129. *The Structure of the Isomeric Diamminoplatinous Chlorides. Discovery of a Third Isomeride.*

By HARRY DUGALD KEITH DREW, FREDERIC WILLIAM PINKARD, WILLIAM WARDLAW, and (in part) ERNEST GORDON COX.

THE problem of the structure of the isomeric diamminoplatinous chlorides is of particular interest because of its bearing both upon the stereochemistry of platinum and of quadrivalent atoms generally, and upon the constitution of the metal ammines. The interest of the problem is enhanced by the fact of its having withstood repeated examination during the past 85 years. A recent study of the isomeric compounds which diethyl sulphide forms with platinous chloride (Angell, Drew, and Wardlaw, J., 1930, 349) suggested to us the possibility of a fresh interpretation of the relationship among the diammino-compounds, and we have therefore re-examined these substances. In the present paper a new view of their structures is suggested.

The first ammino-derivative of platinum was prepared by Magnus in 1828; but in 1845 it was recognised that there exist two quite distinct diammines,* $Pt(NH_3)_2Cl_2$, *viz.*, (1) the α-dichloride, an almost white, usually only microcrystalline substance, prepared from the tetrammine by removal of two molecules of ammonia; and (2) the β-dichloride, which crystallises in yellow needles, is more soluble in water than its isomeride, and is obtained directly from chloroplatinous acid (or one of its salts) and ammonia. These two isomeric diammines are stable substances; they are inappreciably ionised in water, when freshly dissolved; and they give rise to two distinct series of derivatives.

Early in the present work it became evident that there is a marked difference in the inter-relationship of the α- and β-diammines as compared with that of the α- and β-isomerides of the diethyl sulphide series, $Pt(SEt_2)_2Cl_2$. In the sulphine series, the isomerides can be intertransformed directly (by the use of solvents or by heating), and a mixture of the two isomerides may result as the product of a single reaction; in the diammine series, there is no direct intertransformation of isomerides, and a mixture of the two never results from a single reaction. Moreover, whereas the action of an excess of diethyl sulphide on the α-sulphine compound produces the β-sulphine compound when the excess of diethyl sulphide is subsequently eliminated, the action of an excess of ammonia upon the α- or β-diammine produces a tetrammine which gives rise to the α-diammine when the excess of ammonia is subsequently removed. It will be seen later that there are also other minor differences of relationship in the two series, *e.g.*, in the relative colours of the isomerides and in their behaviour towards moist silver oxide. The differences between these two series of apparently analogous substances have escaped sufficient recognition in the literature for reasons which will become apparent.

Numerous structures have been proposed for the isomeric diammines. Blomstrand and Cleve regarded both compounds as derivatives of bivalent platinum (I; II); but Jörgensen, who at one time accepted these formulæ, finally reversed them, (III; IV). Klason returned to the earlier formula (V) for the α-isomeride, but considered the β-isomeride to be a derivative of quadrivalent platinum (VI). Werner came to a fundamentally different conclusion: he formulated the isomerides as *trans*- and *cis*-compounds

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* The literature of these substances has become very complex owing to the changes of nomenclature which arose from periodical alterations of view regarding structure. The α-dichloride has been referred to variously as "Reiset's chloride," the "platosammine chloride," the "β-diammine chloride," and the "*trans*-diammine"; the β-dichloride as "Peyrone's chloride," "the platosemidiammine chloride," "the α-diammine chloride," and "the *cis*-diammine." At times, however, some of the above designations have been interchanged among the two series of names.

of quadricovalent platinum, regarding the valencies as distributed in a plane (VII; VIII). Although there has never been any direct evidence in favour of this view, it has been supported by Hantzsch and by many others, and may be said to meet with general acceptance at the present time.

α-*Dichloride.* β-*Dichloride.*

$\mathrm{Pt}\!<\!\begin{array}{l}\mathrm{NH_3Cl}\\ \mathrm{NH_3Cl}\end{array}$

(I.) B. and C.

$\mathrm{Pt}\!<\!\begin{array}{l}\mathrm{NH_3{\cdot}NH_3Cl}\\ \mathrm{Cl}\end{array}$

(II.) B. and C.

$\mathrm{Pt}\!<\!\begin{array}{l}\mathrm{NH_3{\cdot}NH_3Cl}\\ \mathrm{Cl}\end{array}$

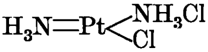
(III.) J.

$\mathrm{Pt}\!<\!\begin{array}{l}\mathrm{NH_3Cl}\\ \mathrm{NH_3Cl}\end{array}$

(IV.) J.

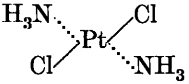
$\mathrm{Pt}\!<\!\begin{array}{l}\mathrm{NH_3Cl}\\ \mathrm{NH_3Cl}\end{array}$

(V.) K.

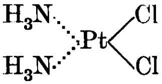


$\mathrm{H_3N{=}Pt}\!<\!\begin{array}{l}\mathrm{NH_3Cl}\\ \mathrm{Cl}\end{array}$

(VI.) K.



(VII.) W.



(VIII.) W.

