# 130. *The Structure of the Simple and Mixed Tetramminoplatinous Dihalides.*

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THE chief obstacle to the theoretical conclusions in the preceding paper lies in the interpretation of the remarkable isomerism found amongst the mixed tetrammino-dihalides, *e.g.*, those of formula $Pt(NH_3)_2py_2Cl_2$. In order to discuss these substances it is necessary to consider first the unmixed tetrammino-dihalides, such as $Pt(NH_3)_4Cl_2$.

We have repeated certain experiments described in the literature and are able to confirm the following facts: (i) Both the α- and the β-diammino-dichloride give, when treated with ammonia, the same tetrammine, a triammine being the intermediate product; (ii) when the tetrammine is heated with hydrochloric acid, it gives, probably through the triammine, the α-diammine, but never the β-diammine. The γ-diammino-dichloride gives with ammonia the same tetrammine, and therefore in all probability the same triammine, as its isomerides.

The tetrammine has two ionised halogens, the triammine only one, so the above reactions may be expressed:

$$\begin{tikzcd}
Pt(NH_3)_2Cl_2 \arrow[rr, shift right, "NH_3"'] & & {[Pt(NH_3)_3Cl]Cl} \arrow[ll, shift right, "HCl"'] \arrow[rr, shift right, "NH_3"'] & & {[Pt(NH_3)_4]Cl_2} \arrow[ll, shift right, "HCl"'] \\
& Pt(NH_3Cl)_2 \arrow[ur, "NH_3"] & & Pt(NH_3)(NH_3Cl)Cl \arrow[ul, "NH_3"'] &
\end{tikzcd}$$

It will be admitted that these expressions, in which are employed the conventional co-ordination formulæ, convey no adequate idea of the nature of the reactions involved. The inadequacy of such formulæ becomes still more evident when the substances containing two different amines are considered.

The α- and the β-dipyridino-compound, $Pt\,py_2Cl_2$, are analogous to the corresponding diammino-compounds; they are prepared by similar methods, undergo many similar reactions, and give rise on treatment with pyridine to the same tetrapyridino-compound, $Pt\,py_4Cl_2$, which with hydrochloric acid gives α-$Pt\,py_2Cl_2$. It cannot therefore be doubted that they correspond in structure with the respective diammino-compounds.

It was discovered by Jörgensen, and confirmed by Klason and others, that the four diammines, α- and β-$Pt(NH_3)_2Cl_2$ and α- and β-$Pt\,py_2Cl_2$, give rise, on treatment severally with an excess of the amine not already in the diammine, to only two (and not four) mixed tetrammines of formula $Pt(NH_3)_2py_2Cl_2$. Each of the two α-diammines generates what may be called the α-mixed tetrammine; whilst each of the two β-diammines produces an isomeric substance of very similar properties, the β-mixed tetrammine:

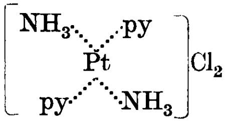
$$Pt(NH_3)_2Cl_2 \xrightarrow{py} \alpha\text{-}[Pt(NH_3)_2py_2]Cl_2 \xleftarrow{NH_3} Pt\,py_2Cl_2;$$
$$Pt(NH_3Cl)_2 \xrightarrow{py} \beta\text{-}[Pt(NH_3)_2py_2]Cl_2 \xleftarrow{NH_3} Pt\,(pyCl)_2.$$

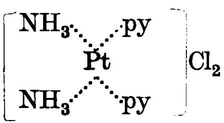
We have re-examined these reactions under several different sets of conditions and are able to confirm the broad facts.

Since it cannot be in doubt that the action of ammonia upon a diammino-compound is similar in nature to its action upon a dipyridino-compound, and since the action of ammonia upon the α- and β-diammino-compounds gives rise to *the same* tetrammine, it follows immediately that the α- and β-mixed tetrammines cannot be structural isomerides, but must be stereoisomerides. If this were not so, then α- and β-isomerides of the formula $Pt(NH_3)_4Cl_2$ would be produced, respectively, from the α- and the β-diammino-compound by the addition of further ammonia.

