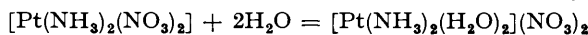


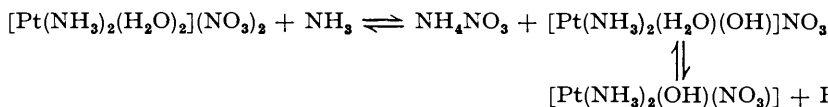
251. *Researches on Ammines. Part IX. Diaquo-, Hydroxoquo-, and Acidhydroxo-diammines of Bivalent Platinum.*

By HERBERT J. S. KING.

It is shown that there are two classes of platinous diammines. Aqueous solutions of the one class, of which *cis*- and *trans*-dichlorodiamminoplatinum are examples, are practically non-electrolytes, but in diammines of the other class, which includes the *cis*- and *trans*-dinitrato-, -dipicrato-, and -sulphato-diammines, the electrical conductivity measurements indicate the presence of salts of bivalent kations. If the platinum atom has a fixed co-ordination number of four, these diacido-compounds must dissolve in water as diaquo-salts, which, however, exist only in solution:

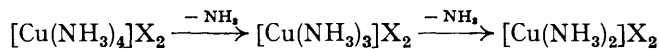


Like other diaquo-salts, these solutions have an acid reaction and are converted by ammonia into hydroxoquo-solutions, though the solids which separate from the hydroxoquo-solutions are acidhydroxodiammines:



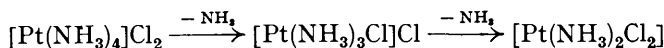
Platinous acidhydroxodiammines, of which the *cis*- and *trans*-nitrato-, -picrato-, and -sulphato-, together with the *cis*-nitro- and *cis*-chloro-derivatives, are now described, have not been prepared previously. *cis*-Nitratohydroxodiamminoplatinum is a non-electrolyte, but conductivity measurements show that the nitrato- and *cis*-sulphato-derivatives dissolve in water as salts of univalent kations, indicating complete conversion into hydroxoquo-diamminoplatinous salts.

It was shown in Part IV (J., 1930, 2307) that the acid radicals of the ammines of bivalent copper are ionised, neither acidotriammines nor diacidodiammines existing in aqueous solution:



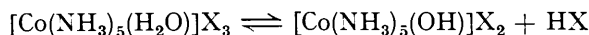
Though it is possible that the solid cuprammine  $[\text{CuA}_2\text{X}_2]$  dissolves in water as  $[\text{CuA}_2(\text{H}_2\text{O})_x]\text{X}_2$ , there is no evidence of this, and no justification for assuming a co-ordination number of four, since hexammines and pentammines are readily obtainable, and are little inferior in stability to the tetrammines. It was also shown that in aqueous solution considerable decomposition of the complex kation occurred, loss of ammonia amounting to  $\frac{1}{2}$  mol. in the case of a 0.1M-solution of tetramminocupric nitrate. This inferior stability of the complex, accompanied by variable co-ordination number and inability to form acido-complexes, characterises the ammines of most bivalent metals.

On the other hand, trivalent cobalt, chromium, etc., form complexes which undergo no decomposition in aqueous solution, and this stability of the complex kation is associated with fixed co-ordination number and formation of stable acido-complexes. Bivalent platinum similarly forms the extremely stable 4-covalent tetramminoplatinous complex, in which acid radicals can replace ammonia with successive formation of acidotriammines and diacidodiammines, sufficiently stable to exist as such in aqueous solution :



Further treatment with ammonia has no effect on the tetramminoplatinous complex.

Werner (*Ber.*, 1907, **40**, 4098) showed that the acid reaction of aquopentamminocobaltic salt solutions is due to incipient conversion into the corresponding hydroxopentammine :



Treatment with excess of concentrated aqueous ammonia resulted in complete conversion into the hydroxopentamminocobaltic salt, with elimination of the ammonium salt of the acid. Aquopentamminochromic salts have similarly been converted into hydroxopentammines (Part II, J., 1925, **127**, 2100). It appeared remarkable that, though the hydroxo-, aquo-equilibrium plays a prominent part in the chemistry of other stable aminocomplexes of fixed co-ordination number, neither hydroxo- nor aquo-salts had been isolated in the platinum series, and the purpose of the present investigation was to ascertain whether such compounds exist.

