[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Stereochemical Considerations of Oxidation–Reduction Reactions of Platinum Complexes

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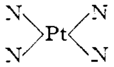
levo-meso-Stilbenediamine-isobutylenediamineplatinum(II), [Pt *i*-bn *m*-stien[2]]$^{+2}$, was oxidized with one and two electron reagents to *levo*-dichloro-*meso*-stilbenediamine-isobutylenediamineplatinum(IV), [Pt *i*-bn *m*-stienCl$_2$]$^{+2}$, and this in turn reduced to the original platinum(II) complex with one and two electron reducing agents. In none of these four different combinations of reactions was there any evidence of racemization. Thus, it is concluded that the platinum-nitrogen bonds



retain a fixed square configuration during these reactions.

The oxidation of bis-(ethylenediamine)–platinum(II), [Pten$_2$]$^{+2}$, to diacido-bis-(ethylenediamine)–platinum (IV), [Pten$_2$X$_2$]$^{+2}$, has been carried out at various experimental conditions by several different investigators. Tschugajeff and Chlopin[3] used both ozone and hydrogen peroxide as the oxidizing agent. Hydrogen peroxide was also used by Babuera,[4] whereas Grinberg and Pitsuin[5] employed potassium permanganate. Chlorine was used by Kurnakow[6] and by Schleicher, Henkel and Spies.[7] Basolo, Bailar and Tarr[8] showed that the reaction products of the chlorine and the hydrogen peroxide oxidation are both the *trans*-isomer. Additional proof of structure is afforded by the isolation of *cis*-[Pten$_2$Cl$_2$]Cl$_2$.[9] It has also been observed[10] that the reduction of *trans*-[Pten$_2$X$_2$]$^{+2}$ yields [Pten$_2$]$^{+2}$. These results suggest that the Pt–N bonds are not broken and that the coplanarity of the two chelate rings is maintained during these reactions.

Rich and Taube[11] report that the exchange of radiochlorine in the system PtCl$_4^{-2}$–*Cl$^-$ is induced by ceric ion but not by chlorine. They attribute the catalysis of the ceric ion, one electron oxidizing agent, to the intermediate formation of the labile anion PtCl$_5^{-2}$. On the other hand the fact that chlorine, a two electron oxidizing agent, has no catalytic effect on the rate of radiochloride exchange in this system is believed to be due to the direct formation of the non-labile intermediate PtCl$_5$OH^{-2}.

The purpose of this investigation was to examine the stereochemistry of platinum(II) and platinum(IV) complexes resulting from oxidation–reduction reactions with one and two electron reagents. Results of the oxidation of *l*-[Pt *i*-bn *m*-stien]$^{+2}$ with ceric ion and chlorine as well as the reduction of *l*-[Pt *i*-bn *m*-stien Cl$_2$]$^{+2}$ with thiosulfate and sulfite ions are reported.

Experimental

1. **Preparation of Compounds.**—Reagent grade chemicals were used and compounds that are not commercially available were prepared and purified essentially by the methods described in the literature. Isobutylenediamine was prepared by converting acetone cyanohydrin into α-aminoisobutyronitrile[12] and subsequent reduction of the nitrile.[13] The synthesis of *meso*-stilbenediamine required first the condensation of benzaldehyde with liquid ammonia to yield hydrobenzamide followed by its rearrangement to amarine.[14] The amarine was then acetylated to give *meso*-N-benzoyl-N-acetyl-1,2-diphenylethylenediamine which was finally hydrolyzed to yield the desired *meso*-stilbenediamine. The method of Catlaway and Parkes[15] was used to prepare diacetyl-*dextro*-tartaric anhydride.

Potassium tetrachloroplatinate(II) obtained by the reduction of K$_2$PtCl$_6$[16] was used for the synthesis of the platinum complexes. The procedure described by Mills and Quibell[12] was used to prepare and resolve [Pt *i*-bn *m*-stien]$^{+2}$. A reaction mixture containing K$_2$PtCl$_4$ and less than one equivalent of isobutylenediamine yielded the yellow crystalline compound [Pt *i*-bnCl$_2$].

Anal. Calcd. for [Pt *i*-bnCl$_2$]: Pt, 55.1. Found: Pt, 55.0.

Equivalent quantities of [Pt *i*-bnCl$_2$] and *meso*-stilbenediamine were allowed to react and [Pt *i*-bn *m*-stien]Cl$_2$ was isolated.

