452. *Amino-compounds of the Platinic Chloro-ammines.*

By Bertram E. Dixon.

Tschugaev (*Z. anorg. Chem.*, 1924, **137**, 401) discovered that, by the action of alkali on chloropentamminoplatinic chloride, one of the ammonia groups was attacked with the formation of an amino-compound, $[Pt(NH_3)_4(NH_2)Cl]Cl_2$. Tscherniaev (*Ann. Inst. Platine*, 1927—8, **5—6**) found that the formation of amino-compounds was general in the nitritoplatinammine series, and also that the $R{\cdot}NH_2$ group was converted into $R{\cdot}NH$ where $R = CH_3$, $NH_2{\cdot}CH_2{\cdot}CH_2$, etc.

It was shown recently (Dixon, J., 1931, 2306) that the reaction can proceed a step farther, with the formation of a second amino-group in the platinic complex of the chloropentammine series. A further study has been made of this reaction in the simple platinic ammines of the dichlorotetrammine, chloropentammine, and hexammine series.

Dichlorotetrammine Series.—By the action of excess ammonia on dichlorotetramminoplatinic nitrate solution, Cleve (*Acta Upsala*, 1866, **6**, No. 5, 78) obtained a light yellow liquid, which on evaporation in air yielded a white deposit containing carbonate and having one of the chlorine atoms replaced by hydroxyl. Raewsky (*Ann. Chim.*, 1848, **22**, 278) had noted the production of a yellow colour by the action of potassium hydroxide.

The action of alkalis on this salt was reinvestigated, carbon dioxide being excluded. Addition of concentrated aqueous ammonia to a solution of the nitrate produces a yellow coloration which gradually disappears on standing. The rapid addition of a concentrated solution of sodium hydroxide to an ice-cold solution of the platinammine precipitates brilliant yellow crystals of *aminodichlorotriamminoplatinic nitrate*, $[Pt(NH_3)_3(NH_2)Cl_2]NO_3$, which require 1 equiv. of hydrochloric acid on titration (methyl-orange).

From disodium hydrogen phosphate and dichlorotetramminoplatinic nitrate in solution, Cleve (*loc. cit.*) obtained white crystals to which Werner ("Neuere Anschauungen," pp. 53, 192) ascribed the structure $[Pt(NH_3)_4Cl(PO_4)]$. It is now found, however, that two totally different products are formed according as the solutions are cold or hot. In the cold, a white precipitate, soluble in water, was produced and shown to be *dichlorotetramminoplatinic hydroxydihydrophosphate* $[Pt(NH_3)_4Cl_2]^{OH}_{H_2PO_4},2H_2O$. In hot solutions, an insoluble faint yellow precipitate was formed, having only one chlorine atom and giving only a trace of precipitate with cold acid molybdate solution. This compound, *chloro(hydrophosphato)tetramminoplatinic hydroxide*, $[Pt(NH_3)_4Cl(HPO_4)]OH$, loses a molecule of water at 130° to form *chloro(hydrophosphato)aminotriamminoplatinum*, $[Pt(NH_3)_3(NH_2)Cl(HPO_4)]$.

Chloropentammine Series.—Attempts were made to isolate other polyamino-compounds (cf. Dixon, *loc. cit.*) by the action of alkalis. Cold concentrated sodium hydroxide led to indefinite results, but upon long shaking with the chloride freshly precipitated silver oxide gave a strongly alkaline solution, and tests on the filtrate indicated the presence of a platinammine capable of combining with 3 equivs. of acid, and of silver hydroxide in the proportion required by the formula $2[Pt(NH_3)_2(NH_2)_3(OH)],3AgOH$.

If only 2 equivs. of silver oxide are used, the filtrate on standing deposits a small quantity of a yellow crystalline *compound* of silver chloride and a diaminochloroplatinammine,

$$2[Pt(NH_3)_3(NH_2)_2Cl]Cl,3AgCl.$$

The chlorine in the nucleus is apparently not attacked by silver oxide until all the ionised chlorine has been removed. If the reaction is arrested after this stage has been reached, a third *compound*, $[Pt(NH_3)_2(NH_2)_3(OH)],2AgCl$, is deposited from the filtrate as well-formed lemon-yellow crystals.