Dichlorodiamminoplatinum has long been known in two isomeric forms, usually regarded as *cis*- and *trans*-modifications of the planar molecule  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , and aqueous solutions of each are practically non-electrolytes, as required by the formula. Although there is thus little tendency for water molecules to displace chloride radicals from the complex, with formation of the chloroquo- or the diaquo-chloride,  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$  or  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{Cl}_2$ , it is significant that in each case the electrical conductivity of an *M*/1000-solution increases noticeably with time (Werner and Miolati, *Z. physikal. Chem.*, 1893, **12**, 49; Drew, Pinkard, Wardlaw, and Cox, J., 1932, 988), presumably owing to formation of a minute equilibrium concentration of aquo-salt. Both compounds interact with soluble silver salts, with complete elimination of chlorine as silver chloride. In this way, both *cis*- and *trans*-dinitro-, -dinitrato-, -sulphato-, and other diammines are obtained, and it was shown by Jensen (*Z. anorg. Chem.*, 1936, **229**, 252) that, whereas the dinitro- and *cis*-di-iodo-diammines resemble the dichloro-compounds in being practically non-electrolytes in aqueous solution, the electrical conductivities of the *cis*- and *trans*-dinitrato- and the *cis*-sulphato-diammines indicate considerable ionisation.

In view of the pronounced tendency of the nitrate radical to form aquo- rather than acido-salts, attempts were made to prepare the diaquo-nitrates. Since the conversion of aquo- into acido-ammines is favoured by heating, the *cis*-dichlorodiammine was shaken with aqueous silver nitrate, and the filtrate evaporated in a vacuum, both operations being conducted at room temperature. Even under these conditions, however, the solid product proved to be the anhydrous dinitratodiammine,  $[\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2]$ . Complete elimination of chlorine from the *trans*-dichlorodiammine was only accomplished by boiling with silver nitrate, and in this case also the solid product was anhydrous dinitratodiamminoplatinum. These substances were much more soluble than the dichloro-compounds, though prolonged warming and shaking were required to dissolve them, and the aqueous solutions were acid to litmus, whereas those of the dichlorodiammines were neutral. They were reconverted into *cis*- and *trans*-dichlorodiamminoplatinum, respectively, when boiled with hydrochloric acid. Jensen (*loc. cit.*) recorded the electrical conductivities of the aqueous solutions at one concentration only, and his values were lower than would be expected for salts of a bivalent kation. The interpretation of the conductivity data which are now recorded for various concentrations is complicated by the acidity of the solutions, but they indicate clearly that both nitrate radicals are ionised in each case (see Table I and discussion on p. 1345). If bivalent platinum has a fixed co-ordination number of four, it is evident that solution of the dinitratodiammines is

accompanied by co-ordination of two molecules of water:  $[\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2] + 2\text{H}_2\text{O} = [\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ . This explains the slow rate of solution. Co-ordination of one water molecule only would yield  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3$ , but the recorded molecular conductivities are approximately double the probable values for this compound. Since the isomeric dinitratodiammines retain their individuality in aqueous solution, it is still necessary to assume the presence of water molecules in the complex of one or both of the ionised solutions, even if the platinum atom is not taken to be quadricovalent, the formula  $[\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$  providing no possibilities of isomerism. The conclusion that the aqueous solutions contain aquo-salts is strongly supported by their acid reaction, which is readily accounted for by partial conversion into the hydroxoquo-salt:  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \rightleftharpoons [\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{OH})]\text{NO}_3 + \text{HNO}_3$ . Measurement of the  $p_{\text{H}}$  values of  $M/256$ -solutions indicated that the proportions of hydroxoquo-salt present in the equilibrium mixtures were 4% for the *cis*- and 10% for the *trans*-compound.

By double decomposition between ammonium picrate and aqueous solutions of the *cis*- and *trans*-dinitratodiammines, the isomeric *dipicratodiammines* were obtained. The conductivity data for the aqueous solutions indicated the presence of two ionised picrate radicals in each case. The yellow products were hydrated (4 and  $3\text{H}_2\text{O}$  respectively) and readily yielded orange anhydrous compounds. This colour change may indicate conversion from the aquo- into the acido-compound, but the water was very readily removed and no difference in electrical conductivity could be detected between the anhydrous and the hydrated compounds. Thus the former, and probably the latter also, were dipicratodiammines, dissolving in water, however, mainly as diaquodiamminoplatinous picrate,  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2$ .

With silver sulphate, *cis*- and *trans*-dichlorodiamminoplatinum yielded the corresponding *sulphatodiammines*, mono- and di-hydrated respectively. Both proved to be ionised in aqueous solution, though the conductivity of the solutions increased on standing, showing that the process of aqutation was slower than in the other cases investigated. The final figures indicated practically complete ionisation of the sulphate radicals. Both solutions had an acid reaction, and measurement of the  $p_{\text{H}}$  values indicated that in each case 10% conversion of the diaquo- into the hydroxoquo-salt had taken place.

