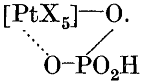
CCCXVI.—*The Reaction between Alkali Phosphates and Chloroplatinic Acid in Ammoniacal Solution.*

By Bertram Eastwood Dixon.

The composition of the precipitate formed by the interaction of soluble phosphates with chloroplatinic acid in ammoniacal solution does not appear to have received attention. In one of his methods for the preparation of chloropentammino- and hexammino-platinic salts, Tschugaev (*Z. anorg. Chem.*, 1924, **137**, 1) obtained an impure phosphate by heating together ammonium chloroplatinate, disodium phosphate, and aqueous ammonia. He did not further investigate this product, but by repeated precipitation from its solution in acid with concentrated hydrochloric acid and with ammonium hydroxide he obtained chloropentamminoplatinic chloride. It has now been found that under certain conditions a pure product of definite composition can be obtained from chloroplatinic acid.

The main reaction may be regarded as consisting of a number of consecutive reactions each involving the replacement of one chlorine atom by an ammonia group from $[PtCl_6]''$ to $[Pt(NH_3)_6]''''$. At certain stages the progress of the main reaction may be checked by the withdrawal of an insoluble product, but unless the conditions of temperature, concentration, time, etc., are specifically suited for the formation of this compound, it is contaminated with the products of simultaneous reactions. From the results of a large number of tests the conditions were determined for the formation of a precipitate of definite composition, namely, *chloroamidotetramminoplatinic hydroxyhydrophosphate.* Briefly, these conditions are: (1) *A relatively great dilution.* The addition of ammonia to fairly concentrated mixed solutions of chloroplatinic acid and sodium or ammonium phosphate yielded immediate light yellow precipitates apparently consisting of mixtures of ammonium chloroplatinate and phosphates of platinammines of high chlorine content. With moderate concentrations of chloroplatinic acid (more than 0·2%) the separation of ammonium chloroplatinate soon commenced; its formation delayed the main course of the reaction and its re-solution in the cold was extremely difficult and probably never complete. (2) *Room temperature.* Analysis of the product obtained in hot, moderately concentrated solution indicated the partial formation of a hexamminoplatinic salt. (3) *Maintenance of an excess of ammonia.* Unless the hydroxyhydrophosphate is allowed to remain in contact with a large excess of ammonia, during both the initial and the subsequent precipitations, it is contaminated with a phosphate of lower alkaline function. This is a monochloroammine salt having a higher phosphate content and is probably the dihydrophosphate (*q.v.*).

For the preparation by this method of several grams of material a period of several weeks is necessary. The almost total insolubility of the hydroxyhydrophosphate in ammonia supports the assumption that it is the first of the successive reaction products which is insoluble under the conditions of the experiment, and that its separation from solution is complete before the replacement of the last chlorine atom in the platinic complex has commenced. The product remains unchanged in composition after solution in hydrochloric acid and reprecipitation by ammonia, as shown by the determination of platinum and chlorine in successive precipitates. It may be noted that this reprecipitation would not necessarily eliminate any hexammine salt that might be present.

Constitution of Chloroamidotetramminoplatinic Hydroxyhydrophosphate.—The chlorine and five nitrogen atoms are firmly bound to platinum. Prolonged boiling of the substance with an acid solution of silver nitrate produces a negligible precipitate, and similar treatment with a dilute solution of potassium hydroxide liberates only traces of ammonia. A yellow precipitate forms readily with a nitric acid solution of ammonium molybdate on warming, and more slowly in the cold. The last reaction, although indicating the presence of some ionised orthophosphate, does not furnish a valid proof of the existence of all the phosphate in the ionised condition. It was found, however, that the phosphate could be completely precipitated by ferric chloride in cold neutral, or very slightly acid, solution; it is thus very improbable that the phosphate is bound directly to platinum, either wholly or with one principal valency out of several available valencies, *e.g.*,  The aqueous solution of the substance reacts alkaline to methyl-orange and litmus. With methyl-orange as indicator, it can be titrated with hydrochloric acid to a sharp end-point, either directly or by solution in excess of standard acid and titration with alkali; two equivalents of hydrochloric acid are required. In accordance with the above evidence and the analysis, the compound may be formulated $\Big[[Pt(NH_3)_4Cl(NH_2)]\Big]^{OH}_{H_2PO_4}$.