Hexammine Series.—The precipitate produced by the addition of ammonium phosphate solution to a solution of the chloride was shown to be a *monoamino*-compound, $[Pt(NH_3)_6]_2{}^{(OH)_2}_{(HPO_4)_3},2H_2O$ or $[Pt(NH_3)_5(NH_2)]_2(HPO_4)_3,4H_2O$.

DISCUSSION.

Dichlorotetrammine Series.—The isolation of aminodichlorotriamminoplatinic nitrate brings the simple dichlorotetrammine series into line with the chloropentammine series as regards its capacity to yield an amino-compound by the action of alkali. The failure of ammonium hydroxide to yield a similar compound in this case may be due to the replacement of one un-ionised chlorine by hydroxyl, a view that is supported by the formation and disappearance of the yellow colour. This comparative instability of one chlorine atom would also provide an obstacle to the formation of polyamino-compounds, although it would appear to be much less pronounced than was believed by the older writers, as shown by the resistance to attack by alkali in the method described above, and also by the formation of the hydroxyhydrophosphate.

Werner's formula for the tetrammine phosphate gains importance from the fact that this compound (together with its bromo- and nitrato-homologues) is the only example cited by this author in which a tervalent radical occupies a single position in the complex. In such a chelate compound the phosphate radical was described as bound to platinum by one direct bond, and to platinum, or to the complex, by two indirect bonds. The expression of this statement in terms of modern views is difficult. The single place in the co-ordination complex occupied by the phosphate radical can be represented by a normal covalent linkage. It is evident, however, that the remaining two valencies would not have the freedom associated with electrovalencies, since the atoms between which they form a link are already spatially related. Nor does the chemical behaviour of the phosphate (or hydrophosphate) radical in this compound accord with the presence of freely ionised links, although this radical seems to be more loosely combined than might be expected from a group within the complex. It seems reasonable to assume, then, that all three valencies of the phosphate radical in this formula would be, at least to some extent, directed forces, whether these valencies are regarded as consisting of one normal covalent linkage and two modified polar linkages, in which the original functions have become merged, or of other forms of covalent links. If this were so, the strain developed by the triple linkage of the phosphate radical forming two adjacent 4-atom rings would be too great to render likely the existence of such a compound. In the formula now proposed for the dehydrated compound, where the number of linkages is reduced to two, this objection no longer holds.

By analogy with the chloropentammine series, the action of excess of alkali might have been expected to yield a diamino-compound by the loss of HX. The product obtained does, in fact, differ from its predecessor by the elements of HCl, but the scission has taken place irregularly and, further, the product is also a mono-amino-compound. The failure to yield a diamino-compound may be attributed to the mobility of the chlorine in the nucleus.

The discovery of the hydroxyhydrophosphate explains an apparent anomaly in the action of alkali phosphate on ammoniacal chloroplatinic acid solution (Dixon, *loc. cit.*). Had the first product of the action of a phosphate on dichlorotetramminoplatinic chloride been the insoluble chlorophosphatotetrammine, this compound would have been formed exclusively in the reaction referred to, and the substitution of NH_3 for chlorine within the nucleus would not have proceeded to give the chloropentammine salt.