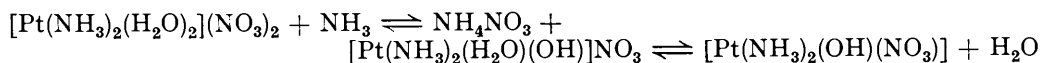
The so-called hydroxides of the *cis*- and *trans*-diamminoplatinous series have been variously described as weakly and strongly alkaline, apparently because their aqueous solutions are sufficiently alkaline to turn litmus blue, and this alkalinity is usually explained by aqutation of the non-valent complex  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$  to  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{OH})]\text{OH}$  or  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{OH})_2$ . The electrical conductivities of aqueous solutions of these compounds have now been determined, and the results indicate that they are practically non-electrolytes, the values obtained at  $25^\circ$  and a dilution of 256 l. being 13.4 and 7.2 mhos: the expected values for the ionised hydroxides  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{OH})]\text{OH}$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{OH})_2$  are about 250 and 500 mhos respectively. The dihydroxodiammines are very soluble in water and their molecular weights have been determined by the cryoscopic method, the results showing that both are monomeric. These compounds must evidently be formulated  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$  both in the solid state and in aqueous solution.

There are thus two well-defined classes of platinum diacidodiammines. In members of the one class, which includes the dichloro-, dinitro-, *cis*-di-iodo-, and dihydroxo-compounds, water molecules are not able to displace acid radicals from the complex, and the equilibrium in the reaction  $[\text{Pt}(\text{NH}_3)_2\text{X}_2] + 2\text{H}_2\text{O} \rightleftharpoons [\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{X}_2$  lies almost entirely to the left. In the case of the other class, to which the dinitrato-, dipicrato-, and sulphato-compounds belong, the equilibrium lies almost entirely to the right. These compounds dissolve in water as ionised diaquo-salts, in equilibrium with a small concentration of hydroxoquo-salt and free acid.

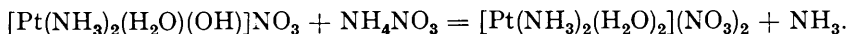
Although both classes are converted into tetrammines by boiling with aqueous ammonia, it was found that, when liquid ammonia was used, ammonia molecules, like water molecules, were unable to displace acid radicals from complexes of the first class. For instance, the *cis*- and *trans*-dichloro- and dinitro-diammines were recovered unchanged from solution in this medium. On the other hand, *cis*-dinitratodiamminoplatinum was

completely converted into tetramminoplatinous nitrate when dissolved in liquid ammonia. Displacement of the nitrate radicals was not quite complete in the case of the *trans*-dinitratodiammine, the product containing between three and four g.-mols. of ammonia for each g.-atom of platinum.

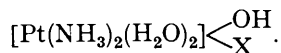
Conversion of *cis*- and *trans*-diaquodiamminoplatinous nitrate in aqueous solution into the corresponding hydroxoquo-salts was readily accomplished by treating the cold solutions with one mol. of aqueous ammonia. The hydroxoquo-diammines, however, like the diaquodiammines, could not be isolated as such, the solid products being anhydrous and hemihydrated *nitratohydroxodiamminoplatinum* respectively:



That the *aqueous solutions* of these substances contained salts of univalent kations was shown by measurement of electrical conductivity (see Table III). The conductivities of the *cis*- and *trans*-compounds at 25° and a dilution of 1024 l. were 123.5 and 132.6 mhos; the corresponding value recorded by Werner and Miolati for  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$  is equivalent to 123.8 mhos (*Z. physikal. Chem.*, 1894, **14**, 511). The platinum atom being assumed to be still 4-covalent, it follows that solution of the nitratohydroxodiammines was accompanied by co-ordination of one molecule of water, with formation of the ionised hydroxoquo-salts,  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{OH})]\text{NO}_3$ . Even if no assumption of quadricovalency is made, it is still necessary to assume the presence of at least one water molecule in one or both of the ionised solutions, the formula  $[\text{Pt}(\text{NH}_3)_2(\text{OH})]\text{NO}_3$  providing no possibilities of isomerism. The ionisation of the nitrate radicals in the aqueous solutions was confirmed by treatment with ammonium picrate; immediate precipitation of the anhydrous *picratohydroxodiammines* then occurred. The *cis*- and *trans-sulphatodihydroxo*-derivatives,  $[\{\text{Pt}(\text{NH}_3)_2(\text{OH})\}_2\text{SO}_4] \cdot 2\text{H}_2\text{O}$ , were obtained by treating aqueous solutions of the sulphato-diammines with the calculated amount of aqueous ammonia. Conductivity data for the former showed that it dissolved in water as  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{OH})]_2\text{SO}_4$ , but the *trans*-compound was too sparingly soluble for its conductivity to be measured. The nitratohydroxo- and sulphatodihydroxo-derivatives proved to be less soluble than the corresponding diacidodiammines, and, as in the case of the latter compounds, solution in cold water was very slow, probably on account of the slowness of the aquation process. The aqueous solutions resembled those of the hydroxopentammino-cobaltic and -chromic salts in liberating ammonia when boiled with ammonium salts:



