(2) The negative viscosity of the glycerol solutions is attributed to the association of the solvent.

(3) The value of the ratio of absolute viscosity to molecular volume has been calculated for fifty non-associated organic liquids. This ratio is approximately constant for members of the same class of compounds in the same series.

(4) By means of this ratio it has been inferred that the degree of association of glycerol must exceed that of water.

(5) The results of the measurements on non-aqueous solutions confirm the conclusions drawn from previous investigations, that the cations of an electrolyte and the association of the solvent are factors causing negative viscosity.

COLUMBIA UNIVERSITY, NEW YORK CITY,
April, 1908.

THE CHARACTER OF THE COMPOUND FORMED BY THE ADDITION OF AMMONIA TO ETHYL-PHOSPHO-PLATINO-CHLORIDE.

BY CHAS. H. HERTY AND R. O. E. DAVIS.

Received March 23, 1908.

By heating together phosphorus pentachloride and spongy platinum, Baudrimont[1] obtained the phospho-platino-chloride $PtCl_2.PCl_3$. Later Schützenberger[2] prepared the compound $PtCl_2.2PCl_3$ by treating Baudrimont's salt with phosphorus trichloride and he studied the various derivatives of these two substances.

The apparent analogy of these compounds to those of platinous chloride with ammonia led one of us (Herty) in 1901 to investigate them further by physico-chemical methods, in order to determine whether the analogy was real and therefore whether they conformed to Werner's[3] extension of the valence hypothesis. If so, various possibilities of isomerism at once suggested themselves.

These views, in abstract form, were presented to the committee in charge of the C. M. Warren Research Fund and a grant was made for the purchase of platinum. Work was begun at once, but unfortunately a call to another field made impossible the completion of the investigation. The platinum was recovered, sold, and the grant returned.

Later, Rosenheim[4] published the results of an investigation covering practically the same ground. He found that the analogy was real and succeeded in obtaining numerous isomers. With the stable ethoxy derivatives, molecular weight determinations, both ebullioscopic and

---

[1] *Ann. chim. phys.* [4], 2, 47.

[2] *Bull. soc. chim.* [2], 17, 482; 18, 101, 148.

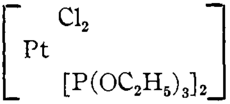
[3] *Z. anorg. Chem.*, 3, 267.

[4] *Ibid.*, 37, 394; 43, 34.

cryoscopic, showed that while the formula of the 1:2 compound is normal, that of the 1:1 compound must be doubled, thus

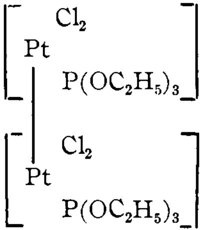
$$PtCl_2.2P(OC_2H_5)_3 \text{ and } (PtCl_2.P(OC_2H_5)_3)_2.$$

These facts show both compounds in strict accord with Werner's coordination ideas, namely, that the coordination number of platinum in platinous compounds is four. Accordingly, their formulas would be



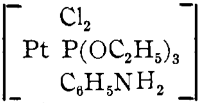
$$\left[\begin{matrix} & Cl_2 \\ Pt & \\ & [P(OC_2H_5)_3]_2 \end{matrix}\right]$$

and



$$\begin{matrix}\left[\begin{matrix} & Cl_2 \\ Pt & \\ | & P(OC_2H_5)_3 \end{matrix}\right] \\ \left[\begin{matrix} | & Cl_2 \\ Pt & \\ & P(OC_2H_5)_3 \end{matrix}\right]\end{matrix}$$

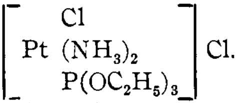
The addition of one molecule of aniline to the former, results in one chlorine atom becoming ionizable, but from the latter, Rosenheim succeeded in obtaining two isomeric substances, a white and yellow modification, each having the formula



$$\left[\begin{matrix} & Cl_2 \\ Pt & P(OC_2H_5)_3 \\ & C_6H_5NH_2 \end{matrix}\right]$$

again conforming to Werner's views.

However, when gaseous ammonia was used instead of aniline an unexpected result was obtained. Two molecules of the base were added for each atom of platinum present, the empirical formula being $PtCl_2.P(OC_2H_5)_3.2NH_3$. According to Werner's views, such a compound should be diionic, as represented by the formula

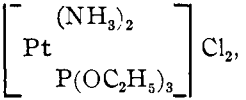


$$\left[\begin{matrix} & Cl \\ Pt & (NH_3)_2 \\ & P(OC_2H_5)_3 \end{matrix}\right] Cl.$$

But Rosenheim found that silver nitrate precipitated at once both chlorine atoms, even at 0°, and that the molecular conductivity at 25° was

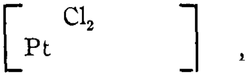
v	32	64	128	256	512
μ	155.9	160.8	160.4	160	162.3

From these facts and from the composition of the double salt with chlorplatinic acid, he concluded that the formula may be