Tschugaev (*Z. anorg. Chem.*, 1924, **137**, 401) on theoretical grounds considered likely the formation of compounds of the hypothetical series $[Pt(NH_3)_3Cl(NH_2)_2]X$, of which the compound just described will constitute a member. By the action of alkalis on chloropentamminoplatinic trichloride, he obtained chloroamidotetramminoplatinic dichloride, $[Pt(NH_3)_4Cl(NH_2)]Cl_2$, which he assumed was formed by the loss of the elements of water from a hypothetical intermediate basic salt, $\Big[Pt(NH_3)_5Cl\Big]^{OH}_{Cl_2}$. The capacity of the amido-salt to combine with one equivalent of hydrochloric acid to reform the chloropentammine he explained by the assumption of partial hydrolysis into the basic salt in aqueous solution. From the ready solubility of the chloroamidotetrammine salts in sodium hydroxide, Tschugaev argued that these might undergo in solution a further change to form the hypothetical compounds $[Pt(NH_3)_3Cl(NH_2)_2]Cl$ and $[Pt(NH_3)_2Cl(NH_2)_3]$ and that the gradual change in the nature of the complex would, by exerting an influence on the function of the bound chlorine atom, render possible the formation of $[Pt(NH_3)_5(OH)](OH)_3$, which occurs when the alkaline solution is warmed.

In the reaction under investigation, the conditions are favourable to the formation and detection of such a salt of higher alkaline function, since (1) the platinic complex is combined, not with hydrochloric acid, but with the weak phosphoric acid, which incidentally has a tendency to form insoluble basic salts, and (2) the solubility relationships involve the removal of the dibasic phosphate from the ammoniacal solution, whereas the corresponding chlorides, if formed, would be soluble in excess of sodium hydroxide and would remain undetected.

When the substance is heated gradually to 130°, a molecule of water is expelled with great difficulty; no loss in weight is then suffered until 155—160°, at which temperature the evolution of ammonia commences. The substance suffered hardly any change in titre with methyl-orange by being heated to 130°, although it did not then dissolve so readily in acid; its solution in nitric acid still gave a precipitate with ammonium molybdate in the cold. The water expelled on heating was also determined directly by collecting and weighing the condensed water. At a much higher temperature, the expulsion of a second molecule of water, accompanied by copious evolution of ammonia and sublimation of ammonium chloride, indicated the disruption of the orthophosphate radical. The formulation of the water as hydroxide, rather than simply as water of crystallisation, which is supported by consideration of the mode of formation of the compound by precipitation with ammonia, and by the tendency of phosphoric acid to form basic salts, receives justification in the difficulty and comparatively high temperature of expulsion.

Chloroamidotetramminoplatinic Dihydrophosphate.—The hydroxyhydrophosphate dissolves readily in dilute or glacial phosphoric acid and is not reprecipitated by excess of the reagent. It is interesting to note in this connexion that when disodium phosphate solution is added gradually to a solution of chloropentamminoplatinic chloride, precipitation is not complete until the supernatant liquid is alkaline to litmus, and the precipitate, after thorough washing, has a definite titre with hydrochloric acid, methyl-orange being used as indicator. A solution of the hydroxyhydrophosphate in a slight excess of phosphoric acid was evaporated gently until of syrupy consistency and allowed to cool. Crystals were formed with some difficulty by scratching the sides of the vessel, or more easily by the addition of alcohol. The substance required one equivalent of hydrochloric acid on titration with methyl-orange, and the analysis agreed with the formula $[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)_2$.