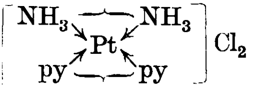
The α- and the β-mixed tetrammine act normally towards hydrochloric acid in that both give rise only to α-diammines; but a remarkable difference of behaviour is nevertheless shown by the two isomerides, for, whilst the α-compound gives a mixture of α-$Pt(NH_3)_2Cl_2$ and α-$Pt\,py_2Cl_2$, the β-compound gives only the mixed diammine α-$Pt(NH_3)pyCl_2$. We have been able to confirm this behaviour, which appears to be without precedent among stereoisomeric compounds.

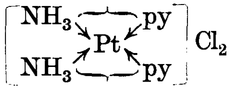
No theory has ever accounted satisfactorily for these facts. Werner regarded the mixed tetrammines merely as *trans-* and *cis-*compounds of planar structure with chlorine ions in the outer sphere of combination :


α-Tetrammine (W.).


β-Tetrammine (W.).

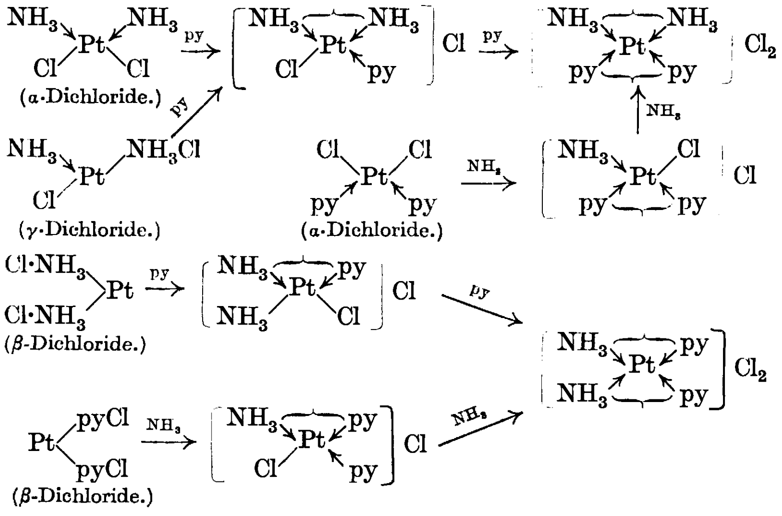
The formulæ become identical if the pyridine groups are replaced by ammonia groups, accounting for the fact that there is only one compound of formula $Pt(NH_3)_4Cl_2$. To explain the decomposition reactions of the mixed tetrammines with hydrochloric acid, however, Werner was obliged to adopt the arbitrary rule that the two ammine groups removed by the acid were always those originally present in relatively *trans*-positions in the tetrammine molecules. This principle has been accepted with little question, although it is without adequate theoretical justification. Werner's explanation rests upon the assumption that the diammines are stereoisomerides and that the entering ammine groups occupy the same positions as the halogens in the diammines. The experimental results given in the foregoing paper render it unlikely that the diammines are stereoisomerides and accordingly an alternative hypothesis is necessary. It is suggested that all of the experimental results so far brought forward may be accounted for if the structure of the platinum atom is such that *the four linkings to the ammino-groups of the tetrammines are differentiated into two equivalent pairs which function independently*, a closer relationship existing between the members of a pair than exists between either member of one pair and either member of the other. The suggestion does not involve valencies of different types, all four linkings being postulated of the same kind and precisely equivalent to one another in the sense of the equivalence of the six linkings to hydrogen in the benzene ring. Such an hypothesis would be equally applicable whether the associated ammine groups had a planar or a tetrahedral distribution. In the following formulæ each ammine group is represented as attached to the platinum atom by a co-ordinate link, and the paired linkings are indicated by brackets :


(α-Mixed tetrammine.)

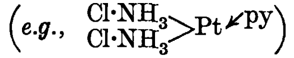

(β-Mixed tetrammine.)