We now find, however, that, when the α-dichloride is converted (by means of an alkali hydroxide or moist silver oxide) into a *base*, and this is neutralised with hydrochloric acid, a third dichloride, which may be called the *γ-dichloride*, is produced. This substance forms yellow needles from water, in which it is not appreciably ionised, resembling in this respect the α- and β-dichlorides. The γ-dichloride gives the same analytical figures as the α- and the β-dichloride; but examination of the crystalline form, minimum refractive index, *X*-ray crystal diagram, and solubility and conductivity in water, of each of the three substances showed that they are all distinct chemical individuals. This was confirmed by their chemical behaviour; for example, they may be transformed into three different thiocyanates. Lastly, the α- and the γ-dichloride, which are very closely related, cannot be merely different crystalline modifications of the same substance, since equivalent hot aqueous solutions differ in colour and deposit on cooling the individual substances originally dissolved.

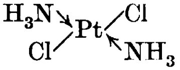
To determine whether the three dichlorides are isomerides or not, the molecular weights in boiling water were observed. Unfortunately the results, which indicated that all three substances are probably monomeric, were not entirely trustworthy owing to the sparing solubility of the α- and the γ-dichloride. The uncertainty was increased by the tendency of the latter to become transformed into the former when boiled for some time with water. That the β-dichloride, which is more soluble in water, is almost certainly monomeric, appears to be proved by the determinations in spite of the fact that slow decomposition of these dichlorides undoubtedly occurs in aqueous solution even in the cold, as is shown by the increase of conductivity with time; this decomposition did not seem to proceed far in more concentrated solutions, even at 100°, since all three dichlorides could be recovered unchanged, so far as microscopic examination revealed, from their solutions under the conditions of experiment. All three substances, indeed, are normally purified from boiling water, and, apart from the not very rapid transformation of the γ- to the α-dichloride, would normally be regarded as stable to the solvent.

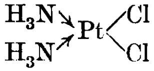
There is, however, considerable indirect evidence to show that the α- and the β-dichloride are both monomeric, for certain of their analogues have already been shown to be monomeric; *e.g.*, Hantzsch found that the α- and the β-dipyridino-dichloride are both monomeric in solution in phenol. It is true that, on the evidence of Reihlen, the α-diammino-dichloride is dimeric in anhydrous ammonia whereas the β-isomeride is monomeric; but ammonia is scarcely a suitable solvent for this purpose. The methods of preparation and the general chemical behaviour of the three dichlorides suggest strongly that all are monomeric; for, if not, unusually complex reactions would have to be assumed in many transformations. This is particularly true in respect of the conversion of the diammines into triammines and then into tetrammines by the simple addition of amine molecules, and of the reversion to diammines on removal of these amine molecules by acid; for the tetrammines are undoubtedly monomeric in aqueous solution. Further, the physical properties of the three dichlorides show a gradation which suggests uniform complexity, *e.g.*, the solubility in water of the γ-dichloride is intermediate between that of the α- and the β-. Still more decisive appears to be the impossibility of devising any rational polymeric formula for a diammino-dichloride which is not already allocated to a known substance. The only possible polymeric formulæ seem to be the following:

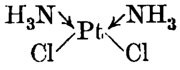
$$[Pt(NH_3)_4]PtCl_4;\ [Pt(NH_3)_3Cl]_2PtCl_4;\ [Pt(NH_3)_4][Pt(NH_3)Cl_3]_2;$$
$$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3].$$

We have prepared all four corresponding substances, three of which are very well known; all have the properties of complex salts and are easily distinguishable from the diammino-dichlorides. The indirect evidence, therefore, seems to be decisively in favour of the monomeric character of the three dichlorides; and the γ-dichloride must then be a third isomeride of the two already known.

The existence of a third isomeride greatly weakens Werner's planar hypothesis as a complete explanation of isomerism in the series, because that hypothesis leaves room for a third isomeride only if the unlikely assumption be made that the four linkings to platinum are inclined at fixed angles which are not right angles, giving formulæ :


(α-.)

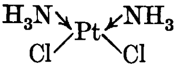

(β-.)

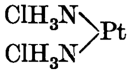

(γ-.)

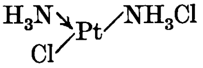
The alternatives to this hypothesis are : (*a*) that both planar and tetrahedral forms occur ; (*b*) that the isomerism is entirely structural and not spatial ; or (*c*) that both spatial and structural types of isomerism occur among the three forms.

In seeking to test these hypotheses we noticed differences in the chemical behaviour of the three isomerides which seem to be too marked to allow of a purely spatial interpretation. It was already known that, besides being different in colour and solubility, the α- and the β-isomeride behave quite differently towards hydrochloric acid. We now find that they also contrast sharply in their behaviour (i) towards caustic alkali or moist silver oxide, (ii) towards phenoxtellurine dibisulphate. With silver oxide, the α-dichloride gives, not an α-base, but the γ-base ; whereas the β-dichloride gives a true β-base. The undoubtedly analogous α- and β-dipyridino-dichlorides give, on the other hand, α- and β-bases respectively ; and, although this difference is readily explicable (see later), it somewhat weakens the argument for a structural differentiation of the diammino-compounds. Of the three diammino-dichlorides, only the β-isomeride gives a coloured complex with phenoxtellurine dibisulphate. Here again, however, the argument is complicated, because the colorations with phenoxtellurine dibisulphate given by the β-dipyridino- and by several other β-diammino-dichlorides are very feeble compared with that given by the β-diammino-dichloride, whilst the plato-salts of the tetrammines and even potassium or ammonium chloroplatinite afford intense colorations. This behaviour will be referred to again later. The third important chemical distinction between the α- and the β-diammino-dichloride is the long-known fact that only the latter reacts with *N*-hydrochloric acid, with which it readily gives Cossa's ammonium salt. The distinction holds true for the pyridino-analogues also.