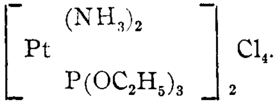
$$\left[\begin{matrix} & (NH_3)_2 \\ Pt & \\ & P(OC_2H_5)_3 \end{matrix}\right] Cl_2,$$

but since such a formula is not in accord with the coordination number of platinous platinum, and since the compound is derived from the double molecule



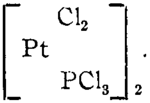
$$\left[\begin{matrix} & Cl_2 \\ Pt & \end{matrix}\right],$$

Rosenheim assigned to it the formula



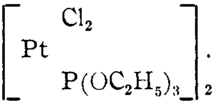
$$\left[\mathrm{Pt}\begin{matrix}(\mathrm{NH_3})_2\\ \mathrm{P(OC_2H_5)_3}\end{matrix}\right]_2\mathrm{Cl_4}.$$

Such a formula appeared to us to be a strained interpretation of Werner's views. Furthermore, the molecular conductivity, as given by Rosenheim, is abnormal in every way. It seemed desirable, therefore, to repeat the preparation of the substance and to study its properties further. Experience gained in the study of the molecular conductivity of complex ammonia compounds at 0°[1] justified the hope that such a study of this compound might throw more light upon its constitution. Following the directions of Schützenberger and of Rosenheim, pure spongy platinum was heated with phosphorus pentachloride, the latter freed from trichloride and oxychloride by heating in a current of dry air at 110°. The fused mass on treatment with hot benzene, free from thiophene and purified by freezing, yielded on cooling an abundant crop of well crystallized



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl_2}\\ \mathrm{PCl_3}\end{matrix}\right]_2.$$

Freed from benzene, at the same time carefully protected from the action of moisture, the compound was immediately treated with absolute alcohol in order to convert it into the ethoxy derivative



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl_2}\\ \mathrm{P(OC_2H_5)_3}\end{matrix}\right]_2.$$

The alcoholic solution was then placed in a desiccator over two vessels, one containing concentrated sulphuric acid, the other powdered lime, and left to evaporate to crystallization. Removal to a new building necessitated cessation of the work for several months. On resuming, it was found that the solution in the desiccator had evaporated to dryness, no distinct crystallization being noticeable. This mass was dissolved in pure benzene and into the solution dry ammonia gas was conducted. The absorption of ammonia was accompanied by a marked elevation of temperature, the original yellowish tint of the solution gradually faded and then, rather suddenly, a mass of white crystals separated, the mass becoming almost solid. The completion of the reaction was indicated by the return to normal temperature. The crystal broth was set aside and owing to the exigencies of other work, two weeks elapsed before the crystals were separated from their mother liquor. The sub-

---

[1] Werner and Herty, *Z. phys. Chem.*, 38, 331.

stance, freed from benzene, was recrystallized from alcohol and obtained in a very pure form.

A portion of the substance dissolved in water showed no acid reaction, although Rosenheim found an immediate acid reaction and explained the peculiar results he obtained from a study of its molecular conductivity by assuming a rapid hydrolysis of the compound Analysis showed:

			Found by Rosenheim		Theoretical for	
	I.	II.	I.	II.	$\left[Pt\begin{matrix}(NH_3)_2\\P(OC_2H_5)_3\end{matrix}\right]_2Cl_4$	$\left[Pt\begin{matrix}Cl\\(NH_3)_2\\P(OC_2H_5)_3\end{matrix}\right]Cl$
Cl (Ionizable)	8.02	7.96	15.08	14.42	15.23	7.62
Pt	42.30	41.40	41.68	...	41.82	41.82
NH_3	7.04	7.18	7.19	...	7.30	7.30

Ionizable chlorine was determined at room temperature by precipitation of the water solution of the substance with excess of silver nitrate. The filtrates remained clear even after standing several weeks. Platinum was determined hy Rosenheim's method,[1] ammonia by the Kjeldahl method.

Effort was then made to determine the total chlorine by Rosenheim's method[1] but concordant results could not be obtained. Determinations of the total chlorine by Stepanow's[2] method gave:

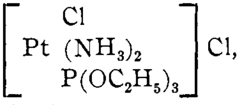
Total chlorine.		
I.	II.	Theoretical.
15.19	15.00	15.23

Determination of the molecular conductivity at 25° showed:

v	32	64	128	256	512	1024	2048
μ	95.79	100.13	106.09	113.49	119.70	127.97	138.98
Found by Rosenheim	155.9	160.8	160.4	160.0	162.3	....	....

The values for μ found by us agree closely with the figures obtained by Werner and Miolati[3] and by Werner and Herty[4] for all diionic complex ammonia compounds. No evidence of hydrolysis could be detected in the solution which had been used for the determination of the molecular conductivity, the reaction was perfectly neutral.

From all the above facts, it is evident that the formula of our compound is



$$\left[Pt\begin{matrix}Cl\\(NH_3)_2\\P(OC_2H_5)_3\end{matrix}\right]Cl,$$

a formula strictly in accord with Werner's coordination law. It would seem further that we have here another case of isomerism of inorganic compounds.

