is not unexpected from theoretical considerations since the difference in the absorption characteristics between the $[PtCl_4]^=$, $[PdCl_4]^=$ ion and the complexes of the system Pt(II) (Pd(II))-trien is very small. Furthermore, replacement of the chloro groups in the tetrachloro compounds by amines is very complex,[16] which makes it very difficult to interpret the results of the continuous variation studies.

Preparations

A. **[Pt trien][PtCl$_4$], a Magnus-type Salt.**[17]—Potassium chloroplatinite was allowed to react with an aqueous solution of trien in the ratio of 2 moles of trien to 1 mole of potassium chloroplatinite. The reddish purple precipitate which settled out after thirty minutes was filtered, washed successively with 200-ml. portions of cold water, 95% ethyl alcohol and finally with ether. It was dried in an oven at 110–120° overnight. The resultant product was a purple-red powder, non-hygroscopic, and only very slightly soluble in water; yield was approximately 20% of theoretical. The salt was found to decompose at temperatures exceeding 260°.

Anal. Calcd. for [Pt trien][PtCl$_4$]: Pt, 57.5; Cl, 20.9; N, 8.26. Found: Pt, 57.4; Cl, 21.2; N, 8.17.

B. **Triethylenetetramineplatinum(II) Ion.**—The $[\text{Pt trien}]^{++}$ ion was prepared by the addition of a large excess of trien to an aqueous solution of potassium chloroplatinite. The color of the solution changes from a cherry red to a light yellow as excess amine is added.

C. **The Aminium Salt of Platinum.**—Five grams of chloroplatinic acid was reduced to the chloroplatinous acid using sulfur dioxide solution as described by Keller.[18] The color of the solution changes from an orange to a cherry red during the course of the reduction. Approximately 0.01 mole of chloroplatinous acid was diluted to 100 ml. and 2 ml. of 70% trien was added, and the solution allowed to stand overnight. It was filtered and the precipitate was washed successively with 600 ml. of cold water, 300 ml. of 95% ethyl alcohol, and finally with 300 ml. of diethyl ether, and dried at 110° overnight. The resultant powder was light orange, non-hygroscopic, and decomposed at 260–265°; yield was about 10%. The complex was slightly soluble in water, insoluble in all common organic solvents. The effect of *p*H on the formation of the aminium salt was investigated. In general it was found that the aminium salt was formed in solutions of low *p*H (2–3), while the Magnus-type salt of platinum and trien was formed in neutral or basic media.

Anal. Calcd. for $(PtCl_4)_2H_4(\text{trien})\cdot 2H_2O$: Pt, 45.6; Cl, 32.8; N, 6.52. Found: Pt, 45.8; Cl, 33.1; N, 6.74.

D. **Triethylenetetraminepalladium(II) Chloropalladite.**—A saturated solution of potassium chloropalladite was prepared by treating palladous chloride with a slight excess of potassium chloride. To 100 ml. of the potassium chloropalladite was added dropwise 0.5 ml. of 70% trien. A light brownish-orange precipitate settled out of solution and was filtered off immediately. It was washed with 200 ml. of cold water, 200 ml. of 95% ethyl alcohol and 100 ml. of diethyl ether and dried in an oven at 110–120° overnight. The resultant product was a light tan, non-hygroscopic powder which decomposed at 230–235°. It was found that on standing the filtrate yielded another crop of crystals which were light yellow in color. The metal analyses for the light tan and yellow precipitates were almost identical. The variation in color may be attributed to differences in precipitation conditions and particle size. The precipitates formed were practically insoluble in all common solvents. Total yield was about 40%.

Anal. Calcd. for [Pd trien][PdCl$_4$]: Pd, 42.6; Cl, 28.3. Found: Pd, 42.7; Cl, 27.9.

E. **Triethylenetetraminepalladium(II) Ion.**—The $[\text{Pd trien}]^{++}$ ion was prepared by adding a large excess of trien to an aqueous solution of potassium chloropalladite. The color of the solution changes from brown to light yellow as excess amine is added.