They were neutral, whereas those of hydroxopentamminocobaltic salts are alkaline to litmus. There was thus no tendency to formation of the basic aquo-salts



It is remarkable that, though the dichloro- and dihydroxo-diammines dissolve in water without aquation, *cis-chlorohydroxodiamminoplatinum*,  $[\text{Pt}(\text{NH}_3)_2(\text{OH})\text{Cl}]$ , which was prepared by interaction of the *cis*-sulphatodihydroxo-derivative and barium chloride, was very soluble in water, and the conductivity data indicated considerable though incomplete ionisation (see Table IV). Thus partial aquation to  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})(\text{OH})]\text{Cl}$  had taken place. On the other hand, *cis-nitrohydroxodiamminoplatinum* proved to be a non-electrolyte, probably because in this case aquation would require preliminary conversion of the nitro-radical into the nitrito-form.

The acidohydroxodiammines, of which nitrate-, picrate-, sulphato-, chloro-, and nitro-derivatives have been obtained, constitute a new class of platinous ammines.

The results obtained in the course of this work are adequately explained by Werner's assumption that the bivalent platinum atom forms a 4-covalent planar complex, of which the two isomeric series of platinous diammines contain *cis*- and *trans*-forms. Striking similarity in the chemical behaviour of the two series is shown, affording strong support to the view that their isomerism is spatial rather than structural. Such differences as

exist appear to depend on the more sparing solubility of the *trans*-compounds. An alternative possibility is that one isomeric series is either *cis*- or *trans*-planar, and the other is tetrahedral, and this would not affect the formulations given. The suggestion of Drew, Pinkard, Wardlaw, and Cox (*loc. cit.*), that the compounds usually formulated as *cis*- and *trans*-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] are structural rather than spatial isomerides, appears very improbable if extended to the dinitratodiammines, since in each case both nitrate radicals are ionised in aqueous solution.

It has been shown that neither diaquo- nor hydroxoquo-diamminoplatinous salts can normally be isolated in the solid state, but it is evident that the *trans*-sulphato-diammine should be either a diaquo- or an aquo-salt. The solid compound was dihydrated, but the low conductivity of freshly prepared solutions was inconsistent with formulation as a diaquo-salt. The solid compound is therefore considered to be  $\left[ \text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\left(\text{O}_2\text{S}\begin{array}{l} \diagup \text{O} \\ \diagdown \end{array}\right) \right]_{-1} \text{O} \cdot \text{H}_2\text{O}$ , the sulphate radical being attached to the platinum atom by a single link only. Diammines containing other dibasic acid radicals are being investigated, since the existence of an anhydrous *trans*-diammine, with such a radical in the complex, would be inconsistent with Werner's formulation of these compounds.

#### EXPERIMENTAL.

*cis*-Dichlorodiamminoplatinum was prepared from ammonium chloroplatinite by Jørgensen's method (*Z. anorg. Chem.*, 1900, **24**, 181). The *trans*-isomeride was obtained by heating tetramminoplatinous chloride for 20 minutes at 250°, and recrystallising the product from boiling water.

*Dinitratodiamminoplatinum*.—(a) *cis*-Compound. 1 G. of *cis*-dichlorodiamminoplatinum was shaken mechanically with 1.1322 g. (1 mol.) of silver nitrate and 15 c.c. of water at room temperature. Separation of silver chloride began almost immediately and was complete in 3 hours. The filtrate, containing *cis*-diaquodiamminoplatinous nitrate, was free from silver and had a slight acid reaction. It was dehydrated over sulphuric acid in a vacuum, leaving pale yellow needles (1.1 g.). 7.88 G. dissolved in 1 l. of water at 18°, but solution was slow (Found: Pt, 55.0; N, 16.2; NO<sub>3</sub>, 34.7. Calc. for [Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]: Pt, 55.2; N, 15.9; NO<sub>3</sub>, 35.1%). The aqueous solution, when boiled with hydrochloric acid, yielded *cis*-dichlorodiamminoplatinum. The compound was previously prepared by Cleve (*K. Sv. Vet. Akad. Handl.*, 1872, **10**, No. 9).

(b) *trans*-Compound. *trans*-Dichlorodiamminoplatinum was mixed as above with aqueous silver nitrate and refluxed for 20 minutes. The slightly acid filtrate was left in a vacuum over sulphuric acid until cream-coloured crystals remained (1.1 g.). The preparation was carried out in diffused light, as the compound darkened in sunlight (Found: Pt, 55.4; N, 15.8%). It dissolved very slowly in water unless this was heated almost to the b. p., but was almost as soluble as the *cis*-compound, 6.62 g. dissolving in 1 l. at 18°. The aqueous solution, when boiled with hydrochloric acid, yielded *trans*-dichlorodiamminoplatinum. Cleve (*loc. cit.*), who prepared the compound from *trans*-di-iododiamminoplatinum, stated that the product prepared from the dichlorodiammine is not chlorine-free: the statement is incorrect.

