

386. *Researches on Ammines. Part X. Triammines of Bivalent Platinum.*

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There are shown to be two classes of platinous triammines. The one class, which includes the chloro-, bromo-, and nitro-triamminoplatinous salts, dissolve in water as such, and are shown by conductivity measurements to behave as salts of univalent kations. Solutions of these compounds also yield *pink* chloroplatinites and acido-triammine picrates. The other class dissolve with complete or substantial conversion into aquo-triammines: $[\text{Pt}(\text{NH}_3)_3\text{X}]\text{X} + \text{H}_2\text{O} = [\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_2$. The nitrate-, sulphato-, and picrato-triammines undergo complete aquation, and conductivity measurements indicate the presence of salts of bivalent kations. Solutions of these salts yield aquotriamminoplatinous chloroplatinite and picrate, the former being green. Conversion into aquo-salt is partial in the cases of carbonato- and oxalato-triammines.

In $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)]\text{Cl}_2$ the ethylenediamine molecule is shown to be attached to platinum at one point only, so that the platinous atom is still 4-covalent. If one molecule of ammonia is expelled, the ethylenediamine molecule occupies *two* positions in the complex. It is concluded that bivalent platinum has no tendency to exist in the 5-covalent state.

THE acidotriamminoplatinous salts are of particular interest since they constitute the only group of metallic ammines hitherto investigated in which an acid radical forms part of a 4-covalent kation. The existence of two classes of platinous diacido-diammines was demonstrated in Part IX (*J.*, 1938, 1338). Members of the one class, which includes the dichloro-, dinitro-, di-iodo-, and dihydroxo-compounds, dissolve in water unchanged, while the other class, to which the dinitrato-, dipicrato-, and sulphato-diammines belong, dissolve as diaquo-salts, which, however, exist only in solution: $[\text{Pt}(\text{NH}_3)_2\text{X}_2] + 2\text{H}_2\text{O} \rightleftharpoons [\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{X}_2$. It has now been shown that there are similarly two types of platinous acido-triammines. In aqueous solution, the equilibrium $[\text{Pt}(\text{NH}_3)_3\text{X}]\text{Y} + \text{H}_2\text{O} \rightleftharpoons [\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{XY}$ lies almost entirely to the left in the one case and to the right in the other, the behaviour depending on the nature of X. In the former case, the solutions are neutral, while in the latter they contain aquotriamminoplatinous salts, the noticeable acidity of which (less pronounced, however, than that of the corresponding diammines) is due to the hydroxo-aquo-equilibrium: $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_2 \rightleftharpoons [\text{Pt}(\text{NH}_3)_3(\text{OH})]\text{X} + \text{HX}$.

The aquotriammine salts, like the diaquodiammines, usually exist only in solution, the solid compounds which separate from the solutions being the original acidotriammines. The solutions containing acido-triammines give, with a soluble chloroplatinite, pink precipitates of the corresponding chloroplatinites, while those containing aquo-triammines yield a green precipitate of aquotriamminoplatinous chloroplatinite. The two classes also react differently with ammonium picrate, the former reacting with one mol. of picrate to form an acidotriamminoplatinous picrate while the latter yield picratotriamminoplatinous picrate with two mols. of picrate. Evidently aquotriamminoplatinous picrate is unstable in the solid state but is present in the aqueous solution of the picrato-picrate (see Table II).

That chloro-, bromo-, and nitro-triamminoplatinous salts dissolve without aquation has been demonstrated by measurement of their electrical conductivities, which are of the order required for salts of univalent kations (see Table I). This conclusion was confirmed by precipitation of pink chloroplatinites and preparation of *chloro-, bromo-, and nitro-triamminoplatinous picrates*.