The same considerations will apply also to the mixed triammines $[Pt(NH_3)_2pyCl]Cl$ and $[Pt(NH_3)py_2Cl]Cl$, each formula being represented by two different substances. The following schemes then account in a simple manner for the observed results :

(*a*) Formation of the α- and β-mixed tetrammines from the several diammines :



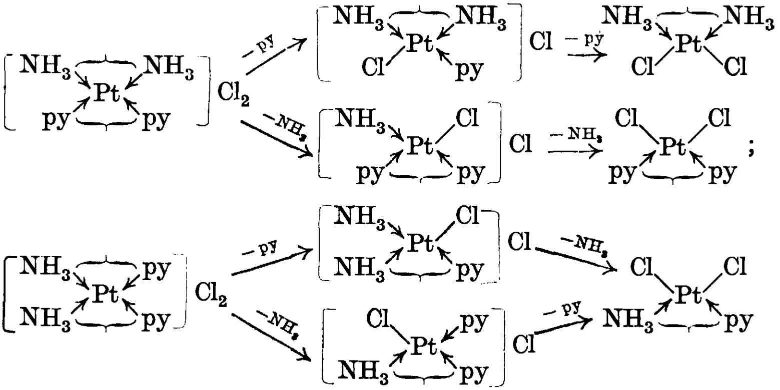
The initial action of amines upon the β-dichlorides is regarded as that of addition, with formation of labile triammines


$$\left(e.g.,\ \begin{matrix}Cl{\cdot}NH_3\\ Cl{\cdot}NH_3\end{matrix}>Pt\leftarrow py\right)$$

which change to the more stable triammines shown; the labile triammines are analogous in type to the γ-diammino-dihalides.

This hypothetical stage of the reaction has been omitted from the above scheme.

(*b*) Degradation of the mixed tetrammines by hydrochloric acid :



It is not intended to imply that a halogen necessarily enters the same angular position as was occupied by the ammine group which it displaces ; but the two positions must nevertheless bear a definite relationship to one another. In the above scheme, the $\gamma$-diamminodichlorides, which are probably the initial products of the action of hydrochloric acid on the triammines, are not shown. It was found that a proportion of $\gamma$-$Pt(NH_3)_2Cl_2$ is always produced when $Pt(NH_3)_4Cl_2$ is decomposed by hydrochloric acid.

The idea of paired valencies for the platinum atom may be considered in connexion with physical evidence adduced in the case of carbon. Lonsdale (*Proc. Leeds Phil. Soc.*, I, Pt. VIII, 346) has shown how models of benzene and naphthalene can be built up from carbon atoms with two pairs of valencies to agree with *X*-ray work and with observations on the absorption spectra of the dichloronaphthalenes (de Laszlo, *J. Amer. Chem. Soc.*, 1928, **50**, 892). Again, Lonsdale (*Phil. Mag.*, 1928, **6**, 433), discussing evidence as to the structures of carbon compounds, particularly hexachloroethane, shows that carbon cannot have spherical symmetry and probably not even tetrahedral symmetry. Lastly, in graphite, *X*-ray observations prove that the carbon atoms are not all crystallographically identical, which can be accounted for by assuming that the carbon valencies are of two different types. It is possible that in the case of platinum, with its high atomic number, the effects due to paired valencies may be more pronounced than in the case of carbon. It should be emphasised, however, that in the case of platinum we do not postulate the presence of valencies which necessarily differ in type but only of two groups of similar valencies, whereas for carbon Lonsdale postulates two different types of valencies associated with the electron orbits ($2_1$) and ($2_2$).

*Stereochemistry of the Tetrammines.**—With the exception of the results published recently by Reihlen (*Annalen*, 1931, **489**, 42), there is no chemical evidence to show whether the four groupings attached to platinum in these substances are arranged in a plane or tetrahedrally. Reihlen's experiments indicate that the formulæ cannot be completely planar, since he claims to have effected resolution of certain tetrammine salts; he has not, however, succeeded in replacing the optically active radicals by inactive radicals while still retaining optical activity due to platinum, and therefore his evidence cannot be considered as final. Somewhat similar results are, in fact, already on record. Our own experiments leave the matter still open. It does, indeed, seem possible to draw the conclusion that the α-positions (shown with brackets in the preceding formulæ) are further apart than the β-positions, because the former cannot be spanned by ethylenediamine and other chelate groupings which are capable of insertion across β-positions; the oxalato-group can similarly replace the halogens of a β-diammine but not of an α-diammine. Reihlen has already made a similar deduction. The important question of the manner in which the positive charges are located in the tetrammine ion cannot at present be discussed.