*Nitratohydroxodiamminoplatinum*.—(a) *cis*-Compound. 1 G. of *cis*-dichlorodiamminoplatinum was converted as above into *cis*-diaquodiamminoplatinous nitrate in aqueous solution, and this was treated at room temperature with 6.66 c.c. (1 mol.) of *n*/2-ammonia. The neutral solution was left in a vacuum over sulphuric acid for 10 hours. The crystals that had then separated were collected, washed successively with a little water, alcohol, and ether, and left overnight in a vacuum over soda-lime. (Unless otherwise stated, the compounds described below were similarly prepared for analysis.) 0.6 G. of four-sided plates was obtained, slightly yellower than the dinitratodiammine (Found: Pt, 63.3; N, 13.8; NO<sub>3</sub>, 19.7. [Pt(NH<sub>3</sub>)<sub>2</sub>(OH)(NO<sub>3</sub>)] requires Pt, 63.3; N, 13.6; NO<sub>3</sub>, 20.1%). The compound was fairly soluble in water, dissolving slowly at room temperature and readily at 40°. It was recovered unchanged from solution in liquid ammonia.

(b) *trans*-Compound. 1 G. of *trans*-dichlorodiamminoplatinum was converted as above into *trans*-diaquodiamminoplatinous nitrate in aqueous solution, and this was treated in the cold with 1 mol. of *n*/2-ammonia. The neutral yellow solution was left overnight in a vacuum over sulphuric acid, and a scanty black precipitate then filtered off. On further concen-

tration, a microcrystalline product separated, yellower and less soluble than the *cis*-isomeride. The *compound* darkened on exposure to sunlight, and the preparation was carried out, as far as possible, with exclusion of daylight (Found : Pt, 61.2; N, 13.3; NO<sub>3</sub>, 19.2. [Pt(NH<sub>3</sub>)<sub>2</sub>(OH)(NO<sub>3</sub>)<sub>2</sub>], ½H<sub>2</sub>O requires Pt, 61.5; N, 13.2; NO<sub>3</sub>, 19.5%).

*Dipicratodiamminoplatinum*.—(a) *cis-Compound*. A solution of *cis*-diaquodiamminoplatinous nitrate, prepared as described above, was added to 3.05 g. (100% excess) of picric acid which had been converted into the ammonium salt in 400 c.c. of water. A yellow precipitate (1.4 g. of acicular aggregates) was obtained almost immediately (Found : Pt, 26.0; N, 14.8; H<sub>2</sub>O, 9.5. [Pt(NH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>O<sub>7</sub>N<sub>3</sub>)<sub>2</sub>], 4H<sub>2</sub>O requires Pt, 25.8; N, 14.8; H<sub>2</sub>O, 9.5%). At 85° the *compound* lost water rapidly, becoming brick-red. Dehydration was complete in 3 hours, without loss of ammonia. The anhydrous dipicratodiammine was also obtained by leaving the tetrahydrate in a vacuum over sulphuric acid for 10 days (Found : N, 16.2. Calc. : N, 16.4%). 1.81 G. of the tetrahydrate dissolved in 1 l. of water at 18°, but solution was very slow unless the water was warmed to 40°.

(b) The *trans-compound* was similarly prepared from a solution of *trans*-diaquodiamminoplatinous nitrate, the theoretical amount of ammonium picrate in 200 c.c. of water being used. No immediate precipitate was obtained, but aggregates of large yellow needles separated during 1 hour (Found : Pt, 26.6; N, 15.0; H<sub>2</sub>O, 7.1. [Pt(NH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>2</sub>O<sub>7</sub>N<sub>3</sub>)<sub>2</sub>], 3H<sub>2</sub>O requires Pt, 26.4; N, 15.2; H<sub>2</sub>O, 7.3%). The water was completely removed in a few days over phosphoric oxide or in 2 hours at 85°; the anhydrous *compound* was orange. The trihydrate was much more soluble than the *cis*-isomeride, 5.63 g. dissolving in 1 l. of water at 18°.

*Picratohydroxodiamminoplatinum*.—(a) *cis-Compound*. 0.5 G. of *cis*-nitratohydroxodiamminoplatinum was dissolved in 20 c.c. of water at 40°, and the cooled solution was added to 0.445 g. (1.2 mols.) of picric acid which had been converted into the ammonium salt in 60 c.c. of water. An immediate microcrystalline yellow precipitate was obtained (0.55 g.) (Found : Pt, 40.9; N, 14.9. [Pt(NH<sub>3</sub>)<sub>2</sub>(OH)(C<sub>6</sub>H<sub>2</sub>O<sub>7</sub>N<sub>3</sub>)] requires Pt, 41.1; N, 14.8%).