The only information available regarding other acidotriamminoplatinous salts is due to Cleve (*K. Svensk Vet. Akad. Handl.*, 1872, **10**, No. 9), who claimed to have obtained the nitrate $\text{Pt}(\text{NH}_3)_3(\text{NO}_3)_2$ and the sulphate $\text{Pt}(\text{NH}_3)_3\text{SO}_4$ by interaction of chlorotriamminoplatinous chloroplatinite (Cleve's salt) and silver nitrate or sulphate. No details were recorded, and attempts to prepare the salts by this method have proved unsuccessful. Two equivalents of silver salt should react with one molecular proportion of Cleve's salt yielding *chlorotriamminoplatinous nitrate* or sulphate, and this has been verified experimentally in the case of the former salt. When, however, four equivalents of silver salt were used, as required by the equation $[(\text{Pt}(\text{NH}_3)_3\text{Cl})_2\text{PtCl}_4 + 4\text{AgNO}_3 = 2[(\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3 + 2\text{AgCl} + \text{Ag}_2\text{PtCl}_4$, the filtrate was not chlorine-free, and this was found to be due to interaction between silver chloroplatinite and silver nitrate (see p. 1914). It was found possible to isolate *nitratotriamminoplatinous nitrate* by carrying out Cleve's preparation in two stages, treating chlorotriamminoplatinous nitrate, prepared as above, with one mol. of silver nitrate, but the compound was more conveniently prepared by treating chlorotriamminoplatinous chloride with silver nitrate. The product is hemi-hydrated so formulation as an aquo-salt is excluded. It dissolved easily in water and the noticeable acidity of the solution suggested that the salt was present in solution, not as

nitratotriammino-, but as aquotriammino-platinous nitrate. This conclusion was confirmed (a) by preparation from it of aquotriamminoplatinous chloroplatinite (green) and *picratotriamminoplatinous picrate*, (b) by measurement of the electrical conductivity of the solution, which was of the order required for a salt of a bivalent kation (see Table II).

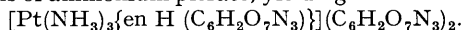
The *sulphato-triammine* was prepared by treating a solution containing aquotriammino-platinous nitrate with excess of sulphuric acid. The product, after drying over phosphoric oxide, contained only half the amount of water required for aquotriamminoplatinous sulphate. It could be formulated alternatively as (I) or (II), the sulphate radical in (II) being attached to



the platinum atom at one point only. A compound of formula (II) would be analogous to the sulphatopentamminocobaltic salts (Jørgensen, *J. pr. Chem.*, 1885, **31**, 262), containing a "bound" sulphate ion, and would be a non-electrolyte if it dissolved without aquation. The aqueous solution, however, was acid to litmus and yielded green aquotriamminoplatinous chloroplatinite when treated with a soluble chloroplatinite. Thus solution had been accompanied by aquation, which might be expected to yield aquotriamminoplatinous sulphate, $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{SO}_4$, whichever formula is adopted for the solid substance. The ease with which aquation occurs favours formula (II). The presence in solution of the aquotriammine salt was confirmed by conductivity measurements (Table II).

Carbonato- and *oxalato-triamminoplatinum* have been obtained by the action of excess of silver carbonate or oxalate on *bromotriamminoplatinous bromide*, and in these cases also formulation of the solid compounds as aquo-salts is excluded, since the former is hemi-hydrated and the latter can be obtained anhydrous. They may be formulated analogously to formulæ (I) and (II) given for the sulphato-triammine. However, it seems unlikely, in view of the strong tendency of the carbonate and the oxalate radical to complex formation, that compounds of structure (I) would undergo aquation. Actually, sufficient aquation occurs for the salts to yield green precipitates with the chloroplatinite ion, though the conductivity data show that this aquation is very incomplete compared with that of the sulphato-triammine. The conductivity data for the oxalato-triammine are so low that formula (I) is definitely excluded.