It seems justifiable to conclude that the weight of evidence at present favours the view that the three diammino-dichlorides are structural isomerides. In that case, the three formulæ shown below are the only ones which it is possible to construct (stereochemical implications being temporarily ignored):


(IX.) α-Dichloride.

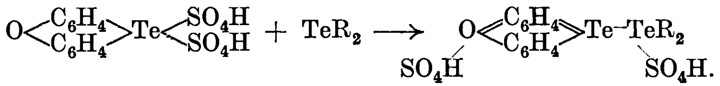

(X.) β-Dichloride.


(XI.) γ-Dichloride.

To assign the three isomerides among these formulæ, it will be necessary to consider some of the foregoing chemical evidence in more detail:

(*a*) The test with phenoxtellurine dibisulphate is made by rubbing a little of that salt with the substance under examination. As already stated, the β-diammino-dichloride at once develops an intensely purple colour, whilst the β-dibromide and β-di-iodide give colours of redder shades; but the α- and γ-isomerides give no coloration. The β-dipyridino-dichloride and several analogous β-dichlorides give less intense colorations, although certain other β-dichlorides do not react. In no case, however, has an α-dihalide been observed to give a coloration.

It has been shown (Drew, J., 1926, 3054) that tellurides, selenides, and sulphides give similar purplish colorations with phenoxtellurine dibisulphate, the reaction being due in each case to the formation of an -ylium complex with the unsaturated metalloidal atom of the telluride or analogous substance, *e.g.*



Here again, not all tellurides, etc., give a coloured complex, but only those whose constitution is such that they are able to exchange an electron for the mobile anion of the dibisulphate. As a series, therefore, the β-diammino-dichlorides behave towards the reagent in a manner parallel to that of the tellurides, and it seems a fair assumption that their structures must be similar to those of the tellurides, *i.e.*, that they are of the form PtR_2.

Of the three formulæ (IX), (X), and (XI), only (X) is of this type, and it must therefore represent the β-dichloride.

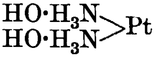
It appears to be a general rule that the plato-salts of the tetrammines and of the triammines, and other similar salts, give colorations with phenoxtellurine dibisulphate, and this can be explained by regarding them as potential sources of monomeric $PtCl_2$ or other substance of this form; *e.g.*, Magnus's salt may be regarded as in equilibrium with its generators: $[Pt(NH_3)_4]PtCl_4 \rightleftharpoons Pt(NH_3)_4Cl_2 + PtCl_2$. In agreement, the salts of chloroplatinous acid give very deep, almost black, colorations with phenoxtellurine dibisulphate:

$K_2PCl_4 \rightleftharpoons 2KCl + PtCl_2$; whereas the salts of chloroplatinic acid and the diammino-tetrachlorides, like the derivatives of quadrivalent tellurium, give no colorations. Platinous chloride, as usually prepared, gives no reaction, and this material cannot therefore possess the simple structure.

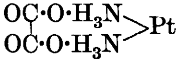
The test with β-$Pt(NH_3)_2Cl_2$ is so sensitive that it enables the presence of traces of the β-dichloride to be detected in admixture with the α- and the γ-isomeride, and we have accordingly employed it to examine whether, as several authorities (notably Klason) have claimed, intertransformation of the α- and the β-dichloride occurs spontaneously or in warm aqueous solution. As already stated, intertransformation never occurs, the deepening of colour of the α-dichloride in hot aqueous solution being due probably to the generation of a small proportion of the γ-form.

(*b*) The platinous diammino-dichlorides react much more slowly with moist silver oxide than do the diethyl sulphide derivatives, perhaps because of their sparing solubility in water, and it is desirable to heat the mixture to cause interaction. The β-isomeride gives a β-base (XII), in the form of a hygroscopic yellow glass, soluble in water to an alkaline solution; the base absorbs carbon dioxide and neutralises halogen acids with formation of β-dihalides; with organic acids, also, it gives β-derivatives [*e.g.*, the β-oxalate (XIII)] which regenerate the β-dichloride when treated with hydrochloric acid.

(XII.)

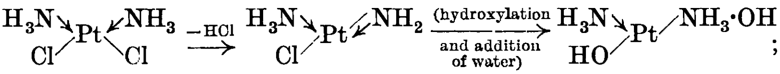


$$\begin{matrix}HO\cdot H_3N\\ HO\cdot H_3N\end{matrix}{>}Pt$$

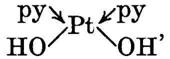


(XIII.)

The α-isomeride, however, gives the same base as the γ-isomeride; and this must be the γ-base (XV), since it yields the γ-dichloride when neutralised by hydrochloric acid. It is suggested that the change is initiated by the removal of a molecule of hydrogen chloride, the hydrogen atom being furnished by one of the ammonia residues :



(XIV.) (XV.)

the intermediate compound (XIV) would thus contain a semipolar triple bond. This theory is supported by the observation that in the dipyridino-series, where there is no hydrogen attached to nitrogen, no γ-base occurs. The β-dichloride gives a glassy β-base, $Pt(py\cdot OH)_2$; whilst the α-dichloride gives a true α-base, , in the form of asbestos-like, hydrated needles. This substance, which, in striking contrast to the β-base, is comparatively sparingly soluble in water to a solution only feebly alkaline, regenerates the α-dichloride with hydrochloric acid. It is possible, but not yet certain, that the corresponding true α-diammino-base occurs as a by-product in the preparation of the γ-base.