(b) *trans-Compound*. *trans*-Nitratohydroxodiamminoplatinum was similarly treated with 1.2 mols. of ammonium picrate, yielding an immediate microcrystalline yellow precipitate (Found : Pt, 41.3; N, 14.6%).

*Sulphatodiamminoplatinum*.—(a) *cis-Compound*. 1 G. of *cis*-dichlorodiamminoplatinum was shaken with 1.0386 g. (1 mol.) of silver sulphate and 20 c.c. of water at room temperature for 4 hours. The slightly acid filtrate, containing diaquodiamminoplatinous sulphate, gave an immediate precipitate in the cold with barium chloride. It was evaporated to dryness in a vacuum over sulphuric acid, yielding 0.87 g. of pale yellow crystals, which darkened on exposure to sunlight. No water was removed at 85° (Found : Pt, 57.0; N, 8.3; SO<sub>4</sub>, 28.0. [Pt(NH<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>)], H<sub>2</sub>O requires Pt, 56.9; N, 8.2; SO<sub>4</sub>, 28.0%). Cleve (*loc. cit.*), who previously prepared the *compound*, described it as anhydrous. It is fairly soluble, but dissolves rather slowly unless warmed.

(b) *trans-Compound*,  $\left[ \text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\left(\text{O}_2\text{S}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\right) \right] \cdot \text{H}_2\text{O}$ . 1 G. of *trans*-dichlorodiamminoplatinum was refluxed with 1 mol. of silver sulphate and 20 c.c. of water for 20 minutes. The slightly acid filtrate was evaporated to dryness in a vacuum over sulphuric acid, yielding 1.1 g. of pale yellow crystals, almost identical in appearance with those of the *cis*-isomeride (Found : Pt, 54.3; N, 8.0; SO<sub>4</sub>, 27.0. Pt(NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O requires Pt, 54.0; N, 7.8; SO<sub>4</sub>, 26.6%). Only ½H<sub>2</sub>O was removed in 3 hours at 85°. The *compound* dissolved much more rapidly in cold water than the *cis*-isomeride, though the actual solubility was about the same. It darkened on exposure to sunlight, which should be excluded during its preparation. Cleve (*loc. cit.*) described it as a monohydrate.

*Sulphatodihydroxotetramminodiplatinum*.—(a) *cis-Compound*. 1 G. of *cis*-dichlorodiamminoplatinum was converted as above into *cis*-diaquodiamminoplatinous sulphate in aqueous solution, and this was treated at room temperature with 6.66 c.c. (1 mol.) of *N*/2-ammonia. It became turbid after a few minutes and after it had been left overnight in a vacuum over sulphuric acid, 0.65 g. of glistening yellow hexagonal prisms had separated (Found : Pt, 62.7; N, 9.2; SO<sub>4</sub>, 15.2. [Pt(NH<sub>3</sub>)<sub>2</sub>(OH)]<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O requires Pt, 62.5; N, 9.0; SO<sub>4</sub>, 15.4%). 1½H<sub>2</sub>O were removed at 85°. The aqueous solution was neutral to litmus and liberated ammonia when boiled with ammonium sulphate, an aqueous solution of diaquodiamminoplatinous sulphate being formed. 3.23 G. of the *compound* dissolved in 1 l. of water at 18°.

(b) *trans-Compound*. Similar treatment of *trans*-dichlorodiamminoplatinum (1 g.) gave 0.65 g. of a microcrystalline yellow *product*, which was extremely sparingly soluble, even in boiling water (Found : Pt, 62.7; N, 9.0; SO<sub>4</sub>, 15.2%).

*cis-Chlorohydroxodiamminoplatinum*.—A suspension of 1 g. of *cis*-sulphatodihydroxotetramminodiplatinum in 20 c.c. of water was boiled for a few minutes with 0.391 g. (1 mol.) of barium chloride. The yellow filtrate was left in a vacuum over sulphuric acid. No solid separated until the water was completely removed; pale yellow crystals then remained (Found: Pt, 67.1; N, 9.8; Cl, 12.0.  $[\text{Pt}(\text{NH}_3)_2(\text{OH})\text{Cl}]_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires Pt, 67.1; N, 9.6; Cl, 12.2%). The compound was readily soluble and the solution was slightly alkaline to litmus. When it was boiled with ammonium chloride, ammonia was liberated, with separation of *cis*-dichlorodiamminoplatinum on cooling. Silver nitrate precipitated silver chloride from the aqueous solution.