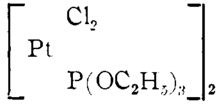
---

[1] *Z. anorg. Chem.*, **37**, 395.

[2] *Ber.*, **39**, 4056.

[3] *Z. phys. Chem.*, **12**, 35; **14**, 506; **21**, 225.

[4] *Ibid.*, **38**, 331.

In order to gain further knowledge of the conditions which determine the formation of the one or the other of these substances, new experiments were begun. A fresh portion of the compound  $\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}_2\\ \\ \mathrm{P(OC_2H_5)_3}\end{matrix}\right]_2$ was prepared. Twenty-one grams of the substance were dissolved in seventy-five cc. of benzene and the solution was divided into three equal portions. In one, designated A, the substance was prepared under the conditions above described. In another, designated B, the crystals were promptly separated from the benzene liquor. In the third portion, designated C, the temperature was maintained at 6° throughout the experiment.

In order to insure as far as practicable a uniform addition of ammonia in the several experiments, thirty-five grams each of finely pulverized lime and ammonium chloride were thoroughly mixed and placed in a 500 cc. round bottom flask and heated in a bath of cottonseed oil. At 220°, copious evolution of ammonia began. The gas, dried over quicklime, was passed through the benzene solution of the ethoxy compound for forty-five minutes, during which time the temperature of the oil bath was gradually raised to 245°.

The benzene solution was placed in a 50 cc. round bottom flask provided with a three-hole rubber stopper through which passed a thermometer dipping into the solution and the inlet and outlet tubes for the ammonia.

Experiment A: The initial temperature of the benzene solution was 22°. When the temperature of the oil bath surrounding the generator reached 220° the temperature in the absorption flask began to rise. After five minutes it was 25°, after ten minutes 33°, after fifteen minutes 38°. Meanwhile the yellow color of the original solution gradually faded. After twenty minutes the temperature was 40°, then suddenly the separation of the white substance took place to such an extent that the mass became almost solid. A portion of the substance was at once removed from the absorption flask, pressed between folds of drying paper and dissolved in water. No evidence of hydrolysis could be detected, the solution being perfectly neutral to indicators. As Rosenheim found that his salt was strongly hydrolyzed, it was decided to continue the passage of the ammonia gas into the crystal broth longer. Accordingly, this was continued for twenty-five minutes more, the temperature of the solution falling gradually. The vessel tightly corked was allowed to stand two weeks. At the end of this time the crystals were filtered from the benzene and pressed between folds of drying paper, then recrystallized from absolute alcohol and labeled "A".

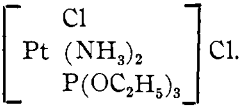
Experiment B: This was a repetition of Experiment A except that the crystals were removed from the benzene immediately after the conclusion of the experiment. The maximum temperature observed in the absorption flask was 44°. The separation of the crystals took place twenty-two minutes after the temperature of the oil bath surrounding the ammonia generator had reached 220°. The substance recrystallized from alcohol was labeled "B."

Experiment C: This was a repetition of Experiment B except that the temperature of the benzene solution was kept constantly at 6°. The crystal separation took place twenty-four minutes from the time the oil bath reached 220°. Recrystallized from alcohol the substance was labeled "C."

The results of the analyses of the three preparations follow:

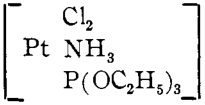
	Ionizable chlorine.		Total chlorine.	Theoretical chlorine for $\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_2\\\mathrm{P(OC_2H_5)_3}\end{matrix}\right]\mathrm{Cl}$.	
	I.	II.		Ionizable.	Total.
A	7.66	7.64	15.16	7.62	15.23
B	7.74	7.66	15.17	....	.....
C	7.47	7.49	15.01	....	.....

From these results it is evident that we have succeeded in preparing only the normal salt



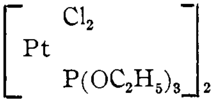
$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_2\\\mathrm{P(OC_2H_5)_3}\end{matrix}\right]\mathrm{Cl}.$$

And yet Rosenheim's directions have been faithfully followed and his description of the absorption experiment coincides with our observations. It is therefore not considered profitable to further undertake the preparation of Rosenheim's compound until more specific directions are given. Meanwhile, it is our intention to try to prepare the compound



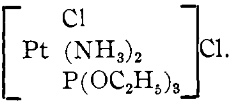
$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl_2}\\\mathrm{NH_3}\\\mathrm{P(OC_2H_5)_3}\end{matrix}\right]$$

analogous to the aniline compound prepared by Rosenheim, and to gain further light upon the character of the reaction by which the addition of ammonia changes the non-ionizable compound



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl_2}\\\\\mathrm{P(OC_2H_5)_3}\end{matrix}\right]_2$$

into the ionizable compound



$$\left[\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\(\mathrm{NH_3})_2\\\mathrm{P(OC_2H_5)_3}\end{matrix}\right]\mathrm{Cl}.$$

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C., March 11, 1908.