F. **The Aminium Salt of Palladium.**—Several attempts were made to prepare the aminium type complex of palladium by treating palladous chloride with excess hydrochloric acid and then adding trien. In all cases, a yellow precipitate was obtained which metal analyses proved to be [Pd trien][PdCl$_4$]. All attempts to form the aminium salt were unsuccessful.

Structural Investigation of Complexes

1. The Complex Compounds Pt$_2$trien Cl$_4$ and Pd$_2$-trienCl$_4$: Conductometric Titrations

Experimental.—One hundred ml. of 5.95×10^{-4} [Pt trien][PtCl$_4$] was titrated with 0.09468 *N* silver nitrate using the conductometric method. The distilled water in all solutions was boiled for one half hour prior to use to remove any dissolved gases. A plot of bridge readings against ml. of silver nitrate added is shown in Fig. 3.

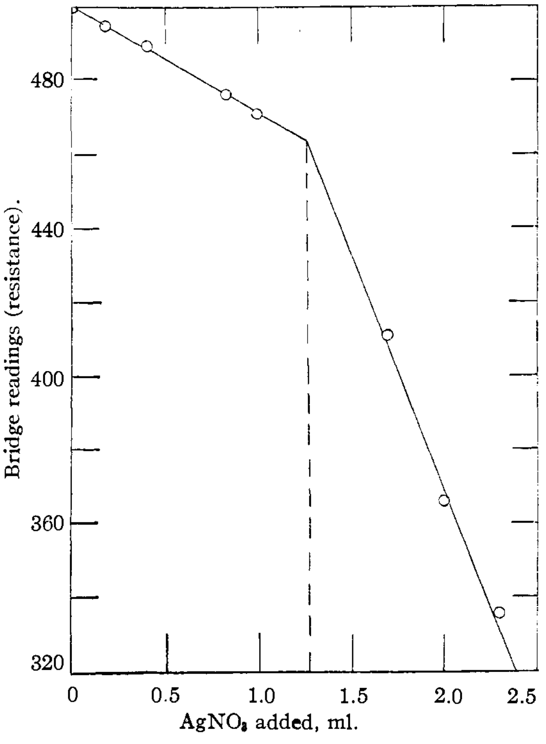

Fig. 3.—Conductometric titration of [Pt(trien)][PtCl$_4$] with AgNO$_3$.

Discussion.—The conductometric titration shows that two equivalents of silver ion is necessary to react with one equivalent of [Pt trien][PtCl$_4$] resulting in a precipitate of silver chloroplatinite. The precipitate formed during this titration has the typical brown color of silver chloroplatinite and analysis showed it to be this compound. These data prove that the 2:1 complex in the basic solution is a Magnus-type salt with a

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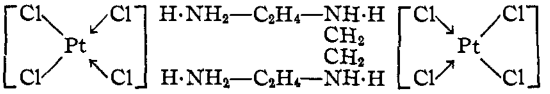
[16] Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1944, p. 105.

[17] G. Magnus, *Poggendorfs Ann.*, **14**, 239 (1828).

[18] G. Keller, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 250.

structural formula of [Pt trien][$PtCl_4$]. Attempts were also made to repeat the above procedure for the 2:1 complex of palladium, but it was so insoluble that no reproducible results could be obtained. By analogy to the platinum complex, however, it would seem that the palladium complex also possesses a Magnus-type structure, *viz.*, [Pd trien][$PdCl_4$].

2. The Complex Compound $Pt_2trienH_4Cl_8$.—The absorption spectrum of a solution of this salt showed the absorption characteristics of the tetrachloroplatinite ion (see Fig. 1) indicating that its structure is



3. The [Pt(trien)]$^{++}$ and [Pd(trien)]$^{++}$ Ions: A. Attempted Optical Resolution

Experimental.—Several attempts were made to precipitate the [Pt(trien)]$^{++}$ and [Pd(trien)]$^{++}$ ions using a large optically active anion. Saturated solutions of *d*-tartaric acid and *d*-α-bromocamphor-π-sulfonate were added to solutions of the ions. Dry air was blown over the solutions for several hours and the resulting precipitate was tested for platinum. In all instances the tests revealed only the presence of organic material.