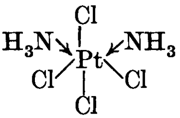
The action of aqueous caustic soda or potash upon the three isomeric diammino-dichlorides is similar to that of silver oxide, but the β-base appears to be readily further changed by the hot reagent. Aqueous caustic alkalis do not react appreciably with α- or β-$\mathrm{Pt\,py_2Cl_2}$, probably because the soluble alkali chloride has here a more pronounced effect in reversing the reaction owing to the insolubility in water of the dipyridino-dichlorides.

The foregoing reactions make it clear that the α-diammino-dichloride must have formula (IX), leaving (XI) for the γ-dichloride. These formulæ exhibit the close relationship which exists between the two substances, and, as will be seen in the following paper, they also offer a reason for the non-conversion of the γ- to the β-dichloride.

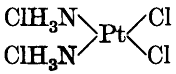
In the dipyridino-series, the β-dichloride is very much less soluble in organic solvents (*e.g.*, chloroform) than is the α-dichloride, suggesting that the former has a greater tendency towards polar character. The structures given [compare (X) and (IX)] are compatible with this behaviour, because the halogens may be assumed to have a greater tendency (however small this may be) to ionise from nitrogen than from platinum.

It is an interesting fact that β-diammines cannot be prepared from tertiary aliphatic amines, of which the salts are strong electrolytes, only platinous oxide and the hydrochloride of the amine resulting. This behaviour supports our conclusion that the β-diammines contain halogen attached to nitrogen with only an extremely feeble tendency to ionise.

Diammine Tetrahalides.—The α- and the β-dichloride each unite with two further chlorine atoms to give respectively the well-known α- and β-tetrachlorides, which are not intertransformable; the α-tetrachloride is tetragonal; the β-tetrachloride, monoclinic or orthorhombic. The γ-dichloride gives on chlorination the α-tetrachloride. It has been shown by Jörgensen, Tschugaeff, and others that each of the tetrachlorides gives back on reduction the particular dichloride from which it was originally formed; it follows, therefore, that if the α- and the β-dichloride are structural isomerides, the tetrachlorides are structural isomerides also. The view which we have suggested leads to the formulæ :



(XVI.) α-Tetrachloride.



(XVII.) β-Tetrachloride.

Whether a planar or a tetrahedral structure be adopted for the α-dichloride, an octahedral structure must be assigned to the α-tetrachloride, whereas, with the suggested formulation (X) for the β-dichloride, the β-tetrachloride may be either tetrahedral or planar. At present the available evidence is insufficient to warrant a decision between these possibilities. An investigation of the *dichlorodibromides* yielded no additional information. The action of bromine on α-diamminoplatinous dichloride gave the same product, apparently α-$Pt(NH_3)_2Cl_2Br_2$, as that of chlorine on the corresponding dibromide, a result which would be expected whether the α-dichloride be planar or tetrahedral. Similar reactions with the β-dichloride gave the same product in each case, apparently β-$Pt(NH_3)_2Cl_2Br_2$. Either on the formulation of the β-dichloride here suggested or on that put forward by Werner, there is a possibility of the occurrence of two distinct β-dichlorodibromides unless a rearrangement of groups takes place. The non-occurrence of these isomeric β-tetrahalides is to be attributed to the fact that the reactions have to be carried out in aqueous solution, in which medium there is sufficient interchange of halogens to give rise to the same (the more stable) form in each case or else to mixtures of the tetrachloride and tetrabromide. The probability of such interchange of halogens follows from the results of Schlesinger and Palmateer (*J. Amer. Chem. Soc.*, 1930, **52**, 4316), as well as from the known interactions in aqueous solution of the α- and the β-dichloride with alkali bromides and iodides. It must be concluded that a study of the products with mixed halogens is of value only when, as is the case in the sulphine series, non-ionising organic solvents can be used.

The formulations proposed in the present paper enable several well-known reactions to be interpreted in a simplified manner :

(*a*) The action of ammonia upon potassium or ammonium chloroplatinite yields a mixture of the β-diammino-dichloride and Klason's compound, $PtNH_3Cl_2$. One and then a second molecule of ammonia becomes inserted between platinum and attached chlorine atoms, these being the only points of the molecule open to attack by co-ordinating groups ; each of the resulting complexes then loses two molecules of alkali chloride :

$$K_2PtCl_4 \xrightarrow{(+NH_3)} K_2Pt(NH_3Cl)Cl_3 \xrightarrow{(-2KCl)} Pt(NH_3Cl)Cl$$

$$K_2PtCl_4 \xrightarrow{(+2NH_3)} K_2Pt(NH_3Cl)_2Cl_2 \xrightarrow{(-2KCl)} Pt(NH_3Cl)_2.$$

This accounts for the fact that α-dichlorides never result from such reactions. The loss of only one molecule of potassium chloride from the complex $K_2Pt(NH_3Cl)Cl_3$ gives Cossa's potassium salt,

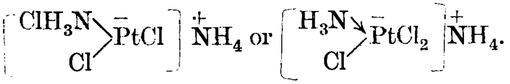
$KPt(NH_3Cl)Cl_2$, which is in all probability an intermediate in the formation of the β-dichloride.