It has frequently been suggested that in the process of ammine formation, the metals tend to simulate the electronic arrangement of the next inert gas. In the case of the bivalent platinum ion, this would require quinquovalency (2, 8, 18, 32, 16 \rightarrow 2, 8, 18, 32, 18, 8). As no well-established examples of quinquovalent platinum have hitherto been described, an attempt was made to prepare such a compound by treating chlorotriamminoplatinous chloride with ethylenediamine. It might be expected that the powerful chelate group present in the molecule of this substance would attach itself directly to the complex, if 5-covalency is possible, yielding ethylenediaminotriamminoplatinous chloride $[\text{Pt}(\text{NH}_3)_3\text{en}]\text{Cl}_2$ (where en = $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$). A compound of this molecular formula has actually been obtained, but it reacted with three molecular proportions of ammonium picrate, yielding



Thus the ethylenediamine molecule is attached to the platinum atom at one point only, and the platinum is still in the 4-covalent state. When $[\text{Pt}(\text{NH}_3)_3\text{en}]\text{Cl}_2$ was titrated with acid or boiled with water, a molecule of ammonia was removed, and the ethylenediamine molecule then occupied two positions in the complex, as was shown by precipitation of $[\text{Pt}(\text{NH}_3)_2\text{en}](\text{C}_6\text{H}_5\text{O}_7\text{N}_3)_2$ by excess of picrate. These results indicate that there is no tendency for bivalent platinum to exist in the 5-covalent state.

EXPERIMENTAL.

Chlorotriamminoplatinous Chloride.—Using Tschugaev's method (*J.*, 1915, **107**, 1249), difficulty was experienced in obtaining the compound pure. The following modification gave excellent results. 3.5 G. of tetramminoplatinous chloride were boiled for 3 minutes with 9.66 g. of Cleve's salt (8% excess) and 350 ml. of water acidified with hydrochloric acid. After cooling, the green Magnus salt and excess of Cleve's salt were removed and the filtrate was concentrated to small bulk at 50° under reduced pressure. After further filtration from traces of Cleve's salt, the remaining water was removed in a vacuum over sulphuric acid, and the solid product left over soda-lime to remove traces of hydrogen chloride (yield 6.1 g.). If less water or smaller excess of Cleve's salt was used, the product was contaminated with tetrammine.

Chlorotriamminoplatinous Nitrate.—3 G. of Cleve's salt were heated to 70° with 1.132 g. (2 mols.) of silver nitrate and 120 ml. of water. After collection of silver chloroplatinite, the colourless filtrate was concentrated to 30 ml. under reduced pressure at 50°. On addition of alcohol and ether, white, irregular, microscopic plates separated (0.57 g.) (Found: Pt, 56.7; N, 16.5; Cl, 10.0. $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$ requires

Pt, 56.8; N, 16.3; Cl, 10.3%). The compound was easily soluble, giving a neutral solution which gave no immediate precipitate with silver nitrate. The silver chloroplatinite was suspended in water and left overnight in contact with a further 2 mols. of silver nitrate. The filtrate from silver chloride and unchanged chloroplatinite contained only 0.32 mol. of silver nitrate. Chlorotriamminoplatinous nitrate was best prepared by adding 0.5355 g. (1 mol.) of silver nitrate dropwise to a solution of chlorotriamminoplatinous chloride (1 g.). The filtrate was evaporated in a vacuum over sulphuric acid, yielding 0.95 g. of square plates (Found: Pt, 56.6; Cl, 10.2%). The aqueous solution gave a pink precipitate with ammonium chloroplatinite.

Chlorotriamminoplatinous picrate was precipitated as large yellow needles (1.5 g.) on mixing solutions of chlorotriamminoplatinous chloride (1 g.) and ammonium picrate (1.2 mols.) {Found: Pt, 38.4; N, 16.3; Cl, 6.7. $[\text{Pt}(\text{NH}_3)_3\text{Cl}](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 38.3; N, 16.5; Cl, 7.0%}.