Anal. Calcd. for [Pt *i*-bn *m*-stien]Cl$_2$: Pt, 34.5. Found: Pt, 34.6.

This complex was resolved by the fractional crystallization of the diacetyl-*dextro*-tartrate salt. After ten recrystallizations the molar rotation of the least soluble fraction was constant, $[M]^{23}_{5461} = -7{,}790$ compared to $-10{,}600$ reported by Mills and Quibell.

Anal. Calcd. for [Pt *i*-bn *m*-stien] C$_8$H$_8$O$_8$·2H$_2$O: Pt, 26.2. Found: Pt, 26.3.

This diastereomer was converted to the iodide by treatment with potassium iodide and then to the chloride by shaking with freshly precipitated silver chloride. The chloride salt isolated contained 34.6% platinum in accord with theory and had a molecular rotation, $[M]^{23}_{5461}$, of $-1{,}980$ compared to $-4{,}850$ reported by Mills and Quibell. It is not known why there should be such a discrepancy in molecular rotations. However, as the value obtained was satisfactory for this investigation, no attempt was made to duplicate the higher value.

***trans*-Dichloroisobutylenediamine-*meso*-stilbenediamineplatinum (IV) Chloride.**—This compound has not been reported previously. It could not be prepared by the reaction of chlorine with an aqueous solution of [Pt *i*-bn *m*-

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[1] Northwestern University Fellowship, 1954. Union Carbide Fellowship, 1955. U. S. Atomic Energy Commission Contract AT(11-1)89-Proj. No. 2 summers 1954 and 1955.

[2] *i*-bn = isobutylenediamine, 1,2-diamino-2-methylpropane; *m*-stien = *meso*-stilbenediamine, 1,2-diamino-1,2-diphenylethane.

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[8] F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, THIS JOURNAL, **72**, 2433 (1950).

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[10] D. I. Ryabchekov, *Doklady Akad. Nauk, USSR*, **42**, 182 (1944); S. A. Borisov-Pototskii, *Ann. secteur platene. Inst. chem. gen. USSR*, No. **16**, 41 (1939).

[11] R. L. Rich and H. Taube, THIS JOURNAL, **76**, 2608 (1954).

[12] W. H. Mills and T. H. H. Quibell, *J. Chem. Soc.*, 839 (1935).

[13] F. Basolo, R. K. Murmann and Y. T. Chen, THIS JOURNAL, **75**, 1478 (1953).

[14] F. Lifschitz and J. G. Bos, *Rec. trav. chem.*, **59**, 173 (1940).

[15] F. D. Catlaway and G. D. Parkes, *J. Chem. Soc.*, 663 (1923)

[16] R. N. Keller, *Inorg. Syn.*, **II**, 247 (1946).

stien]Cl$_2$.[8] Such a reaction resulted in the separation from solution of an unidentified yellow sticky material. This difficulty was not encountered whenever the oxidation was carried out in methanol–water. Chlorine was slowly bubbled through a solution of 5 g. of [Pt *i*-bn *m*-stien]Cl$_2$ dissolved in 25 cc. of concentrated hydrochloric acid and 75 cc. of methanol. After approximately 30 min. at room temperature, the excess chlorine was swept out of the reaction mixture by means of a vigorous stream of air. The solution was then placed on a steam-bath and evaporated almost to dryness. This residue was in turn dissolved in 25 cc. of methanol and ether was slowly added to the solution until it became turbid. The mixture was cooled in an ice–salt-bath and the yellow crystalline product was collected on a filter and washed with a minimum amount of alcohol followed by ether. The salt was dried at 100° and found to weigh 5.3 g. (yield 94% of theoretical).

Anal. Calcd. for [Pt *i*-bn *m*-stienCl$_2$]Cl$_2$·H$_2$O: C, 33.0; H, 4.6; Pt, 29.7. Found: C, 33.2; H, 4.8; Pt, 29.8.

The anhydrous salt was obtained when the monohydrate was kept at 120° for 24 hr.

Anal. Calcd. for [Pt *i*-bn *m*-stienCl$_2$]Cl$_2$: C, 33.9; H, 4.4; N, 8.8; Pt, 30.7; ionic Cl$^-$, 11.1. Found: C, 33.7; H, 4.8; N, 8.7; Pt, 30.8; ionic Cl$^-$, 11.1.