Chloropentammine Series.—The three products obtained in this series evidently contain silver in the form of a complex ion. If, now, the platinammine component is regarded as functioning in these compounds chiefly or exclusively in its capacity as amine, a remarkable parallel is afforded with the well-known compounds, $[Ag(NH_3)_2]OH$ and $[Ag_2(NH_3)_3]Cl_2$. The compounds would then be formulated as $[Ag_3\{(NH_2)_3Pt(NH_3)_2(OH)\}_2](OH)_3$ and $[Ag_2\{(NH_2)_3Pt(NH_3)_2(OH)\}]Cl_2$. The similarity between the two series of silver compounds is brought out by a consideration of their composition, properties, and method of preparation. This view of the predominance of the rôle played by the amino-group over that of the platinic complex as a whole may be justified by consideration of the activity of the amino-group in general, and of the fact that in two of these compounds the platinic complex is null-valent. In the third compound $[Ag_3\{(NH_2)_2Pt(NH_3)_3Cl\}_2]Cl_5$, the influence of the two amino-groups is modified by the fact that here the platinic complex has one available electron. This may explain why this compound has no counterpart among the common silver ammines (with the possible exception of a superficial resemblance to $Ag_3PO_4,4NH_3$).

If this view be accepted, it means that these silver compounds represent a new type of ammine, in which the place of a saturated radical, such as NH_3, inside the complex of one metal is taken by the null-valent complex of another metal. The rôle of the second metallic complex is thus essentially different from that played, *e.g.*, in $[Co\{Co(NH_3)_4(OH)_2\}_3]Br_6$, by the dihydroxotetramminocobaltic complexes, which have contributed three to the number of electrons available from the shell of the main cobaltic atom. It may be assumed that the linkages between the platinic complex and the silver are formed through the nitrogen of the amino-groups. The linkage through nitrogen, which is probably present in silver–ammonia compounds, would tend to weaken the influence of the platinic complex as such.

Hexammine Series.—This series falls into line with the two previous series in yielding an amino-salt. The end-points obtained on neutralisation with acid are, however, poor, and this seems to indicate that the aminopentammine base is weaker than the aminochlorotetrammine base. Gerdes (*J. pr. Chem.*, 1882, **26**, 257), in an attempt to prepare the free base of this series by the action of silver oxide on the chloride, obtained a powder containing silver, which he did not further investigate.

General.—The primary amino-reaction is now proved to be general for the simple platinic chloroammines. Moreover, the isolation of the silver compounds, following that of diaminochlorotriamminoplatinic hydrophosphate, shows that the replacement of NH_3 by NH_2 within the complex can continue, under suitable conditions, until the formation of an electrically neutral platinic complex ends the possibility of further reaction. Since, subject to this limitation, there is no reason to suppose that this process of replacement does not proceed indefinitely in a solution with a sufficiently great hydroxyl-ion concentration, the products actually obtained will depend on the solubility relationships. It is evident, therefore, that the formulæ given to many of the salts which have been formed in such solutions should be reviewed in the light of these new facts; *e.g.*, this reaction may account for the confusion existing as to the constitution of some tetramminoplatinic salts containing multivalent radicals.

From the ease with which an NH_2 group is reconverted into an NH_3 group it might be expected that the difficulty of separation of polyamino-compounds would increase with the number of NH_2

groups. The failure to isolate by simple means the compounds $[Pt(NH_3)_3(NH_2)_2Cl]Cl$ and $[Pt(NH_3)_2(NH_2)_3Cl]$, for both of which a superficially stable electronic configuration can be provided, may be explained in this way by the assumption of a residual valency due to the amino-groups. On the other hand, the stability of the silver compounds isolated is in accord with the assumption of co-ordinate links between the nitrogen of the amino-groups and the silver chloride or hydroxide. The similar stability of the other type of polyamino-compound prepared, diaminochlorotriamminoplatinic hydrophosphate, may possibly be due to the stabilising influence of the two positively charged hydrogen ions attached to the phosphate radical.

EXPERIMENTAL.

Dichlorotetramminoplatinic nitrate was obtained by the action of HNO_3 on tetramminoplatinous chloride, prepared by Ramberg's method from K_2PtCl_4. Titration values, whether of acid or of alkali, are expressed as percentages of HCl of the titrated substance; in those designated by (i), the indicator was methyl-orange, in (ii) it was phenolphthalein in presence of $CaCl_2$ aq., and in (iii) it was phenolphthalein alone.