Bromotriamminoplatinous bromide does not appear to have been isolated previously, though Tschugaev (*loc. cit.*) obtained the bromoplatinite $[\text{Pt}(\text{NH}_3)_3\text{Br}]_2\text{PtBr}_4$. The salt has now been prepared by converting chlorotriamminoplatinous chloride (2 g.) into aquotriamminoplatinous nitrate in 20 ml. of water (see nitratotriamminoplatinous nitrate below). The ice-cooled product was treated with colourless fuming hydrobromic acid (20 ml.), whereupon an immediate cream precipitate was obtained (1.8 g. of microscopic, acicular aggregates). It was washed successively with alcohol and ether and dried over soda-lime (Found: Pt, 48.2; N, 10.2; Br, 39.4. $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Br}$ requires Pt, 48.1; N, 10.3; Br, 39.4%). 0.636 G. of the salt dissolved in 100 g. of water at 20°. The aqueous solution was neutral to litmus and yielded a pink precipitate with ammonium chloroplatinite.

Bromotriamminoplatinous picrate was obtained as irregular, microscopic, yellow plates when a solution of the bromide was treated with one mol. of ammonium picrate (Found: Pt, 35.2; N, 14.9; Br, 14.2. $[\text{Pt}(\text{NH}_3)_3\text{Br}](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 35.2; N, 15.2; Br, 14.4%).

Nitrotriamminoplatinous Nitrate.—The very unstable nitrite of this series has been described by Tschugaev (*J.*, 1916, **109**, 1286). The much more stable *nitrate* has now been prepared. 2 G. of chlorotriamminoplatinous chloride were converted as above into a solution of chlorotriamminoplatinous nitrate. This was shaken for an hour with 0.970 g. (1 mol.) of silver nitrite and left overnight. The neutral, colourless filtrate was evaporated to small bulk in a vacuum over sulphuric acid and treated with excess of alcohol and ether, whereupon a voluminous white product separated (1.3 g. of acicular aggregates, very soluble in water) (Found: Pt, 55.3; N, 20.0; NO_3 , 17.2. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{NO}_3$ requires Pt, 55.1; N, 19.8; NO_3 , 17.5%). (Sunlight should be excluded during precipitation, or some decomposition occurs.) The salt gave a salmon-pink chloroplatinite (microscopic, acicular aggregates).

Nitrotriamminoplatinous picrate was precipitated as slender yellow needles when a solution of the nitrate was treated with one mol. of ammonium picrate (Found: Pt, 37.2; N, 18.6. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 37.5; N, 18.9%).

Nitratotriamminoplatinous Nitrate.—Cleve (*loc. cit.*, p. 64) claimed to have obtained this compound, in monohydrated form, by double decomposition between Cleve's salt and silver nitrate. Several preparations were made, refluxing with four mols. of silver nitrate, but in no case was the filtrate chlorine-free. The hemihydrated salt was readily obtained pure when chlorotriamminoplatinous chloride (2 g.) was shaken for an hour with 2.142 g. (2 mols.) of silver nitrate and 30 ml. of water. After being left overnight, the product was filtered and the filtrate, which was colourless and acid to litmus, was (a) treated with 400 ml. of alcohol and ether, whereby 1.9 g. of a white micro-crystalline precipitate were obtained (Found: Pt, 51.5; N, 18.8. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 51.5; N, 18.5%), or (b) taken to dryness in a vacuum over sulphuric acid, the anhydrous salt then being obtained (Found: Pt, 52.7. Calc.: Pt, 52.7%).

Aquotriamminoplatinous chloroplatinite was obtained as an immediate acicular green precipitate when the aqueous solution of nitratotriamminoplatinous nitrate (*i.e.*, aquotriamminoplatinous nitrate) was treated with ammonium chloroplatinite (Found: Pt, 64.9; N, 7.3. Calc. for $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{PtCl}_4$: Pt, 64.9; N, 7.0%). No loss of weight or change of colour occurred when the compound was left over phosphoric oxide for two weeks. This compound and the corresponding bromoplatinite were described by Tschugaev and Tschernjaeff (*Compt. rend.*, 1915, **161**, 792), and appear to be the only aquotriammines which exist in the solid state.