This complex was also prepared by the oxidation of [Pt *i*-bn *m*-stien](ClO$_4$)$_2$ with cerium(IV) perchlorate and subsequent reaction with excess hydrochloric acid. An aqueous solution containing 1.3 g. of [Pt *i*-bn *m*-stien]Cl$_2$ in 10 cc. of water was shaken with 10 cc. of a solution containing an equivalent amount of silver perchlorate. The silver chloride was removed on a filter and to the filtrate was added 46 cc. of 0.1 *N* Ce(ClO$_4$)$_4$ in 1 *M* HClO$_4$. This cerium(IV) perchlorate solution had been prepared by the dissolution of 17.21 g. of CeO$_2$ in 160 cc. of HClO$_4$ (70%) and 340 cc. of H$_2$O and then dilution to 1 l. The reaction mixture was allowed to stand 30 min., after which time 50 cc. of HCl (concd.) was added and the solution was concentrated to 50 cc. on a steam-bath. This solution was cooled in an ice–salt-bath and the crystalline perchlorate was isolated and dried at 65° (1.0 g. or 58% of theory). An attempt to analyze this salt by the usual combustion technique was not successful. At elevated temperatures there is a violent explosion and almost complete loss of sample. Therefore, an aqueous solution of the complex was reduced with sulfur dioxide and the chloride ion released was determined volumetrically. A further check was that the perchlorate salt of the product obtained by chlorine oxidation has an infrared spectrum identical with that of this compound.

Anal. Calcd. for [Pt *i*-bn *m*-stienCl$_2$](ClO$_4$)$_2$: coördinated Cl$^-$, 9.3. Found: coördinated Cl$^-$, 9.3.

2. **Oxidation of *l*-[Pt *i*-bn *m*-stien]$^{+2}$.**—Oxidation of *l*-[Pt *i*-bn-*m*-stien]$^{+2}$ was carried out with cerium(IV) ion and with chlorine, a one and a two electron oxidizing agent, respectively. In one set of experiments the reaction product, *l*-[Pt *i*-bn *m*-stienCl$_2$]X$_2$, was isolated, characterized by a comparison of its infrared spectrum with that of the known compound and its optical rotation determined. In a second set of experiments the reaction product was not isolated but instead the optical rotation of the resulting solution was measured.

Chlorine.—The procedure already described for the chlorine oxidation of the *racemic* complex was repeated using the optically active material. Four grams of *l*-[Pt *i*-bn *m*-stien]Cl$_2$ yielded 4.2 g. of *l*-[Pt *i*-bn *m*-stienCl$_2$]Cl$_2$, [M]$^{28}_{5461}$ −4,420. This salt contained 30.8% Pt and had an infrared spectrum identical with that of the known compound.

The chlorine oxidation *in situ* was performed on 50 cc. of methanol–hydrochloric acid solution containing 2.018 g. of *l*-[Pt *i*-bn *m*-stien]Cl$_2$. In the usual way, the excess chlorine was swept out of solution by a stream of air. Then the reaction mixture was diluted to 100 cc. and its optical rotation was measured, [M]$^{28}_{5461}$ −4,380.

Cerium(IV) Ion.—The procedure described for the cerium(IV) oxidation method was repeated using the optically active complex. Three grams of *l*-[Pt-*i*-bn *m*-stien]Cl$_2$, yielded 2.3 g. of *l*-[Pt *i*-bn *m*-stienCl$_2$](ClO$_4$)$_2$, [M]$^{28}_{5461}$ −4,310.

For the investigation *in situ,* 2.606 g. of *l*-[Pt *i-bn m*-stien]Cl$_2$ was dissolved in 15 cc. of water and 10 cc. of a solution containing 1.94 g. of AgClO$_4$ was added. The silver chloride was removed on a filter, thoroughly washed with water and the volume of the filtrate was adjusted to 50 cc. This solution had a molecular rotation of [M]$^{28}_{5461}$ −1,850. To this solution was added 95 cc. of 0.1 *N* Ce(ClO$_4$)$_4$ in 1 *M* HClO$_4$ and the mixture was concentrated to 80 cc. on a steam-bath. The reaction mixture was cooled to room temperature and a small amount of oil separated which was readily dissolved upon the addition of 20 cc. of ethanol. The molecular rotation of this solution, believed to contain *l*-*trans*-[Pt *i*-bn *m*-stien(H$_2$O)$_2$]$^{+4}$, was found to be [M]$^{28}_{5461}$ −3,370. The addition of 50 cc. of HCl (concd.) to 50 cc. of this solution followed by evaporation on a steam-bath to approximately 40 cc. yielded upon cooling to room temperature, 1 g. (58% of theory) of *l*-*trans*-[Pt *i*-bn *m*-stienCl$_2$](ClO$_4$)$_2$. Analysis of coördinated chloride and its infrared spectrum were used to characterize this compound which had a molecular rotation of [M]$^{28}_{5461}$ −4,330.