The evidence given in our previous paper (*loc. cit.*) on the α- and β-diethyl sulphide compounds, $Pt(SEt_2)_2Cl_2$, shows that the sulphur atoms cannot correspond in a stereochemical sense with the nitrogen atoms of the α- and β-diammines, unless radical changes of configuration occur when the sulphines are intertransformed. In both sulphines, therefore, the sulphur atoms probably occupy β-positions. The α- and β-sulphines thus correspond structurally, but not stereochemically, with the α- and β-diammines.

## EXPERIMENTAL.

Triamminoplatinous dichloride, $[Pt(NH_3)_3Cl]Cl$, prepared from β-$Pt(NH_3)_2Cl_2$ by Tschugaev's method (J., 1915, **107**, 1244), formed very pale cream-yellow, rectangular needles, only moderately soluble in water (Found: Pt, 61·25. Calc.: Pt, 61·55%). With aqueous potassium chloroplatinite it gives the flesh-coloured plato-salt, $[Pt(NH_3)_3Cl]_2PtCl_4$, which crystallises from hot water in plates; this salt has the same empirical formula as the diamminoplatinous dichlorides (Found: Pt, 65·15. Calc.: Pt, 65·05%). It gives with phenoxtellurine dibisulphate a slowly-developed reddish coloration.

Tetramminoplatinous dichloride, $[Pt(NH_3)_4]Cl_2$, prepared from

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* See note by E. G. Cox (p. 1015).

any of the three isomeric diamminoplatinous dichlorides and aqueous ammonia, formed colourless needles or prisms, sometimes several inches long, of the monohydrate. The same product was obtained from all three methods of preparation, so far as could be seen [Found, in sample dried over calcium chloride: Pt, 55·0. Calc. for $Pt(NH_3)_4Cl_2,H_2O$ : Pt, 55·45%]. It is readily soluble in water and may be crystallised from dilute hydrochloric acid. The tetrammine appears to be without action upon α- or β-Pt $py_2Cl_2$ in aqueous solution at 100°, even after several hours. With aqueous potassium chloroplatinite it gave almost invariably the green salt of Magnus, but on one occasion a freshly prepared sample gave on a first test (but not in any of ten subsequent tests) the pink form of Magnus's salt.

Tetrapyridinoplatinous dichloride, $[Pt\,py_4]Cl_2$, was prepared by the action of aqueous pyridine upon the α- or β-dipyridino-dichloride; in each case apparently the same product resulted, *viz.*, large, colourless, rhombic bipyramidal crystals of the trihydrate (from aqueous alcohol and ether) [Found: Pt, 30·7, 30·65. Calc. for $Pt(C_5H_5N)_4Cl_2,3H_2O$ : Pt, 30·7%]. The substance is readily soluble in water; it has no action upon aqueous ammonium chloride or aqueous $Pt(NH_3)_4Cl_2$ at 100°. With potassium chloroplatinite, it gives a pale-pink, microcrystalline plato-salt, very sparingly soluble in water [Found: Pt, 45·55, 45·65. Calc.: Pt. 46·0%].

α-Diamminodipyridinoplatinous dichloride, $[Pt(NH_3)_2py_2]Cl_2$, was prepared, under a variety of different conditions, from α-$Pt(NH_3)_2Cl_2$ and aqueous pyridine, and from α-Pt $py_2Cl_2$ and aqueous ammonia. The main product was apparently the same in both reactions, and it was immaterial whether the reactions were carried out at 100° or at laboratory temperature. The first reaction, however, was smoother than the second, since ammonia tended to replace to a small extent the pyridine groups in α-Pt $py_2Cl_2$. At 100°, the diammines dissolve in the aqueous bases in less than an hour, but at laboratory temperature dissolution may be incomplete after several weeks. The tetrammine is usually obtained from water, or from dilute hydrochloric acid, in long, colourless, glistening, rectangular prismatic needles of the monohydrate [Found: Pt, 41·1, 41·05, 41·1; N, 12·2. Calc. for $Pt(NH_3)_2(C_5H_5N)_2Cl_2,H_2O$ : Pt, 41·0; N, 11·8%]. The tetrammine is very readily soluble in hot water, but less soluble in the presence of hydrochloric acid; in cold water it is only moderately soluble.