The reverse process is seen in the action of hydrochloric acid upon the β-dichloride, whereby first Cossa's ammonium salt and then ammonium chloroplatinite are formed; a grouping $\cdot NH_3Cl$ is first removed by a molecule of hydrochloric acid as ammonium chloride with formation of Klason's $Pt(NH_3Cl)Cl$, which was shown by him (*J. pr. Chem.*, 1903, **175**, 17) to add on alkali chlorides with formation of Cossa's salts; repetition of the same types of reactions with the remaining $\cdot NH_3Cl$ group gives ammonium chloroplatinite :

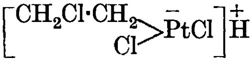
$$Pt(NH_3Cl)_2 \xrightarrow{+HCl} Pt(NH_3Cl)Cl + NH_4Cl \longrightarrow \underset{\text{(Cossa's ammonium salt)}}{NH_4[Pt(NH_3Cl)Cl_2]};$$

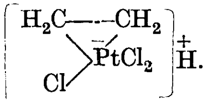
$$Pt(NH_3Cl_2) \xrightarrow{+2HCl} PtCl_2 + 2NH_4Cl \longrightarrow (NH_4)_2[PtCl_4].$$

Cossa's ammonium salt may, therefore, have either of the following structural formulæ, of which the first seems the more probable [see (*b*)] :



$$\left[\begin{matrix}ClH_3N\\Cl\end{matrix}\!>\!\overset{-}{Pt}Cl\right]\overset{+}{NH_4} \text{ or } \left[\begin{matrix}H_3N\\Cl\end{matrix}\!>\!\overset{-}{Pt}Cl_2\right]\overset{+}{NH_4}.$$

(*b*) Zeise's acid, formulated by Jörgensen as $HCl\cdot Cl\cdot Pt\cdot C_2H_4\cdot Cl$, becomes on our view the analogue of Cossa's acid and must be written :  $\left[\begin{matrix}CH_2Cl\cdot CH_2\\Cl\end{matrix}\!>\!\overset{-}{Pt}Cl\right]\overset{+}{H}$. This analogy affords valuable evidence in favour of our contention that the groupings NH_3Cl, py Cl, etc., are present in such platinum compounds; for, in the case of Zeise's acid, it is not possible, owing to the quadrivalency of carbon, to write the group $\cdot CH_2\cdot CH_2\cdot Cl$ otherwise than in that manner, the alternative formula (below) being that of a platinic instead of a platinous compound :



Cossa's platotetrammine salt of Zeise's acid, which Jörgensen describes as platodiamminoplatosemiethylene chloride and to which he ascribes the formula $Pt(NH_3\cdot NH_3\cdot Cl\cdot Cl\cdot Pt\cdot C_2H_4Cl)_2$, is the analogue of the platotetrammine salt of Cossa's first acid and must be written : $\overset{-}{[Pt(C_2H_4Cl)Cl_2]_2}\overset{++}{[Pt(NH_3)_4]}$.

(*c*) Fassbender's acid, $H(py)PtCl_5$, was obtained by the action of pyridine on H_2PtCl_6; Anderson's end-product of this reaction was shown by Jörgensen, who reduced it to β-$Pt\,py_2Cl_2$, to be identical with β-Pt py_2Cl_4, the analogue of Cleve's chloride, β-$Pt(NH_3)_2Cl_4$. These reactions now become :

$$H_2[PtCl_6] \xrightarrow{py} H_2[Pt(py\,Cl)Cl_5] \xrightarrow{-HCl} \underset{\text{(Fassbender's acid.)}}{H[Pt(py\,Cl)Cl_4]}$$

$$H[Pt(py\,Cl)Cl_4] \xrightarrow{py} H[Pt(py\,Cl)_2Cl_3] \xrightarrow{-HCl} \underset{\text{(Anderson's end-product.)}}{Pt(py\,Cl)_2Cl_2}$$

Jörgensen assigned to Anderson's end-product the formula which we now regard as correct.

Fassbender found that the first action of pyridine upon sodium chloroplatinate was the displacement of sodium chloride by pyridine, giving NaPt py Cl_5. This substance, which must be assigned the formula $Na[Pt(py\,Cl)Cl_4]$, is precisely analogous to Cossa's second salt, $K[Pt(NH_3Cl)Cl_4]$. It is clearly a product of the loss of sodium chloride from the unstable primary substance $Na_2[Pt(py\,Cl)Cl_5]$. These reactions demonstrate that the first action of an amine upon potassium chloroplatinate, as upon the chloroplatinite, is the insertion of a molecule of amine between platinum and a chlorine atom, the latter becoming attached to nitrogen. In this lies the explanation of the fact that amines of β-structure are invariably the products of such interactions.