3. **Reduction of *l-trans*[Pt *i*-bn *m*-stienCl$_2$]$^{+2}$.**—Some reducing agents will reduce *trans*-[Pt *i*-bn *m*-stienCl$_2$]$^{+2}$ to metallic platinum. In order to have some estimate of the reducing agent required, the electrode potential was determined for the half-cell reaction

$$[\mathrm{Pt}\ i\text{-bn}\ m\text{-stien}]^{+2} + 2\mathrm{Cl}^- \rightleftarrows [\mathrm{Pt}\ i\text{-bn}\ m\text{-stien}\ \mathrm{Cl}_2]^{+2} + 2e^-$$

An average E^0 value of −0.70 volt was obtained for solutions containing different amounts (~10^{-3} *M*) of the platinum complexes in 1.0 *N* KCl. Measurements were made with a Beckman *p*H meter using a calomel reference electrode and a platinum indicator electrode.

Just as in the case of the oxidation reactions, the reduction was performed with a one electron, thiosulfate ion, and a two electron, sulfur dioxide, reducing agent. Much as before, in one set of experiments the reduction product was isolated whereas in another set it was not isolated.

Sulfur Dioxide.—Sulfur dioxide was passed through a solution of 1.0 g. of *l-trans*[Pt *i*-bn *m*-stienCl$_2$]Cl$_2$, obtained by the chlorine oxidation, in 100 cc. of water for approximately 30 min. The excess sulfur dioxide was then removed by bubbling a vigorous stream of air through the reaction mixture. A concentrated solution containing 0.7 g. of KI was added and the mixture was cooled in an ice–salt-bath. The iodide salt was collected on a filter, washed with cold water and finally converted to the chloride by allowing it to react with an equivalent amount of freshly precipitated silver chloride. The desired salt, *l*-[Pt *i*-bn *m*-stien]Cl$_2$, weighed 0.47 g. (53% of theory), contained 34.7% Pt and had an infrared spectrum identical with that of the known compound. The molecular rotation of this compound was [M]$^{28}_{5461}$ −2,030. A similar reduction of *l-trans*[Pt *i*-bn *m*-stienCl$_2$](ClO$_4$)$_2$, obtained by the cerium(IV) oxidation, yielded *l*-[Pt *i*-bn *m*-stien](ClO$_4$)$_2$ with a molecular rotation of [M]$^{28}_{5461}$ −1,860.

A portion of the reaction mixture, [M]$^{28}_{5461}$ −4,380, resulting from the oxidation of *l*-[Pt *i*-bn *m*-stien]Cl$_2$ with chlorine was then reduced with sulfur dioxide. The volume of this solution was adjusted to 25 cc. and the molecular rotation of the regenerated platinum(II) complex measured *in situ*, [M]$^{28}_{5461}$ −1,890. In the same way the solution produced by the cerium(IV) oxidation, [M]$^{28}_{5461}$ −3,370, was reduced with sulfur dioxide and its optical rotation determined, [M]$^{28}_{5461}$ −1,950.

Thiosulfate Ion.—A reaction mixture made up of 1.3 g. of *l-trans*[Pt *i*-bn *m*-stienCl$_2$]Cl$_2$ that had been isolated from the chlorine reaction, 50 cc. of water and 0.65 g. of Na$_2$S$_2$O$_3$ was allowed to stand at room temperature for approximately 1 hr. A concentrated aqueous solution containing 0.9 g. of KI was then added and the mixture was cooled in an ice–salt-bath. This iodide salt gave 0.71 g. (61% of theory) of the chloride salt which contained 34.4% Pt and had an infrared spectrum identical with that of the known chloride. The product of this reduction had a molecular rotation of [M]$^{28}_{5461}$ −1,960. Similarly the reduction of the perchlorate obtained by the cerium(IV) oxidation yielded *l*-[Pt *i*-bn *m*-stien](ClO$_4$)$_2$ with an optical rotation of [M]$^{28}_{5461}$ −1,860.