All samples of the tetrammine gave with potassium chloroplatinite a salmon- or chamois-coloured plato-salt,

$$α\text{-}[Pt(NH_3)_2py_2]PtCl_4,$$

which crystallised as needles and prisms; it gave an almost black coloration with phenoxtellurine dibisulphate. Fractional precipitation of the plato-salt in five successive crops from an aqueous solution of the tetrammine indicated that it was homogeneous [Found in successive crops (not recrystallised): Pt, 53·55, 53·65, 53·85, 53·9, 53·9. Calc.: Pt, 53·9%]. The salt was also examined by fractional crystallisation from boiling hydrochloric acid (20 c.c. of concentrated acid diluted to 100 c.c. with cold water). The fraction which separated on cooling was repeatedly recrystallised from the hot solvent; its solubility (0·16 g. in 100 c.c. at 20°) remained unaltered throughout, and its composition remained the same (Found, in final crop: Pt, 53·5%). Transformation of the final crop to the tetrammine, by heating in faintly acid solution with the calculated quantity of $Pt(NH_3)_4Cl_2$, gave nearly the theoretical quantity of Magnus's salt (0·29 g. of the plato-salt gave 0·227 g. Calc.: 0·24 g.), together with the mixed tetrammine, which was obtained from the filtrate in the characteristic form regenerating the chamois plato-salt with potassium chloroplatinite. The tetrammine was decomposed by hot 15% hydrochloric acid into a mixture of $\alpha$-$Pt(NH_3)_2Cl_2$ and $\alpha$-$Pt\,py_2Cl_2$. The decomposition of the plato-salt by means of aqueous $Pt(NH_3)_4Cl_2$ was repeated on a larger scale, and the recovered $\alpha$-$Pt(NH_3)_4py_2Cl_2$ was recrystallised from water and obtained as the monohydrate [Found: Pt, 41·1. Calc. for $Pt(NH_3)_4py_2Cl_2,H_2O$: Pt, 41·0%]. The possibility that the chamois plato-salt is a mixture of the plato-salts of two triammines is thus negatived. It was shown also that a mixture in equimolecular proportions of $Pt(NH_3)_4Cl_2$ and $Pt\,py_4Cl_2$ does not undergo change when heated in water, and that a mixture in equimolecular proportion of the plato-salts of these two tetrammines does not produce the chamois plato-salt when crystallised from hydrochloric acid. There can thus be little doubt but that the mixed tetrammine and its plato-salt are simple substances.

The decomposition of the $\alpha$-mixed tetrammine by hot hydrochloric acid was repeatedly examined to see whether the two $\alpha$-diamminedichlorides, which are the products, were formed in equimolecular proportions. This was found not to be the case, the proportion apparently depending upon the concentration of the acid used; but the dipyridino- invariably predominates over the diamminodichloride. With stronger acid (about 24% HCl), the total product may contain up to 80% by weight (75% by mols.) of the dipyridino-compound; with weaker acid (approx. 15% HCl), the total product contains some 68% by weight of the latter (an equimolecular mixture would contain 58·6% by weight). These figures were obtained without separation of the two products, by analysis of the various weighed crops. The decomposition requires some 4—6 hours at 100° for completion; but the yield is never quantitative, being some 90% of that calculated if the reaction proceeded to completion with the products in the ratio obtained. Air must be excluded as far as possible during the heating, since the products tend to become oxidised to tetrachlorides (Found, under various conditions of experiment, in total product: Pt, 48·6, 49·7, 50·6, 52·0. Calc. for equimolecular mixture: Pt, 53·9%).

The two products were easily separated in a pure state by fractional crystallisation from chloroform or hydrochloric acid, and were identified both by analysis and by their conversion with ammonia into tetrammines giving the known plato-salts in a pure condition. Search was made for $\alpha$-$Pt(NH_3)pyCl_2$ among the products, but no trace of this substance could be detected.

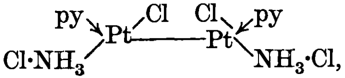
No appreciable difference was detected in the behaviour towards hydrochloric acid under comparable conditions of specimens of the $\alpha$-diamminodipyridino-dichloride prepared by the two alternative methods already given.