*cis-Nitrohydroxodiamminoplatinum*.—1 G. of *cis*-sulphatodihydroxotetramminodiplatinum was boiled for a few minutes with 0.3961 g. (1 mol.) of barium nitrite and 40 c.c. of water. The liquid was filtered hot and concentrated in a vacuum over sulphuric acid; yellow acicular aggregates, similar in colour to the dichlorodiammine, were obtained. The product was fairly soluble, 8.13 g. dissolving in 1 l. of water at 18° (Found: Pt, 66.4; N, 14.2.  $[\text{Pt}(\text{NH}_3)_2(\text{OH})(\text{NO}_2)]$  requires Pt, 66.8; N, 14.4%). The aqueous solution was slightly alkaline, and liberated ammonia when boiled with ammonium salts.

*Dihydroxodiamminoplatinum*.—(a) *cis-Compound*. *cis*-Sulphatodihydroxotetramminodiplatinum was heated to boiling with the calculated amount of barium hydroxide solution, and the filtrate evaporated to dryness in a vacuum over sulphuric acid (Found: Pt, 73.7; N, 10.7. Calc. for  $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$ : Pt, 74.1; N, 10.6%).

(b) *trans-Compound*. The sulphatodiammine was boiled with the calculated amount of barium hydroxide (Klason, *J. pr. Chem.*, 1903, 67, 27), and the filtrate evaporated to dryness in a vacuum over sulphuric acid (Found: Pt, 74.3; N, 10.4%).

*Action of Liquid Ammonia on Diacidodiammines*.—The substances were dissolved in liquid ammonia, and the excess allowed to evaporate. The products were analysed with the following results:

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ —Found: N, 9.1 ( <i>cis</i> ), 9.2 ( <i>trans</i> ). Calc.: N, 9.3%.
$[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ —Found: Pt, 60.6 ( <i>cis</i> ), 60.5 ( <i>trans</i> ). Calc.: Pt, 60.7%.
$[\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2]$ —Found: Pt, 50.1 ( <i>cis</i> ), 51.8 ( <i>trans</i> ); N, 21.7 ( <i>cis</i> ), 19.8 ( <i>trans</i> ). Calc. for $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ : Pt, 50.4; N, 21.7%.

*Molecular-weight Determinations*.—Cryoscopic method. The Beckmann apparatus was used, with water as solvent.

	w, g.	Δ.	Water, g.	M.
<i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$ .....	0.2835	0.127°	17.09	243
<i>trans</i> - $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$ .....	0.3530	0.150	17.39	252
		0.3707	17.21	253
				Calc., 263.3

*PH Values*.—The colorimetric method was used. With m/256-solutions, the following values were obtained:

<i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2]$ ... 3.8	<i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{OH})(\text{NO}_3)]$ ..... 7.0	<i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{SO}_4)]$ ... 3.4
<i>trans</i> -" ... 3.4	<i>trans</i> -" ..... 7.0	<i>trans</i> -" ... 3.4

*Electrical Conductivities at 25°* (see Part II, *loc. cit.*).—The conductivities at infinite dilution were obtained by means of the  $1/\lambda - (C\lambda)^{n-1}$  graph. The specific conductivity of the water was  $0.99 - 1.3 \times 10^{-6}$  mho at 25°.

TABLE I.

*Diaquodiammino- and Tetrammino-platinous Salts.*

<i>v</i> .....	128	256	512	1024	2048	∞
$\lambda$ for <i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ * .....	225.7	237.7	250.5	263.9	—	—
" <i>trans</i> - .....	—	250.2	267.3	277.4	—	—
" $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ .....	244.5	261.3	274.5	283.9	—	312.0
						( <i>n</i> = 1.54)
" <i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{C}_6\text{H}_5\text{O}_7\text{N}_3)_2$ .....	—	—	—	182.6	214.4	—
" <i>trans</i> - .....	—	186.1	195.1	224.0	252.5	—
" <i>cis</i> - $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4$ { <i>a</i> , zero time .....	138	159	186	217	—	—
		148.9	173.8	198.4	234.1	—
" <i>trans</i> - .....	—	109	125	—	—	—
		—	176.3	219.3	240.2	—
" $[\text{Pt}(\text{NH}_3)_4]\text{SO}_4$ .....	168.2	217.3	242.4	260.6	—	—

\*  $\lambda = 213.6$  mhos for *v* = 64.

The solutions were prepared rapidly, by shaking and warming to 40°. The conductivities of the tetramminoplatinous salts, and of the diaquodiamminoplatinous nitrates and picrates, showed no variation on standing. In the case of *cis*-diaquodiamminoplatinous sulphate, however, the conductivities increased rapidly during the first hour (5% at a dilution of 1024 l.) and had reached equilibrium after 24 hours. The values recorded for zero time were obtained by extrapolation. The increase in conductivity with time was still more rapid in the case of *trans*-diaquodiamminoplatinous sulphate, a 4% increase taking place in 10 minutes at a dilution of 1024 l. Equilibrium in this case was reached after 3 days.