Reductions *in situ* required first the neutralization of the acid reaction mixtures by the careful addition of aqueous sodium hydroxide. A portion of the solution resulting from the oxidation with chlorine, [M]$^{28}_{5461}$ −4,380, was reduced with an excess of sodium thiosulfate. After the volume was adjusted to 25 cc. the optical rotation of this solution was determined, [M]$^{28}_{5461}$ −1,760. Thiosulfate reduction of the reaction mixture obtained by the cerium(IV) oxidation, [M]$^{28}_{5461}$ −3,370, yielded a solution with [M]$^{28}_{5461}$ −1,840.

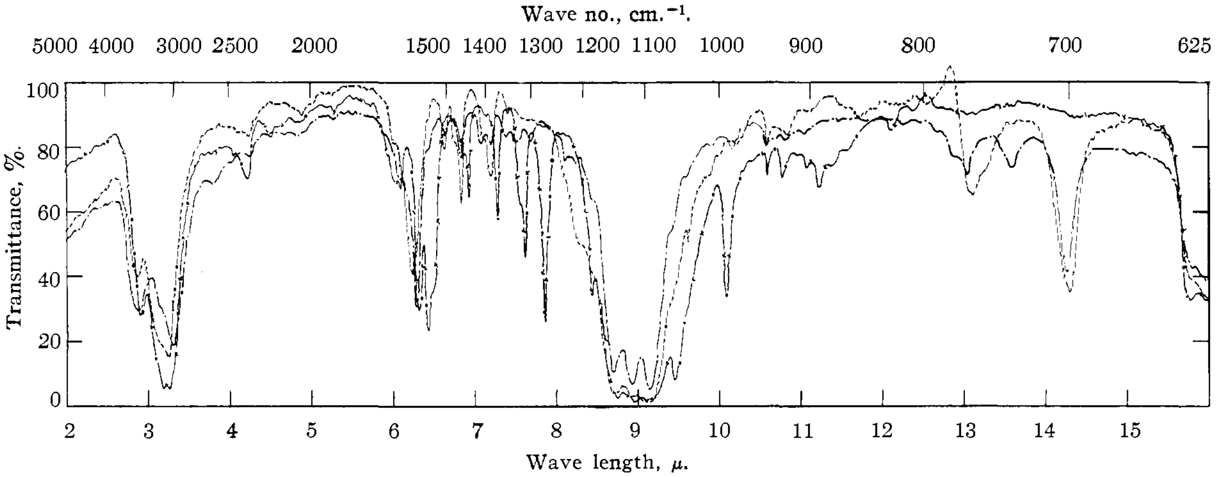

Fig. 1.—*trans*-[Pt en$_2$ Cl$_2$] (ClO$_4$)$_2$ — × —; *trans*-[Pt *i*-bn *m*-stien Cl$_2$]ClO$_4$ — - —; [Pt *i*-bn *m*-stien] (ClO$_4$)$_2$- - - - -

4. **Polarimetric Measurements.**—Measurements of optical rotation were made with a Bellingham and Stanley polarimeter using a 2 dm. light path. A mercury lamp was used as a light source in conjunction with a prismatic eyepiece on the polarimeter to permit the use of the 5461 Å. line. The concentrations of the solutions were approximately 4% for the platinum(II) complexes and 2% for the platinum(IV) compounds.

5. **Measurements of Absorption Spectra.**—The infrared absorption spectra were measured in the rock salt region (5,000–625 cm.$^{-1}$) with a Baird Model AB-2 double beam recording instrument. Measurements were all made on the solid compounds employing the potassium bromide disk technique.[17]

Results and Discussion

The Mills and Quibell[12] complex, [Pt *i*-bn *m*-stien]$^{2+}$, was successfully oxidized and salts of the new complex *trans*-[Pt *i*-bn-*m*-stienCl$_2$]$^{2+}$ were isolated. This cation was obtained in the optically active (average $[M]^{28}_{5461}$ −4,370) form by starting with *l*-[Pt *i*-bn *m*-stien]$^{2+}$ ($[M]^{28}_{5461}$ −1,980). The platinum(IV) compound is not optically pure because the optical activity of the platinum(II) compound employed had a molecular rotation of only approximately half of that reported by Mills and Quibell. No attempt was made to resolve *racemic-trans*·[Pt *i*-bn *m*-stienCl$_2$]$^{2+}$.