$\beta$-*Diamminodipyridinoplatinous dichloride*, $[Pt(NH_3)_2py_2]Cl_2$, which appears not to have been isolated hitherto in a pure state, was prepared, under several sets of conditions, by the action of aqueous pyridine upon $\beta$-$Pt(NH_3)_2Cl_2$ and by that of aqueous ammonia upon $\beta$-$Pt\,py_2Cl_2$. The two methods gave apparently identical products, and the result was substantially the same whether the reaction temperature was that of the laboratory or 100°. The action of pyridine in the cold upon $\beta$-$Pt(NH_3)_2Cl_2$ gives the above $\beta$-mixed tetrammine as practically the sole product; that of ammonia upon $\beta$-$Pt\,py_2Cl_2$ gives a mixture of this tetrammine with the tetrammine $Pt(NH_3)_3pyCl_2$, and the proportion of the latter is large if the reaction proceeds at 100°. The separation of the two tetrammines can be effected by fractionation from aqueous alcohol and ether.

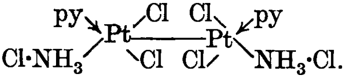
The $\beta$-diamminodipyridino-dichloride separates from water, in which it is much more soluble than the corresponding $\alpha$-tetrammine, in massive, transparent, colourless, bipyramidal crystals of the tetrahydrate (Found: Pt, 36·9, 36·8, 37·1, 36·75. $C_{10}H_{16}N_4Cl_2Pt,4H_2O$ requires Pt, 36·8%). From aqueous ethyl alcohol it separates in bushes of rectangular plates, consisting of the *monohydrate* (Found: Pt, 40·95. $C_{10}H_{16}N_4Cl_2Pt,H_2O$ requires Pt, 41·0%). Some evidence was obtained that a *trihydrate* also exists, forming pearly, rectangular platelets from aqueous alcohol and ether (Found: Pt, 37·95. $C_{10}H_{16}N_4PtCl_2,3H_2O$ requires Pt, 38·1%). The tetrammine frequently forms crystals of triangular outline.

The $\beta$-mixed tetrammine gives with aqueous potassium chloroplatinite a pink or flesh-coloured *plato-salt*, β-$[Pt(NH_3)_2py_2]PtCl_4$, which crystallises in hexagonal needles or plates from water, in which it is very sparingly soluble, or from hydrochloric acid [Found : Pt, 53·55, 53·65, 53·8, 53·8, 54·1. $Pt_2(NH_3)_2py_2Cl_4$ requires Pt, 53·9%]. This salt, like Magnus's salt, gives an almost black coloration with phenoxtellurine dibisulphate. That it is the homogeneous salt of a tetrammine, and not a mixture of the plato-salts of two triammines, was shown by its double decomposition with the calculated quantity of $Pt(NH_3)_4Cl_2$, which gave almost the theoretical yield of Magnus's salt (0·4826 g. of the plato-salt gave 0·38 g. Calc. : 0·40 g.) and the β-mixed tetrammine, isolated as the monohydrate (Found : Pt, 40·95. Calc. : Pt, 41·0%). There is thus no doubt that the β-mixed tetrammine is a simple substance and that structural rearrangement does not occur when it is converted into the plato-salt.

The decomposition of the β-mixed tetrammine dichloride with hot hydrochloric acid was studied to test whether any α-$Pt(NH_3)_2Cl_2$ or α-Pt $py_2Cl_2$ resulted along with the main product α-$Pt(NH_3)pyCl_2$, but these two substances were absent. When the decomposition is carried out with moderately dilute hydrochloric acid at 100°, the product consists of yellow needles, sometimes several cm. long, and short yellow prisms; these two forms both consist of α-$Pt(NH_3)pyCl_2$, possibly containing also some of the γ-form. They give no coloration with phenoxtellurine dibisulphate. The mixed dichloride is moderately soluble in hot water to a neutral, yellow solution. The freshly formed substance polymerises in presence of hydrochloric acid to a light red prismatic form, which reverts to the yellow form when crystallised from water and cannot then be reconverted into the red form. When allowed to stand with concentrated hydrochloric acid in presence of air, the red form is oxidised to a darker red material, which is practically insoluble in water (Found : Pt, 49·7. Calc. : Pt, 49·1%). Jörgensen (*J. pr. Chem.*, 1886, **33**, 511) gives an analysis of this substance. It seems probable that the γ-form of $Pt(NH_3)pyCl_2$ is first produced and that this polymerises to the light red form,



which gives on oxidation the stable dark red platinic compound,



The yellow form of $Pt(NH_3)pyCl_2$ prepared by the action of hydrochloric acid on the β-mixed tetrammine was the same whichever of the alternative methods was used for the preparation of the latter (Found : Pt, 53·75, 54·15, 53·5, 54·15, 53·45; N, 7·7. Calc. : Pt, 53·9; N, 7·7%). When dissolved in ammonia it gave the following tetrammine.