Aminodichlorotriamminoplatinic Nitrate.—Excess of cold 30% NaOH aq. (free from Na_2CO_3) was added to a conc. solution of dichlorotetramminoplatinic nitrate immersed in ice, and stirred. The brilliant yellow ppt. which appeared almost immediately was washed with EtOH till free from NaOH, then with Et_2O, and dried in a desiccator {Found: Pt, 49·2; N, 17·5; Cl, 18·3; titration (i), acid, 9·3. $[Pt(NH_3)_3(NH_2)Cl_2]NO_3$ requires Pt, 49·4; N, 17·7; Cl, 17·95; titration (i), acid, 9·25%}. If CO_2 is not excluded, the ppt. is contaminated with a white carbonate.

Dichlorotetramminoplatinic Hydroxydihydrophosphate.—3 Equiv. of cold Na_2HPO_4 aq. were added to a solution of 1 equiv. of dichlorotetramminoplatinic nitrate. The bulky white ppt. formed on stirring was washed with ice-cold H_2O, and dried in a desiccator. It contained un-ionised Cl and readily gave a ppt. with a HNO_3 solution of $(NH_4)_2MoO_4$ {Found: Pt, 40·1; N, 11·7; Cl, 14·9; P, 6·5; titration (i), acid, 7·6; titration (ii), alkali, 7·3. $[Pt(NH_3)_4Cl_2](OH)H_2PO_4,2H_2O$ requires Pt, 40·3; N, 11·6; Cl, 14·65; P, 6·4; titration (i), acid, 7·55; titration (ii), alkali, 7·55%}. At 110° the loss in wt. was 3·9% ($1H_2O$ requires 3·7%). At higher temp. more H_2O was expelled but decomp. set in before the loss in wt. reached 11·1%.

Chloro(hydrophosphato)tetramminoplatinic Hydroxide.—2 Equiv. of hot Na_2HPO_4 aq. were poured into a boiling solution of dichlorotetramminoplatinic nitrate, and the mixture boiled and stirred for 4 min. The ppt. was well washed with H_2O and dried in a desiccator; it was granular, faintly buff-coloured, and practically insol. in H_2O. It contained un-ionised Cl. Only a trace of ppt. was obtained with cold acid molybdate solution, although a small ppt. was formed on warming; no ppt. was formed with $FeCl_3$ in cold neutral, or very slightly acid, solution. The *compound* dissolved in 1 equiv. of HCl to form a solution neutral to methyl-orange; this solution could then be titrated (phenolphthalein) with 1 equiv. NaOH, which pptd. the ammine from solution {Found: Pt, 47·1; N, 13·4; Cl, 8·5; P, 7·45; titration (i), acid, 8·85; titration (iii), acid, nil. $[Pt(NH_3)_4Cl(HPO_4)]OH$ requires Pt, 47·4; N, 13·6; Cl, 8·6; P, 7·55; titration (i), acid, 8·85; titration (iii), 0%}. When the hydroxide was heated at 130°, $1H_2O$ was expelled (Found: loss, 4·1. $1H_2O$ requires loss, 4·4%) without causing any change in the titre or other chemical properties [Found: titration (i), acid, 8·8; (iii), alkali, 0·2%]. The substance formed was presumably the anhydride, *chloro(hydrophosphato)-aminotriamminoplatinum*, $[Pt(NH_3)_3(NH_2)Cl(HPO_4)]$.

Chloropentammine Series.—Exposure of the reactants to the atm. was reduced to a min. Since the speed of reaction depends largely on the degree of agitation, the times given are only approx., and the progress of the reaction must be followed by frequent tests.