Picratotriamminoplatinous Picrate.—0.4 G. of chlorotriamminoplatinous chloride was treated as above with 2 mols. of silver nitrate and the resulting solution of aquotriamminoplatinous nitrate was added to 0.636 g. (2.2 mols.) of picric acid which had been converted into the ammonium salt. 0.75 G. of large needles was precipitated (Found: Pt, 28.1; N, 17.6. $[\text{Pt}(\text{NH}_3)_3(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 27.8; N, 18.0%). There was no loss of weight at 100°.

Sulphatotriamminoplatinous could not be obtained by Cleve's method (*loc. cit.*) or by interaction of chlorotriamminoplatinous chloride or bromotriamminoplatinous bromide and silver sulphate. 2 G. of chlorotriamminoplatinous chloride were converted as above into an aqueous solution of aquotriamminoplatinous nitrate, which was concentrated to 25 ml. in a vacuum over sulphuric acid, treated with an equal volume of dilute sulphuric acid, and precipitated with alcohol and ether (120 ml.). The voluminous white microcrystalline product (1.6 g.) was dissolved in the minimum amount of water, and reprecipitated with alcohol and ether. The compound was fairly soluble, giving a slightly acid solution, but considerable heating and shaking were required to dissolve it. The solution yielded a green chloroplatinite. If dried overnight over soda-lime, the compound was monohydrated (Found: Pt, 54.6; N, 11.7; SO_4 , 26.6. $[\text{Pt}(\text{NH}_3)_3(\text{SO}_4)] \cdot \text{H}_2\text{O}$ requires Pt, 54.2; N, 11.7; SO_4 , 26.7%), but if it was left for a week in a vacuum over phosphoric oxide, a *hemihydrate* was obtained (Found: Pt, 55.6; N, 11.9; SO_4 , 27.2. $[\text{Pt}(\text{NH}_3)_3(\text{SO}_4)] \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 55.6; N, 12.0; SO_4 , 27.3%).

Carbonatotriamminoplatinous.—3 G. of bromotriamminoplatinous bromide were shaken for 3 hours with silver carbonate freshly precipitated from 12 g. of silver nitrate and suspended in 50 ml. of water. After removal of silver bromide, the filtrate was ice-cooled and precipitated with alcohol and ether. 1.7 G. of very soluble white needles were obtained and dried over magnesium perchlorate (Found: Pt, 61.8; N, 13.6; C, 4.0; H, 3.1. $[\text{Pt}(\text{NH}_3)_3(\text{CO}_3)] \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 61.9; N, 13.3; C, 3.8; H, 3.2%). The substance yielded a green chloroplatinite.

Oxalatotriaminoplatinum was obtained when 4 g. of silver nitrate were converted into silver oxalate and the moist product was shaken for 3 hours with 1 g. of bromotriaminoplatinous bromide and 15 ml. of water. The filtrate was free from bromine and was treated with alcohol and ether (100 ml.), yielding 0.55 g. of white needles, easily soluble to a neutral solution. The product was dried over soda-lime (Found: Pt, 55.3; N, 11.7; C₂O₄, 24.7; H₂O, 4.7. [Pt(NH₃)₃(C₂O₄)]₂·H₂O requires Pt, 55.4; N, 11.9; C₂O₄, 25.0; H₂O, 5.1%). The compound was completely dehydrated over phosphoric oxide. A pure product could not be obtained by treating hydroxotriaminoplatinous hydroxide with one mol. of oxalic acid, owing to contamination with an acid oxalate. The oxalato-triammine yielded a green chloroplatinite.