*Triamminopyridinoplatinous dichloride*, $[Pt(NH_3)_3py]Cl_2$, was prepared (1) as indicated above, or (2) by the action of aqueous ammonia at 100° upon β-Pt $py_2Cl_2$, partial replacement of pyridine by ammonia occurring. The products from the two sources were identical. The substance crystallises from aqueous alcohol in flat, nacreous, square-ended plates of the monohydrate (Found: Pt, 46·95, 46·65, 46·8. $C_5H_{14}N_4Cl_2Pt,9H_2O$ requires Pt, 47·15%). It is readily soluble in cold water, but easily precipitated by alcohol. It yields a plato-salt, $[Pt(NH_3)_3py]PtCl_4$, which crystallises from water or dilute hydrochloric acid as the monohydrate and is exceptionally readily soluble (Jörgensen, *Z. anorg. Chem.*, 1900, **25**, 360). The monohydrate forms lustrous, strawberry to violet needles or plates of rectangular or hexagonal outline [Found: Pt, 57·4, 57·3, 57·3, 57·25. Calc. for $(NH_3)_3(C_5H_5N)Pt_2Cl_4,H_2O$: Pt, 57·4%]. The plato-salt was proved to be the salt of a tetrammine by decomposition with $Pt(NH_3)_4Cl_2$, whereby the correct proportion of Magnus's salt was obtained, and the original tetrammine recovered and identified.

Decomposition of the tetrammine with hydrochloric acid at 100° gave a mixture of α-diammino and -amminopyridino-dichlorides, but not in molecular proportion (Found: Pt, 57·5, 57·3. Calc. for equimolecular mixture: Pt, 58·95%). Thus, there is preferential elimination of ammonia residues.

When the mixed diammine was dissolved in aqueous pyridine, a tetrammine (not isolated) was produced, which gave a sparingly soluble plato-salt in pale pink microcrystals consisting probably of $[Pt(NH_3)py_3]PtCl_4,H_2O$ (Found: Pt, 48·75. Calc.: Pt, 48·55%).

Cossa's ammonium salt was prepared by Jörgensen's method (*Z. anorg. Chem.*, 1900, **24**, 165), *i.e.*, by heating β-$Pt(NH_3)_2Cl_2$ for some 30 hours with *N*-hydrochloric acid. If the aqueous solution was allowed to evaporate spontaneously, it left a little unchanged β-$Pt(NH_3)_2Cl_2$ and Cossa's ammonium salt (I); but if, instead, the equivalent of aqueous $Pt(NH_3)_4Cl_2$ was added, the tetrammine salt (II) was deposited in glistening, golden plates, often of square outline. This salt is sparingly soluble in water, but crystallises readily from dilute hydrochloric acid (Found: Pt, 64·9. Calc.: Pt, 65·05%); hot concentrated hydrochloric acid partially decomposes it into Magnus's salt. The salt gives a slowly developed light red coloration with phenoxtellurine dibisulphate, in marked contrast to the deep colours given by the salts containing the anion $\overline{Pt}\overline{Cl}_4$. The changes may be interpreted as follows

$$Pt(NH_3Cl)_2 \xrightarrow{HCl} [Pt(NH_3Cl)Cl_2]NH_4 \qquad \text{(I.)}$$

$$[Pt(NH_3)_4]Cl_2 + 2[Pt(NH_3Cl)Cl_2]NH_4 \longrightarrow$$

$$\text{(II.)} \quad [Pt(NH_3)_4]^{++}[Pt(NH_3Cl)Cl_2]_2^{-} + 2NH_4Cl.$$

By double decomposition of (II) with aqueous potassium chloroplatinite, Cossa's potassium salt (III) was obtained in the filtrate from the precipitated Magnus's salt. The salt formed large, rhombic, orange-red plates, soluble in water to a deep yellow solution. Like the corresponding ammonium salt, it gives an intense dark-red coloration with phenoxtellurine dibisulphate. When the potassium salt is heated with a few drops of hydrochloric acid and a little ammonia is then added, the salt (II) is precipitated, a reaction probably due to the formation of Cossa's acid and its dissociation to hydrogen chloride and $Pt(NH_3Cl)Cl$, a proportion of the latter then adding on ammonia to give $Pt(NH_3)_4Cl_2$ which combines with unchanged $Pt(NH_3Cl)Cl$.