Titrations.—Since methyl-orange is unaffected by the primary phosphate radical, the titration of both salts offers no difficulty if the solutions are kept fairly concentrated, and the titration carried to a yellow end-point. The hydroxyhydrophosphate and the dihydrophosphate, dissolved in two and one equivalents respectively of hydrochloric acid, can be titrated fairly sharply with alkali in the presence of excess of calcium chloride with phenolphthalein as indicator. If the titration is carried out in the absence of the calcium chloride, the precipitate is formed so slowly after each addition of alkali that no end-point can be reached; for the same reason it is impossible to detect the point at which conversion into secondary phosphate is complete, *e.g.*, by titration with phenolphthalein in a cold saturated solution of sodium chloride. The acid solution of hydroxyhydrophosphate required just over two equivalents of alkali, and that of the dihydrophosphate four equivalents. The slight excess of alkali can be explained by the fact that chloroamidotetramminoplatinic chloride, which is a slightly weaker base than ammonia at the same dilution (Grünberg and Faermann, *Z. anorg. Chem.*, 1930, **193**, 193), can only be approximately titrated with phenolphthalein, which changes when about 90% of the theoretical amount of acid has been added. The error is less serious in the case of the dihydrophosphate than of the hydroxyhydrophosphate, and, as is to be expected, increases when indicators of higher alkaline exponent are used. However, when due allowance is made for this error, the results of the titrations with phenolphthalein afford a valuable confirmation of the condition of the primary orthophosphate radical in the two salts. It was found impossible to titrate electrometrically the acid solutions of the phosphates by means of a hydrogen electrode, owing to a gradual alteration in potential after each addition of alkali.

The hydroxyhydrophosphate possesses a twofold theoretical interest. As already mentioned, in the dehydrated condition as chlorodiamidotriamminoplatinic hydrophosphate, it forms a member of a new series, $[\mathrm{Pt(NH_3)_3Cl(NH_2)_2}]\mathrm{X}$, capable of combining with two equivalents of hydrochloric acid. Secondly, in its capacity as basic salt, it furnishes a concrete example of the type of intermediate basic salt assumed by Tschugaev in the formation and in the hydrolysis of the chloroamidotetrammine series:

$$\left[\mathrm{Pt(NH_3)_5Cl}\right]^{\mathrm{OH}}_{\mathrm{X_2}} \rightleftharpoons [\mathrm{Pt(NH_3)_4ClNH_2}]\mathrm{X_2} + \mathrm{H_2O}.$$

Significance in General Analytical Work.—It is evident that the conditions of formation of chloroamidotetramminoplatinic hydroxyhydrophosphate are those obtaining on the addition of alkali phosphates to ammoniacal solutions containing small amounts of platinum as platinic chloroammines of the Werner series. The amount of metal dissolved from platinum apparatus during the course of a silicate analysis, especially during the evaporation in platinum dishes of natural silicates containing much iron or chromium, may be appreciable, often reaching 0·01 g. or more. Owing to the complicated reactions involved, any assumption as to the condition of the platinum during the course of the analysis must be made with reserve. It is probable, however, that the platinum is present in solution chiefly as chloroplatinic acid, since the greater part of the metal has been dissolved during the formation of nascent chlorine, *e.g.*, by the action of hydrochloric acid on small amounts of manganate, chromate or vanadate, or by the reduction of ferric chloride by the platinum of the dish. Upon the addition of ammonia a mixture of ammines will be formed, which will pass into the filtrate together with calcium and magnesium salts.

Tests carried out with small known amounts of chloroplatinic acid indicated that in the course of an ordinary silicate analysis small amounts of platinum (2—3 mg.) are precipitated with the magnesium ammonium phosphate. This was confirmed by the examination of ignited magnesium pyrophosphate residues obtained in the actual analyses of a number of rocks of the type referred to above. It appears likely, then, in these circumstances, that some of the dissolved platinum is precipitated with the magnesium in the form of compounds identical with, or similar to, those described in this paper. It is therefore recommended that, in the accurate analysis of silicate rocks and minerals containing appreciable amounts of the elements mentioned above, the dissolved platinum should be separated by means of hydrogen sulphide after the removal of the silica.

EXPERIMENTAL.

Chloroamidotetramminoplatinic Hydroxyhydrophosphate.—Chloroplatinic acid corresponding to 10 g. of platinum, and 100 g. of sodium ammonium hydrogen phosphate were dissolved in 14 litres of water in a loosely-stoppered, wide-mouthed bottle and 50 ml. of aqueous ammonia (*d* 0·880) were added. The solution was kept in a cool place and stirred frequently. In a day or two a white crystalline deposit commenced to form, and more ammonia was then added from time to time. (The separation of ammonium chloroplatinate, which may take place if the solution is too strongly ammoniacal before much phosphate has formed, is to be avoided, as it is difficult to redissolve in cold ammoniacal solution, and heating may result in some hexammine salt formation. Although an appreciable amount of chloroplatinate may be masked by much phosphate, the yellow isometric crystals of the former are easily distinguished microscopically from the anisotropic needles of the phosphate.) At the end of a month the yellow colour of the solution had disappeared and the precipitate was filtered off, washed with cold water, redissolved in dilute hydrochloric acid, and filtered from a small amount of insoluble matter. A few drops of ammonium phosphate solution were added and then ammonium hydroxide was added gradually with constant stirring until reprecipitation was complete. Finally 10 ml. excess ammonia were added and the mixture was kept overnight. The precipitate was filtered off, washed by decantation with cold, then with hot water, and dried. At the end of 2 months, 75% of the platinum had been precipitated from solution.