It will be seen that our formula (X) represents the β-diamminodichloride as two molecules of ammonium chloride in each of which a hydrogen atom has been substituted by the same platinum atom ; and it might be anticipated, therefore, that the halogens would be ionised. Since ionisation is actually absent or only very minute, it follows that the nitrogen atoms of (X) must be quinquecovalent, being associated with a decet of electrons. It may be suggested that this violation of the octet rule, and of the rule that the co-ordination number for an element of the first series cannot exceed four, is due to the attraction of the massive and unsaturated platinum atom for electrons, whereby it restrains the valency electrons of the nitrogen atoms and prevents their capture by the halogens. A somewhat similar effect is seen in the case of the mercury atom in mercuric chloride. That nitrogen may occasionally be quinquecovalent becomes probable from the evidence recently cited in the cases of the dihalides of pyridine [*e.g.*, pyridine iodochloride is not ionised in pyridine solution (Williams, J., 1931, 2783)] and even of certain aromatic and aliphatic nitro-compounds (Hendricks and Hilbert, *J. Amer. Chem. Soc.*, 1931, **52**, 4280). Wynne-Jones, too, has shown (J., 1931, 795) that salts of piperidine, dipropylamine, and other partially substituted ammonias, with hydrochloric, picric, and perchloric acids, exist to a greater or less extent in the form of non-ionic molecules.

It has been deduced from *X*-ray crystal measurements that the four chlorine atoms of potassium chloroplatinite are in one plane, which also contains the platinum atom (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44** 2404); but this deduction appears to afford no special support to a planar theory of the structure of the diammines and tetrammines. The tacit assumption that the chlorine atoms in the ion $\bar{\bar{P}}tCl_4$ have the same stereochemical disposition as those in $PtCl_4$ and that the ammonia groups in the α-diammines merely replace these chlorine atoms, is entirely without proof at the present time.

We conclude that there is no longer a valid reason for assuming a planar distribution of four valencies to platinum in the platodiammines.

EXPERIMENTAL.

Isomeric Diamminoplatinous Dichlorides, $Pt(NH_3)_2Cl_2$.—*α-Dichloride* (IX). Prepared by heating the tetrammine $Pt(NH_3)_4Cl_2$ alone, or, better, with concentrated hydrochloric acid, this was obtained as small, faintly yellow prisms from hot water (Found: Pt, 65·2, 65·1; H, 1·9, 2·25; N, 9·5. Calc. for $H_6N_2Cl_2Pt$: Pt, 65·05; H, 2·0; N, 9·3; Cl, 23·6%); it neither reacts with aqueous potassium chloroplatinite nor gives a coloration with phenoxtellurine dibisulphate. When its aqueous solution is heated for some hours at 100° an equilibrium mixture with a small proportion of the γ-dichloride is produced. The α-dichloride is oxidised to the α-tetrachloride (XVI) on prolonged contact with hydrochloric acid in presence of air.

β-Dichloride (X). Reaction between ammonium chloroplatinite and ammonia yielded this dichloride as bright yellow, flat, rectangular needles from water (Found: Pt, 64·95, 64·95, 64·9, 64·9; H, 2·0, 2·05; N, 9·35; Cl, 23·5%). It does not interact with aqueous potassium chloroplatinite; gives an intensely purplish-violet coloration with phenoxtellurine dibisulphate; is unchanged when heated at 100° in aqueous solution during 48 hours; is substantially unchanged when heated with water in a sealed tube at 140° for 6 hours; gives a red coloration when warmed with phenoxtellurine; is unchanged in the presence of cold concentrated hydrochloric acid, but is transformed to Cossa's ammonium salt when heated with *N*-hydrochloric acid.

γ-Dichloride (XI). Addition of dilute hydrochloric acid to the solution of the base formed by the action of silver oxide and water, or of warm aqueous caustic soda, on the α-dichloride afforded the γ-isomeride, which crystallised as golden-yellow to orange-yellow needles or plates from hot water; the crystals are frequently curved or serrated when crude (Found: Pt, 65·0, 64·95, 65·3, 65·2, 64·9; H, 2·1; N, 9·6; Cl, 23·55%). This *substance* is mainly transformed into the α-dichloride when heated at 100° in aqueous solution during a few hours; it does not combine with aqueous potassium chloride or chloroplatinite. The aqueous solution is neutral and has a pronounced yellow colour. Towards halogens or bases, the substance reacts like the α-dichloride.

Diamminoplatinous Dibromides and Di-iodides.—These substances were prepared by the action of a large excess of the aqueous potassium halide on a solution of the α- or β-dichloride; or, in the case of the β- and γ-compounds, by neutralising an aqueous solution of the base with the appropriate halogen acid.

α-$Pt(NH_3)_2Br_2$ (Found: Pt, 49·9. Calc.: Pt, 50·15%); sulphur-yellow prismatic needles; gives no coloration with phenoxtellurine dibisulphate. α-$Pt(NH_3)_2I_2$ (Found: Pt, 40·35. Calc.: Pt, 40·4%); pale yellow, crystalline powder. β-$Pt(NH_3Br)_2$ (Found: Pt, 50·25, 50·3%); orange needles, giving orange-brown coloration with phenoxtellurine dibisulphate. β-$Pt(NH_3I)_2$ (Found: Pt, 40·35%); orange-yellow prismatic needles, giving reddish-brown coloration with phenoxtellurine dibisulphate. γ-$Pt(NH_3)_2Br_2$ (Found: Pt, 50·3. $PtH_6N_2Br_2$ requires Pt, 50·2%); clusters of small, dark orange prisms from water.