A *trans* configuration is assigned [Pt *i*-bn *m*-stienCl$_2$]$^{2+}$ on the basis of the following evidence. (1) A large number of examples of the oxidation of platinum(II) complexes[18] have been investigated in considerable detail and in every case the platinum(IV) product was found to possess the two entering ligands in *trans* positions. There is no *a priori* reason to suspect that the complex described here should behave differently. (2) If it is assumed that the diamine–platinum chelate rings rearrange so as to give the *cis*-isomer, then some racemization is expected. However, the results obtained clearly show that there is essentially no racemization accompanying these reactions. (3) Finally, the infrared spectrum of [Pt *i*-bn *m*-stienCl$_2$](ClO$_4$)$_2$ is similar to that of *trans*-[Pten$_2$Cl$_2$](ClO$_4$)$_2$ in the N–H stretching (*ca.* 3.2 μ) and N–H bending (*ca.* 6.2 μ) regions and almost identical with that of [Pt *i*-bn *m*-stien](ClO$_4$)$_2$. Since the spectrum shows no sign of the additional band splittings expected of the *cis*-isomer[19] (Fig. 1), it is concluded that [Pt *i*-bn *m*-stienCl$_2$)$^{+2}$ has a *trans* structure.

Results of the experiments on the oxidation of *l*-[Pt*i*bn *m*-stien]$^{2+}$ and the reduction of *l-trans*-[Pt *i*-bn *m*-stienCl$_2$]$^{2+}$ are summarized in Table I. These data show that the reactions investigated take place without racemization. Rich and Taube[11] observed that the presence of cerium(IV) enhanced the rate of radiochloride exchange in the system PtCl$_4^{-2}$–*Cl$^-$. They attribute this catalysis to the formation of a labile intermediate, PtCl$_5^{2-}$. Data in Table I show that neither a one electron oxidizing agent (cerium(IV)) nor a one electron reducing agent (thiosulfate) gives rise to racemization in these systems. It must therefore be concluded that the Pt–N bonds in the pentacoördinated intermediate are not labile. This result is not too surprising, even though PtCl$_5^{-2}$ is labile, in view of the fact that ethylenediamine derivatives are known to form very stable chelate rings.[20]

TABLE I

OXIDATION OF *l*-[Pt *i*-bn *m*-stien]$^{+2}$ AND REDUCTION OF *l-trans*-[Pt *i*-bn *m*-stien Cl$_2$]$^{+2}$

Pt(II) $[M]^{28}_{5461}$	Oxidizing agent	Pt(IV) $[M]^{28}_{5461}$	Reducing agent	Pt(II) $[M]^{28}_{5461}$
Isolation of products				
−1,830[a]	Ce(IV)	−4,310	S$_2$O$_3^{-2}$	−1,860
			SO$_2$	−1,860
−1,980	Cl$_2$	−4,420	S$_2$O$_3^{-2}$	−1,960
			SO$_2$	−2,030
Reactions *in situ*				
−1,830	Ce(IV)	−3,370[b]	S$_2$O$_3^{-2}$	−1,840
			SO$_2$	−1,950
−1,830	Cl$_2$	−4,380	S$_2$O$_3^{-2}$	−1,760
			SO$_2$	−1,890

[a] Precision of all $[M]^{28}_{5461}$ values is ±150. [b] The complex in this solution is *l-trans*-[Pt *i*-bn *m*-stien(H$_2$O)$_2$]$^{+4}$ rather than the dichloro compound.

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[17] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

[18] A. A. Grinberg, "Introduction to the Chemistry of Complex Compounds," State Scientific-Technical Publications of Chemical Literature, Moscow, 1951, page 155 (in Russian).

[19] J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954).