Discussion.—Although the 1:1 complex had been isolated for either the Pt(II) or Pd(II) systems, its existence in solution has been shown. By treatment with [$PtCl_4$]$^=$ or [$PdCl_4$]$^=$ ions the corresponding Magnus-type salts precipitate.

If a covalent tetrahedral [Pt trien]$^{++}$ or [Pd trien]$^{++}$ ion were present in solution a large optically active anion should bring about resolution. Since the fractions obtained contained no platinum the resolving agents must be more insoluble than the platinum salts. No structural information can therefore be obtained from these data.

B. Magnetic Behavior

Experimental.—The magnetic behavior of the solid complexes prepared, *viz.*, [Pt trien][$PtCl_4$], [$PtCl_4$]$_2H_4$(trien)·$2H_2O$, and [Pd trien][$PdCl_4$] was investigated on a Curie–Cheneveau type balance.[19,20] The investigation was made at room temperature (25°). Previously boiled distilled water was used to calibrate the balance. In all instances the salts under investigation were found to be diamagnetic. Average mass susceptibilities found for [Pt trien][$PtCl_4$], H_4(trien)($PtCl_4$)$_2$·$2H_2O$ and [Pd trien][$PdCl_4$] were found to be -0.22×10^{-6}, $-0.31 \times 10-^{6}$ and -0.42×10^{-6} units, respectively.

Discussion.—The diamagnetism exhibited by all of the complexes investigated is in accord with the predictions of theory and constitutes further evidence for the planar structure of bivalent platinum and palladium complexes.[12]

Summary

1. The absorption spectra of the system triethylenetetramine and platinum(II) or palladium(II) ions indicate that one or more complexes are present in these systems.

2. The complex compounds [Pt trien][$PtCl_4$], [Pd trien][$PdCl_4$] and [trienH_4 ($PtCl_4$)$_2$]·$2H_2O$ were prepared and their structures determined.

3. Attempts to resolve the [Pt trien]$^{++}$ and [Pd trien]$^{++}$ ions were unsuccessful.

4. Magnetic investigations of the complex compounds show them to be diamagnetic, indicating planar dsp^2 linkage.

(19) Cheneveau, *Phil. Mag.*, **20**, 357 (1910).

(20) Grey and Farquharson, *J. Sci. Instruments*, **9**, 1 (1932).

NEW ORLEANS, LOUISIANA RECEIVED APRIL 22, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

The Kinetics of the Reaction of Ozone and Chloride Ion in Acid Aqueous Solution

BY LE ROY BROUGH YEATTS, JR.,[1,2] AND HENRY TAUBE

Kinetic investigations of reactions of ozone with reducing agents are in most instances difficult. The reactions are often so rapid that it is difficult to follow the rate, as for example in the reactions with stannous ion, iodide ion or ferrous ion. Often, too, the reaction with the reducing agent induces decomposition of ozone. This is observed in the reactions of ozone with hydrogen peroxide,[3] formic acid,[4] oxalic acid and phosphorous acid.[5] By contrast, in the system under present study, the main net reaction

$$2H^+ + 2Cl^- + O_3 = O_2 + H_2O + Cl_2 \qquad (A)$$

proceeds slowly enough so that the rate may be followed by ordinary methods, and it accounts almost completely for the change in the system. A very slight decomposition of ozone is observed, but since it varies in an erratic way from experiment to experiment it appears to be unrelated to reaction A. Elsewhere[3] it has been shown, and this observation is confirmed by the present work, that the spontaneous decomposition of ozone in acid solution is inhibited by chloride ion.

(1) From a thesis submitted by Le Roy B. Yeatts, Jr., to the Department of Chemistry, Cornell University, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Present address, Lafayette College, Easton, Penna.

(3) Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

(4) Taube, *ibid.*, **63**, 2453 (1941).

(5) Taube, unpublished observations.