Diamminoplatinous Tetrahalides.—α-$Pt(NH_3)_2Cl_4$ (Found, in preparation dried over phosphoric oxide: Pt, 52·3, 52·5. Calc. for $PtH_6N_2Cl_4$: Pt, 52·6%), prepared by the action of chlorine upon the α-dichloride in aqueous solution, formed small, bright yellow cubes or octahedra from water.

β-$Pt(NH_3)_2Cl_4$, similarly prepared from the β-dichloride, crystallised as lemon-yellow, rhombic or hexagonal plates (Found: Pt, 52·65. Calc.: Pt, 52·6%).

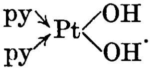
Dipyridinoplatinous Dichlorides.—α-$Pt\,py_2Cl_2$, prepared by the action of concentrated hydrochloric acid upon the tetrapyridinodichloride, or by the action of dilute hydrochloric acid upon the corresponding α-base, formed a very pale yellow, microcrystalline powder, soluble in chloroform (which is the best solvent for its recrystallisation) and other organic solvents, but almost insoluble in water (Found, in sample from chloroform: Pt, 45·9. Calc.: Pt, 46·0%). It gives no coloration with phenoxtellurine dibisulphate, and is unchanged by long boiling with aqueous ammonium chloride.

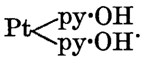
β-$Pt\,py_2Cl_2$ was prepared from pyridine and aqueous potassium chloroplatinite; it is a very pale yellow, microcrystalline powder, very sparingly soluble in water, gives a red coloration with phenoxtellurine dibisulphate, and is less soluble in organic solvents than the α-isomeride (Found : Pt, 46·0. Calc. : Pt, 46·0%).

Bases.—*γ-Diammino-base* (XV). The α-diammino-dichloride was boiled with water and excess of silver oxide during some 20 minutes. The filtrate was evaporated in a vacuum over phosphoric oxide, short, very pale yellow, hexagonal prisms being obtained [Found : Pt, 69·8, 70·2, 70·35, 70·5. $Pt(NH_3)_2(OH)_2$ requires Pt, 74·15. $Pt(NH_3)_2(OH)_2,H_2O$ requires Pt, 69·4%].

The aqueous solution of the *base* was alkaline to litmus and was free from chlorine and from silver; it readily absorbed carbon dioxide, and was somewhat hygroscopic. When neutralised with dilute hydrochloric acid it gave the γ-dichloride.

β-*Diammino-base* (XII). Prepared from the β-diammino-dichloride, as above, this *base* formed a transparent yellow glassy solid, free from halogen and from silver, and was very hygroscopic [Found (in specimens prepared in a stream of nitrogen and dried over phosphoric oxide) : Pt, 71·0, 71·0, 72·1, 71·8. Other samples prepared in air gave variable results : Pt, 67·8, 69·1, 67·8, 65·7, 64·0, 68·2%]. Its solution in water was alkaline, absorbed carbon dioxide, and gave with dilute hydrochloric acid the β-dichloride. The solid base gave a green coloration with phenoxtellurine dibisulphate.

α-*Dipyridino-base,*  $\begin{smallmatrix}\mathrm{py}\searrow & & \diagup\mathrm{OH}\\ & \mathrm{Pt} & \\ \mathrm{py}\nearrow & & \diagdown\mathrm{OH}\end{smallmatrix}$. This *base*, prepared in a similar manner from α-Pt py_2Cl_2, forms long, asbestos-like needles from water, in which it is only moderately soluble [Found (in air-dried product) : Pt, 35·05. Pt $py_2(OH)_2,9H_2O$ requires Pt, 35·5%. Found (in product dried over phosphoric oxide) : Pt, 46·5. Pt $py_2(OH)_2,2H_2O$ requires Pt, 46·1%]. The aqueous solution, which is somewhat feebly alkaline, gives only α-Pt py_2Cl_2 with dilute hydrochloric acid; with aqueous sodium chloride it slowly interacts giving the same product.

β-*Dipyridino-base,*  $\mathrm{Pt}\begin{smallmatrix}\diagup\mathrm{py{\cdot}OH}\\ \diagdown\mathrm{py{\cdot}OH}\end{smallmatrix}$. Prepared by the action of moist silver oxide on β-Pt py_2Cl_2, this *base* forms a hygroscopic, yellow glassy mass, readily soluble in water to an alkaline solution, from which dilute hydrochloric acid precipitates the β-dichloride [Found : Pt, 49·8. Pt $(py{\cdot}OH)_2$ requires Pt, 50·4%].

β-*Oxalate* (XIII). Neutralisation of the β-base with oxalic acid, or treatment of the β-dichloride with silver oxalate, or warming ammonium chloroplatinite and ammonium oxalate with aqueous ammonia afforded this *oxalate* as almost white needles with pearly lustre (Found : Pt, 61·5. $C_2H_6O_4N_2Pt$ requires Pt, 61·5%); it decomposes near 230°, is very sparingly soluble in water, gives the β-dichloride when treated with warm hydrochloric acid, but does not give a coloration with phenoxtellurine dibisulphate.

Physical Properties of the Isomeric Diamminoplatinous Dichlorides.