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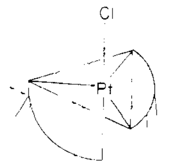
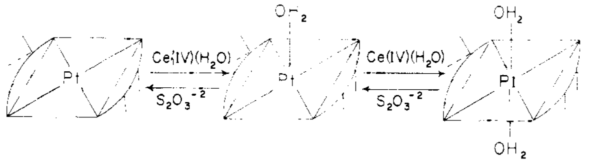
Finally, the results obtained suggest the stereochemical changes diagrammed in Table II. The tetragonal pyramid structure is assigned the pentacoordinated intermediate in the one electron reactions on the basis of the following evidence. (1) Calculations by Daudel and Bucher[21] show that this stucture is possible for the dsp^3 hybridization assigned this complex. (2) K. A. Jensen and B. Nygaard[22] report that the nickel(III) complex, $NiBr_3 \cdot 2Et_3P$, has a tetragonal pyramid structure. Since nickel and platinum are members of the same group in the periodic table and have the "same" valence electronic configuration, it is believed that the platinum(III) complexes will have the same structure as do those of nickel(III). (3) The quantitative conversion of platinum(II) complexes to the analogous platinum(IV) compounds which contain the entering groups in *trans* positions suggests that rearrangement to a trigonal bipyramid structure is unlikely. (4) The fact that one electron reactions do not induce racemization is likewise consistent with the tetragonal pyramid structure. There are ten geometric isomers theoretically possible for a trigonal bipyramid structure of $[\mathrm{Pt}\ i\text{-bn}\ m\text{-stienCl}]^{+2}$. Six of these are asymmetric but four of them are symmetrical, as for example



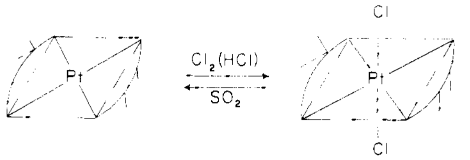
It would therefore appear that if the pentacoördinated intermediate had such a structure then some racemization would have accompanied these reactions.

TABLE II

STEREOCHEMISTRY OF PLATINUM COMPLEXES IN OXIDATION-REDUCTION REACTIONS



One electron reagent



Two electron reagent

Finally the octahedral structure of platinum(IV) is well known and the evidence for the *trans* configuration cited for the two electron reactions has been discussed already.

Acknowledgment.—The authors wish to thank Dr. F. P. Dwyer for suggesting the use of the Mills and Quibell complex. We are also indebted to Dr. R. G. Pearson for stimulating discussions in connection with this investigation.

EVANSTON, ILL.

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[21] R. Daudel and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

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[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. III. Thermal and X-Ray Phase Diagrams of the System K_2O or K_2CO_3 with Ta_2O_5

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The phase diagram of the system K_2O or K_2CO_3 with Ta_2O_5 has been determined using differential and conventional thermal analysis, optical pyrometry and X-ray techniques. Four compounds corresponding to the formulas (I) $K_2O \cdot 5Ta_2O_5$, (II) $K_2O \cdot 2Ta_2O_5$, (III) $K_2O \cdot Ta_2O_5$ and (IV) $3K_2O \cdot Ta_2O_5$ have been identified. Compounds I, II and III melt incongruently at 1645, 1520 and 1370°, respectively. Within experimental limits the ferroelectric compound III occurs at a singular point between congruent and incongruent melting. The density of III has been determined as 6.96 g./cm.^{3} at 25°. Compound IV melts congruently at 1330°. The polymorphism of Ta_2O_5 has been reinvestigated from room temperature to its melting point. A low temperature form, β, melts at $1785 \pm 30°$ and has a density of 8.18 g./cm.^{3} at 25°. At $1360 \pm 5°$, β transforms to a high temperature modification, α, with a melting point of $1872 \pm 10°$, and a density of 8.37 g./cm.^{3} at 25°. On the basis of a combination of geometric and electronic factors this system was expected to exhibit model behavior with respect to the K_2O-Nb_2O_5 system, but differed markedly. X-Ray powder data for all the anhydrous compounds have been determined and ambiguities concerning Ta_2O_5 interplanar spacings have been resolved.

Introduction

This paper is the third in a series involving a study of the high temperature reactions of alkali oxides and carbonates with the group VB pentoxides[1,2] and marks completion of that portion of the investigation in which K_2O is the basic component.

Mellor[3] reports the existence of only one anhydrous potassium tantalate, *viz.*, $KTaO_3$. This is interesting in view of the large number of anhydrous potassium niobates and vanadates listed in this treatise. Potassium metatantalate exhibits the perovskite structure with cell constant a =

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[1] A. Reisman and F. Holtzberg, THIS JOURNAL, **77**, 2115 (1955).

[2] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **78**, 1536 (1956).

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1952, p. 901.