Hydroxotriaminoplatinous hydroxide was obtained in aqueous solution when 1 g. of bromotriaminoplatinous bromide was left in contact with freshly prepared moist silver oxide (from 4 g. of silver nitrate) for 5 hours, with occasional trituration. The colourless, strongly alkaline filtrate was found to be free from bromine and gave the theoretical yield of picratotriaminoplatinous picrate when treated with 2 mols. of picric acid. The hydroxide could not be obtained in the solid state, decomposition occurring when the solution was taken to dryness over sulphuric acid or precipitated with alcohol and ether. If chlorotriaminoplatinous chloride was substituted for the bromo-bromide, the product was not chlorine-free, even after boiling with silver oxide. The hydroxide might have been expected to yield, with 1 equiv. of acid, hydroxotriaminoplatinous salts, analogous to the acidohydroxodiammines described in Part IX. These could not, however, be isolated, probably owing to their great solubility.

Ethylenediaminotriaminoplatinous chloride was obtained by triturating 1 g. of chlorotriaminoplatinous chloride with a little ethylenediamine hydrate for a few minutes till a white paste was obtained. Alcohol was then added, and the product transferred to a filter and washed with alcohol to remove excess of ethylenediamine hydrate. It was dried in a vacuum over soda-lime (Found: Pt, 51.6; N, 18.8; Cl, 18.4. [Pt(NH₃)₃en]Cl₂ requires Pt, 51.7; N, 18.6; Cl, 18.8%). The solid product had no smell; it lost 4.8% of its weight when heated at 100° (Calc. for loss of 1NH₃: 4.5%). The aqueous solution was only faintly alkaline to litmus, but could be titrated with standard acid, the end-point corresponding to neutralisation of exactly 4.5% of ammonia. The same amount of ammonia was removed by boiling the aqueous solution for 15 mins.

Action of Ammonium Picrate on Ethylenediaminotriaminoplatinous Chloride.—3.3 Mols. of ammonium picrate were used, giving an immediate precipitate of large yellow needles in 75% yield (Found: Pt, 19.9; N, 19.8. [Pt(NH₃)₃enH(C₆H₃O₇N₃)](C₆H₃O₇N₃)₂ requires Pt, 19.7; N, 19.8%).

Ethylenediaminodiamminoplatinous picrate was obtained when 3 mols. of ammonium picrate were added to a solution of ethylenediaminotriaminoplatinous chloride which had been boiled for 20 minutes to expel one mol. of ammonia (Found: Pt, 26.0; N, 18.7. [Pt(NH₃)₂(H₂N·CH₂·CH₂·NH₂)](C₆H₃O₇N₃)₂ requires Pt, 26.2; N, 18.8%).

p-Values.—The colorimetric method was used, with bromophenol-blue as indicator. For M/256-solutions, the values obtained were: [Pt(NH₃)₃(NO₃)]NO₃, pH 4.2; [Pt(NH₃)₃(SO₄)]₂, pH 4.4.

Electrical Conductivities at 25°.—In the tables, *v* is the reciprocal of the concentration in g.-mols. per litre and *λ* is the corrected molecular conductivity in mhos. Measurements in Table I were made (*a*)

TABLE I.

Acido-triammines which dissolved without aqutation.

<i>v</i>	32.	64.	128.	256.	512.	1024.	∞
<i>λ</i> for [Pt(NH ₃) ₃ Cl]Cl { <i>a</i>	100.4	102.6	104.4	106.0	108.8	116.2	—
{ <i>b</i>	100.4	103.7	106.5	109.4	117.5	130.5	—
„ [Pt(NH ₃) ₃ Cl]NO ₃ { <i>a</i>	107.1	109.5	111.4	113.0	115.2	117.8	—
{ <i>b</i>	107.1	117.8	122.8	134.3	146.6	160.2	—
„ [Pt(NH ₃) ₃ Br]Br { <i>a</i>	—	—	109.4	113.0	116.1	118.2	—
{ <i>b</i>	—	—	111.5	116.0	120.0	122.8	—
„ [Pt(NH ₃) ₃ (NO ₂)]NO ₃	101.7	107.3	111.6	115.0	117.9	120.1	125.8
							(<i>n</i> = 1.48)