(i) Molecular-weight determinations were attempted by the ebullioscopic method in water, McCoy's modification of Beckmann's apparatus being used. The following results were obtained :

	W (g.).	e.	v (c.c.).	M.
α-Isomeride	0·1901	0·010°	30·0	(342)
	0·1201	0·009	27·0	(279)
β-Isomeride	0·5272	0·036	24·8	313
	0·3808	0·025	27·8	296
γ-Isomeride	0·1230	0·008	27·1	(306)
	0·1758	0·010	29·8	(298)

[Calc. for $Pt(NH_3)_2Cl_2$: M, 300.]

It is clear that only in the case of the β-isomeride can it be concluded that the results afford reliable evidence as to the degree of complexity.

(ii) Molecular conductivities in water were determined in the apparatus previously described (*loc. cit.*). The initial conductivities were very low in the case of each of the three isomerides; but, in confirmation of the work of Werner and others, it was noticed that there was a rapid increase of conductivity with time. This increase was found to be due neither to the development of free acid by hydrolytic action of the solvent nor to catalytic effect of the platinised platinum electrodes. The latter explanation, proposed by Werner, was disproved by keeping the solution for the requisite interval of time before inserting the electrodes, and comparing the conductivity then obtained with that of a solution kept in the cell during the same period. Chemical tests indicated that the increase of conductivity is probably due to the generation of ammonium chloride by the disruptive action of water; this decomposition appears to be appreciable only in very dilute solutions.

The conductivities were extrapolated to zero time, and the values reduced to a common dilution for purposes of comparison. The following values were obtained for M at 25°, t being the time (in minutes) and v the dilution (in litres/g.-mol.) :

α-Isomeride.

t	0	62	131	174	2752
M (v = 2866)	17·0	21·0	26·1	32·7	89·8
M (v = 1234)	7·5	9·0	11·2	14·1	38·7

β-Isomeride.

t	0	66	193	1397
M (v = 1234)	7·7	14·4	36·8	86·0

γ-Isomeride.

t	0	67	139	1410
M (v = 4690)	21·3	30·3	56·0	116·6
M (v = 1234)	5·6	7·9	14·7	30·7

(iii) Solubilities in water at 25° were determined after several days' shaking in the thermostat. Measured volumes of solution were evaporated over phosphoric oxide, and the amounts of solute obtained by weighing. Results :

100 G. of water at 25° dissolve 0·0366 g. of α-isomeride;
0·2523 g. of β-isomeride;
0·0491 g. of γ-isomeride.

Crystallographic Investigation of the Diamminoplatinous Dichlorides.

(By E. G. Cox.)

(a) *Microscopic Examination.*—The three isomerides were obtainable only in small, imperfectly formed crystals, the largest being about 0·1 mm. long. The refractive-index determinations noted below were made by the immersion method with sodium light; owing to the high values of the indices, it was not possible to make the determinations with very great accuracy, except for one of the indices of the γ-isomeride, but the examination was sufficient to show very appreciable differences between the three substances.

(i) α-$Pt(NH_3)_2Cl_2$. Pale yellow crystals; tabular, often elongated, with straight extinction and positive elongation. Refractive indices about 1·76. Twinning fairly common.

(ii) β-$Pt(NH_3)_2Cl_2$. Yellow crystals, deeper in colour than the α-compound. Mostly acicular, usually with straight extinction but frequently inclined; positive elongation. Refractive indices about 1·76; birefringence apparently somewhat higher than that of the α-isomeride. Twinning fairly common, but on a different law from the α-compound.

(iii) γ-$Pt(NH_3)_2Cl_2$. Crystals orange-yellow, deeper than α- or β-. Acicular, with a great tendency to parallel growths and dendritic formations; radiated growths also occur. Straight extinction with negative elongation. One refractive index 1·715; another about 1·76. The comparatively low index of this isomeride distinguishes it immediately from the other two.

(b) X-*Ray Examination.*—Powder photographs of the α- and the γ-isomeride showed definitely that the two have entirely different structures. Photographs were taken of two different specimens of the former and of three of the latter. The three γ-photographs were exactly alike, as were also the two α-photographs. Owing to the technical difficulties of obtaining suitable powder photographs of substances containing such a high percentage of platinum, reproduction is not feasible, but the differences between the α- and γ-photographs are considerable and immediately discernible. Since it is evident from the microscopic examination that the two substances are either orthorhombic or monoclinic, it is not possible at present to gain much information of value as to the structures of the individual isomerides from the photographs. It is clear that the two differ considerably, and it is hoped later to investigate all three isomerides more closely by *X*-ray methods.

Summary.

(1) It is shown that there are *three* isomeric diamminoplatinous dichlorides, and that they are probably structural isomerides.

(2) It is suggested that only the α-isomeride has four groups arranged round the platinum atom and that there is at present no positive evidence to decide whether the distribution is tetrahedral or planar.

(3) The α- and the β-diammino-tetrachloride are shown, on the basis of the formulæ proposed for the dichlorides, to be likewise structural and not stereo-isomerides.

(4) The isomeric series of α- and β-diammino-compounds differ notably from those of the α- and β-sulphines, particularly in the non-interconvertibility of the former among themselves.

(5) Mechanisms are suggested for the formation of Cossa's salts and of several other well-known groups of substances.

We desire to express our thanks to the Department of Scientific and Industrial Research, to the Chemical Society, and to Imperial Chemical Industries, Ltd., for grants which have partly defrayed the cost of the work; also to Dr. F. G. Angell for making some of the physical measurements.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

EAST LONDON COLLEGE.

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