Bis(hydroxotriaminodiamminoplatinic)silver Hydroxide.—Excess of moist Ag_2O was shaken vigorously with a solution of chloropentamminoplatinic chloride for 1—2 hr. in a corked flask until a small filtered portion gave a ppt. on addition of HCl, but no more than a trace on addition of HNO_3. The main solution was filtered quickly; it was strongly alkaline and readily absorbed CO_2 from the air with formation of a white ppt. The solution was analysed by titrating an aliquot portion with HCl, which neutralised the platinammine base and pptd. AgCl, and by determining the Pt and N in other portions acidified and evaporated to dryness {Found: Pt, 3·88; N, 1·35; AgOH, 3·70; titration, HCl, 3·16. A solution of

$$[Ag_3\{(NH_2)_3Pt(NH_3)_2(OH)\}_2](OH)_3$$

(9·57 mg. per ml.) requires Pt, 3·88; N, 1·39; AgOH, 3·72; titration, HCl, 3·26 mg. per ml.}. The alk. solution, which was stable out of contact with air, yielded on evaporation under reduced press. a white pasty mass, which evolved NH_3 slowly on standing.

Bis(chlorodiaminotriamminoplatinic)silver Chloride.—2 Equiv. of Ag_2O were shaken with a solution of the chloropentammine salt for about 1 hr. A test portion of the pale greenish-yellow filtrate gave a ppt. of AgCl on acidification with HNO_3, and the filtrate from the AgCl contained Cl'. On standing overnight, the main solution deposited a small quantity of pale yellow isotropic adherent crystals, which were unaffected by light. They were analysed by titrating with HNO_3, filtering off the separated AgCl, and estimating in aliquot portions of the filtrate the ionised and un-ionised Cl {Found: Pt, 34·7; N, 12·6; AgCl, 37·7; Cl (complex) 6·6; Cl (free), 6·1; titration (i), acid, 13·2. $[Ag_3\{(NH_2)_2Pt(NH_3)_3Cl\}_2]Cl_5$ requires Pt, 34·6; N, 12·4; AgCl, 38·1; Cl (complex), 6·3; Cl (free), 6·3; titration (i), acid, 12·9%}.

(Hydroxotriaminodiamminoplatinic)silver Chloride.—A solution of chloropentamminoplatinic chloride was shaken for about 3 hr. with 4 equiv. of Ag_2O until a portion of filtered solution, on being acidified with HNO_3, yielded a ppt. of AgCl and a solution containing $Ag^{\cdot}$ but no Cl'. After filtration and 24 hrs.' standing, the greenish-yellow liquid deposited well-formed bright yellow crystals. These were collected, dried in a desiccator and analysed by the method used for the diamino-compound {Found: Pt, 33·1; N, 11·9; AgCl, 49·9; Cl (complex), 0·1; titration (i), acid, 18·9.

$$[Ag_2\{(NH_2)_3Pt(NH_3)_2(OH)\}]Cl_2$$

requires Pt, 33·6; N, 12·05; AgCl, 49·35; Cl (complex), nil; titration (i), acid, 18·85%}.

All the three foregoing Ag compounds on treatment with HCl and filtration yielded the corresponding hydroxo- or chloro-pentamminoplatinic compounds.

Hexamminoplatinic Hydroxyhydrophosphate.—Hexamminoplatinic chloride was prepared by Tschugaev's method (*Z. anorg. Chem.*, 1924, **137**, 1), but was found to be contaminated with hydroxopentamminoplatinic chloride, which has a similar solubility in water. Separation was effected by fractional solution of the two phosphates in dil. AcOH, hexamminoplatinic phosphate being the less sol. The yield was poor.

The *phosphate* was pptd. from an NH_3 aq. solution of $[Pt(NH_3)_6]Cl_4$ by addition of excess $(NH_4)_2HPO_4$ aq. It was filtered off, dissolved in HCl, repptd., and dried at 105° {Found: Pt, 41·15; N, 17·9; P, 9·55; titration (i), acid, 8·5; titration (ii), alkali, 4·2. $[Pt(NH_3)_6]_2(OH)_2(HPO_4)_3,2H_2O$ requires Pt, 41·0; N, 17·65; P, 9·75; titration (i), acid, 7·65; titration (ii), alkali, 3·8%}. At 130° the loss in wt. was 3·3% ($2H_2O$ requires loss, 3·8%).

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GOVERNMENT LABORATORY,
LONDON.

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