Nevertheless, an aqueous solution of Cossa's potassium salt, when treated with aqueous ammonia in the cold, gives almost quantitative precipitation of $\beta$-$Pt(NH_3)_2Cl_2$. This striking reaction is readily interpreted on the basis of the theory of the foregoing paper :

$$\text{(III.)}\quad [Pt(NH_3Cl)Cl_2]K \xrightarrow{+NH_3} [Pt(NH_3Cl)_2Cl]K \xrightarrow{-KCl} Pt(NH_3Cl)_2$$

When Cossa's potassium salt was treated with aqueous pyridine, it gave a yellow precipitate, which, after recrystallisation from water, developed no coloration with phenoxtellurine dibisulphate and was not distinguishable from $\alpha$-$Pt(NH_3)pyCl_2$ obtained by the action of hydrochloric acid upon $\beta$-$Pt(NH_3)_2py_2Cl_2$ (Found : Pt, 54·15. Calc.: Pt, 53·9%); with ammonia it gave $Pt(NH_3)_3pyCl_2$, identical with the substance previously described. The reaction of pyridine with Cossa's potassium salt appears to be more complex than that of ammonia, and needs further study (compare Klason, *Ber.*, 1904, **37**, 1355).

The triammine salt, $[Pt(NH_3)_3\overset{+}{Cl}][\overset{-}{Pt}(NH_3Cl)Cl_2]$, which, like (II), is empirically isomeric with the diammino-dichlorides, was prepared by mixing equivalent solutions of Cossa's potassium salt and of the triammine. The voluminous pinkish form which first separates changes rapidly to denser yellow crystals (Found : Pt, 65·0. Calc. : Pt, 65·05%). It crystallises from water in dendritic yellow scales; from dilute hydrochloric acid in well-defined, square plates of orange shade. The substance gives with aqueous potassium chloroplatinite a precipitate of the pink plato-salt of the triammine, Cossa's potassium salt remaining in solution.

### *Crystallographic Examination of the Tetrammines.*

(By E. G. Cox.)

Goniometric examination has confirmed that the tetrammines $Pt(NH_3)_4Cl_2$ prepared from either the $\alpha$- or the $\beta$-diammine are identical. An $X$-ray examination of this substance, which crystallises with one molecule of water, is now nearing completion. It is tetragonal, with $a = 7{\cdot}30$, $c = 4{\cdot}23$ Å.U.; space-group probably $D_4^1$ or $D_{4h}^1$. The evidence obtained so far seems to indicate that the four ammonia groups are situated at the corners of a square around the platinum atom, the water molecules lying midway between platinum atoms in a direction inclined to the plane of the ammonias.

An examination of the mixed tetrammine, $\alpha$-$Pt(NH_3)_2py_2Cl_2,H_2O$ is also being made; by means of $X$-ray photographs it has been found that the two substances of the above formula prepared by the action of pyridine on the $\alpha$-diammine, and of ammonia on the $\alpha$-dipyridine, respectively, are identical. The compound is either monoclinic, or triclinic with $\alpha$ and $\gamma$ nearly 90°. In any case, it seems that the molecule has at most a plane or an axis of symmetry.

## *Summary.*

(1) It is shown that the isomeric mixed tetrammines, $Pt(NH_3)_2py_2Cl_2$ are not necessarily *cis*- and *trans*-isomerides of planar configuration, as supposed by Werner; this isomerism can be explained by the assumption that the co-ordinate links between the ammino-groups and platinum are paired.

(2) There is, so far, no definite chemical evidence as to whether the ammino-groups in the tetrammines have a planar or a tetrahedral distribution.

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