Chloroamidotetramminoplatinic hydroxyhydrophosphate appears as long colourless prismatic needles when formed in very dilute solution, and as small crystals of great lustre when reprecipitated by ammonia from acid solution. It is readily soluble in dilute acetic acid, and, on warming, in dilute sodium hydroxide solution; one part by weight dissolves in 10,000 parts of water at 15°, in 5,000 parts of water at 100°, and in 50,000 parts of 5% ammonium hydroxide solution at 15° {Found in material dried at 100° : Pt, 45·6; N, 16·4; Cl, 8·2; P, 7·3. $[Pt(NH_3)_4Cl(NH_2)](OH)H_2PO_4$ requires Pt, 45·5; N, 16·3; Cl, 8·3; P, 7·2%}.

For the approximate estimation of the ionised phosphate, a known weight of the substance was dissolved in a little hydrochloric acid, a slight excess of ferric chloride solution added, and then sodium hydroxide until the mixture was alkaline to litmus. A mixture of acetic acid and ammonium acetate was added until the solution was just acid, and the precipitated phosphate was filtered off in the cold and estimated in the usual way. Only traces of platinum were found in the precipitate (Found : PO_4, 21·25. Calc. : total PO_4, 22·15%).

The substance was heated in an air-oven, the temperature being increased by intervals of 5°. The loss in weight was very gradual, 2—3 hours often being required in order to reach a constant weight at a given temperature. At 130° the loss in weight was 4·01% (1 equivalent H_2O requires 4·20%); the weight was then constant until 155—160°, when the evolution of ammonia commenced. The water was also directly determined by cautiously heating the substance in a modified form of Brush and Penfield's tube, the closed end of the tube being enclosed in copper gauze. At a dull red heat a sublimate of ammonium chloride formed at a short distance from the source of heat and water condensed farther on. The part of the tube containing the water was drawn off and weighed, the contents were washed into a vessel, and the empty tube was weighed. The small amount of dissolved ammonia was determined by titration; no trace of chloride or phosphate was present. A correction in the weight of water was made for the weight of ammonia and for the buoyancy due to ammonia gas (Found : H_2O, 8·27, 8·90. Two equivalents H_2O require 8·40%).

Chloroamidotetramminoplatinic Dihydrophosphate.—The preparation has been described in the theoretical part. The crystals, which showed a tendency to clot, were filtered off, ground in a mortar with water, and washed until free from phosphoric acid. The substance was similar in appearance to the hydroxyhydrophosphate and unaffected by boiling water {Found: Pt, 38·15; P, 12·15. $[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)_2$ requires Pt, 38·35; P, 12·2%}.

Titrations.—All titration values, whether of acid or of alkali, are expressed as percentages of HCl of the titrated substance. With methyl-orange, the volume of solution was kept below 100 ml. and the end-point taken as yellow (p_H 4·0). For titrations with phenolphthalein, the substance was dissolved in two or one equivalents of 0·05*N*-hydrochloric acid respectively, 20 ml. of 50% calcium chloride solution and a few drops of indicator were added, and the titration was carried to a decided pink. With indicators of higher exponent than thymolphthalein (p_H 9·3—10·5), *e.g.*, tropæolin O (p_H 11·0—13·0), no end-point could be obtained.

	Methyl-orange.		Phenolphthalein.		Thymolphthalein.
	Found.	Calc.	Found.	Calc.	Found.
Hydroxyhydrophosphate	16·95 acid	17·00 acid	1·07 alk.	nil	4·2 alk.
Dihydrophosphate	7·09 acid	7·16 acid	21·30 alk.	21·48 alk.	24·7 alk.

For the purpose of calculating the theoretical values for phenolphthalein, the base is assumed to be perfectly titratable in the presence of this indicator.

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