immediately after solution, (*b*) after 24 hours. The conductivities of the chlorotriaminoplatinous salts increased with time and had reached equilibrium after 24 hours. The (*a*) values for these salts have been obtained by extrapolation to zero time. The $\lambda-c^{1/3}$ graphs drawn from these (*a*) values indicate negligible aqutation for dilutions up to 256 litres, increasing rapidly, however, on further dilution (see Part II, *J.*, 1925, 127, 2105). At a dilution of 1024 litres, the (*a*) value for the chloride indicates 5% aqutation, increasing to 15% at equilibrium. For bromotriaminoplatinous bromide, the values obtained immediately after solution gave a linear graph, indicating absence of aqutation. At a dilution of 1024 litres, the equilibrium value indicated only 3% aqutation.

The values for nitrotriaminoplatinous nitrate showed no increase on standing, and the linear $\lambda-c^{1/3}$ graph showed that no aqutation occurred on dilution. This might be expected, since aqutation would necessarily be preceded by conversion of the nitro- into the nitrito-triammine; λ_{∞} for this compound was obtained by means of the $1/\lambda-(c\lambda)^{n-1}$ graph, and gives a value of 54.4 mhos for the mobility of the nitrotriaminoplatinous ion at 25°, 71.4 mhos being taken as the mobility of the nitrate ion. The values for nitratotriaminoplatinous nitrate showed no increase on standing and indicate immediate and complete aqutation to [Pt(NH₃)₃(H₂O)](NO₃)₂. They differ but little from the values previously recorded for the *cis*-dinitratodiammine, which has been shown to dissolve as *cis*-[Pt(NH₃)₂(H₂O)₂](NO₃)₂ (see Part IX, *loc. cit.*). The values recorded for picratotriaminoplatinous picrate agree well with the previously recorded value of 182.6 mhos for the *cis*-dipicratodiammine at a dilution of 1024 litres, and indicate complete aqutation to aquotriaminoplatinous picrate. The data obtained for the sulphato-triammine increased on standing, reaching equilibrium in an hour. In this case, aqutation was evidently slower, but conversion into [Pt(NH₃)₃(H₂O)]SO₄ was fairly complete. The values agree closely with those previously recorded for the *cis*-sulphatodiammine, which has similarly been shown to dissolve as

TABLE II.

Acido-triammines which dissolved with complete or substantial aquation.

v		64.	128.	256.	512.	1024.
λ for	$[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3$	—	232.1	250.5	259.0	267.0
,,	$[\text{Pt}(\text{NH}_3)_3(\text{C}_6\text{H}_5\text{O}_7\text{N}_3)](\text{C}_6\text{H}_5\text{O}_7\text{N}_3)$	—	—	—	178.3	190.4
,,	$[\text{Pt}(\text{NH}_3)_3(\text{SO}_4)]$ equilibrium values	—	—	165.4	205.9	229.6
,,	$[\text{Pt}(\text{NH}_3)_3(\text{CO}_3)]$	69.1	79.4	86.4	91.3	104.4
,,	$[\text{Pt}(\text{NH}_3)_3(\text{C}_2\text{O}_4)]$	42.3	44.6	46.6	48.1	48.9

cis- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4$. The conductivities of the carbonatotriammine increased on standing, reaching equilibrium in from 15 to 45 minutes, according to the concentration. At a dilution of 256 litres, this increase amounted to 15% in 25 minutes. Even at the lower concentrations, the equilibrium values indicate less than 50% aquation. In the case of the oxalato-triammine, the increase in conductivity on standing was much less (2% at a dilution of 256 litres) and equilibrium was reached in 20 minutes. Aquation was, however, very incomplete, amounting only to about 20% even at the lower concentrations.

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

NORTHERN POLYTECHNIC, LONDON, N.7.

[Received, January 13th, 1948.]