TABLE II.

*Diacidodiamminoplatinum Complexes.*

$\nu$ .....	128	256	512	1024
$\lambda$ for <i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] .....	—	—	—	4.50
„ <i>trans</i> - .....	—	—	—	3.82
„ <i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> ] .....	12.5	13.4	—	—
„ <i>trans</i> - .....	6.6	7.2	11.4	—

The conductivities of the dinitrodiammines confirm those recorded by Jensen (*loc. cit.*) for higher concentrations, and showed no increase after 24 hours. Those of the dihydroxodiammines increased very slightly with time (1% in 24 hours for the *trans*-compound at a dilution of 128 l.).

TABLE III.

*Hydroxo-aquodiamminoplatinous Salts.*

$\nu$ .....	64	128	256	512	1024	2048	$\infty$
$\lambda$ for <i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)(OH)]NO <sub>3</sub> .....	108.1	113.3	117.3	121.0	123.5	—	130.2
„ <i>trans</i> - .....	—	109.9	—	126.5	132.6	—	( $n = 1.50$ )
„ <i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)(OH)] <sub>2</sub> SO <sub>4</sub> .....	—	—	161.9	184.6	206.5	238.2	—

There was no variation of conductivity with time.

TABLE IV.

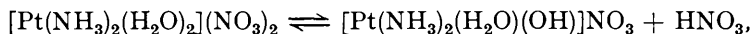
*Acidohydroxodiamminoplatinum Complexes.*

$\nu$ .....	128	256	512	1024
$\lambda$ for <i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (OH)(NO <sub>2</sub> )] .....	{ a —	10.4	11.6	—
	{ b —	—	13.5	—
„ <i>cis</i> -[Pt(NH <sub>3</sub> ) <sub>2</sub> (OH)Cl] .....	{ a 64.0	69.7	—	—
	{ b 76.9	84.8	93.5	95.6
	{ c 82.0	88.2	96.6	114.7

Measurements were made (a) immediately after solution, (b) after 24 hours, (c) after 7 days.

## DISCUSSION OF RESULTS.

In Table I the conductivities of the *cis*- and *trans*-diaquodiamminoplatinous nitrate solutions are compared with those of tetramminoplatinous nitrate, which are of the same order. The acidity of these solutions being assumed to be due to the equilibrium reaction



an approximate correction can be applied. For the *cis*-solution at a dilution of 256 l., the  $p_{\text{H}}$  of 3.8 indicates a hydrogen ion and [Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)(OH)] ion concentration of 0.000159. The corrected molecular conductivity due to diaquo-salt only is 225 mhos, the uncorrected value of 237.7 mhos given in the table being 5.5% too high. Similarly the value of 250.2 mhos given in the table for the *trans*-solution is subject to a correction of 14%, the corrected value being 216 mhos. These corrected values are 14% and 17% lower than the corresponding value for tetramminoplatinous nitrate. It was similarly found by Lamb and Yngve (*J. Amer. Chem. Soc.*, 1921, **43**, 2352) that the mobility of the diaquotetramminocobaltic ion is 9% lower than that of the hexamminocobaltic ion.

The final recorded values for the *cis*- and *trans*-diaquo-sulphates are subject to similar corrections and comparison with the corresponding values for tetramminoplatinous sulphate indicates fairly complete aquation.



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The conductivities of the aqueous solutions of the nitratohydroxo- and sulphatodihydroxo-compounds are given in Table III. It was shown in Part II (*loc. cit.*) that ammine salt solutions normally give a rectilinear  $\lambda-C^{1/3}$  graph, curvature of the graph usually indicating progressive aquation. For *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(OH)(NO<sub>3</sub>)] a rectilinear  $\lambda-C^{1/3}$  graph was obtained, indicating complete aquation to the hydroxoaquo-salt, even at the higher concentrations. The data recorded in Table IV for *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(OH)Cl] indicate very incomplete aquation at the higher concentrations, and equilibrium was reached very slowly, but the final value obtained for a dilution of 1024 l. was only 11% lower than the expected value for the fully ionised salt [Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)(OH)]Cl.

*Ionic Mobilities.*—The mobilities of the tetramminoplatinous and *cis*-hydroxoaquodiamminoplatinous ions, deduced from the data for the nitrates, are 169.2 and 58.8 mhos respectively at 25°. The values employed for the mobilities of the nitrate and hydrogen ions are 71.4 and 350 mhos.

The author is indebted to the Chemical Society for a grant.

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[Received, May 21st, 1938.]

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