295. *Wolffram's Red Salt and the Possibility of Tervalent Platinum.*

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In 1850, Wurtz described a colourless plato-tetrammine having the formula [Pt etn$_4$]Cl$_2$,2H$_2$O, where etn = C$_2$H$_5$·NH$_2$; Wolffram (Diss., Königsberg, 1900) obtained from this, by the action of hydrogen peroxide in hydrochloric acid, a crystalline dihydrated red salt, which he considered to be isomeric with Wurtz's salt.

We undertook the re-examination of this substance because, not only is there no other known case of isomerism among unmixed plato-tetrammines, but the work of earlier investigators and our own previous observations had suggested that a coloured platinum compound of this nature should be capable of being formulated as a compound of tervalent platinum, simple or dimeric; and in fact, we soon found that the red substance had the empirical formula Pt etn$_4$Cl$_3$,2H$_2$O, and that only two of the three chlorine atoms were ionised. While we were attempting to discover the structural formula, however, Reihlen and Flohr (*Ber.*, 1934, **67**, 2010) anticipated our publication; they found that Wolffram's salt could be prepared directly by mixing aqueous solutions of the colourless [Pt etn$_4$]Cl$_2$ and its yellow plati-analogue, [Pt etn$_4$Cl$_2$]Cl$_2$, and they concluded that the most probable structural formula was that of the double salt, [Pt etn$_4$]Cl$_2$ + [Pt etn$_4$Cl$_2$]Cl$_2$ + 4H$_2$O. This was supported by the fact that the red salt was only pale yellow in aqueous solution (Wolffram) and that it gave (Reihlen and Flohr), both with sodium chloroplatinate and with potassium chloroplatinite, products which could readily be accounted for by assuming normal reactions of the components of the double salt.

Reihlen and Flohr thus regard the red salt as a special lattice compound, and find confirmation of this in the fact that the red colour changes to yellow when the salt is de-

hydrated (Wolffram) and the lattice destroyed. They reject as improbable the formula [Pt etn$_4$Cl]Cl$_2$,2H$_2$O, on the ground that "no compounds of tervalent platinum are known," and they do not consider the possibility of a dimeride of this, in which the two platinum atoms are attached to one another. Whilst our parallel experimental results agree substantially with those of Reihlen and Flohr, some fresh data lead us to conclude that the formulation of Wolffram's salt as a double salt is erroneous.

It is well known that [Pt etn$_4$]Cl$_2$ and its aqueous solution are colourless, and it is now found that [Pt etn$_4$Cl$_2$]Cl$_2$ is cream-white when pure, and gives an almost colourless solution in water. The red salt is colourless in cold water, but the saturated hot solution is pale yellow; when dehydrated, it is yellow, but it is soon completely rehydrated in moist air, with restoration of the red colour. The hypothesis that both the aqueous solution of the red salt and the anhydrous salt contain merely a mixture of the two simple components is scarcely adequate to account for the yellow colours. It is very improbable, too, that the red colour of the dihydrate is due to a special lattice, since this would have in a sense to be broken down on dehydration and restored by the action of moist air.

Reihlen and Flohr prepared the analogous bromide, but did not analyse it or determine its hydration. This *substance*, Pt etn$_4$Br$_3$,2H$_2$O, has an important bearing on the structure, and is now found to crystallise from cold water in green needles of the dihydrate, the streak being green; from warm water, however, it separates in scarlet needles of the anhydrous substance, having an orange streak. When the green salt is warmed with a little water, it becomes scarlet without dissolving, suggesting a structural change rather than dichroism. The green salt is completely dehydrated in dry air at 100°, becoming somewhat darker, but if disturbed, this anhydrous salt becomes suddenly reddish-chocolate in colour (orange streak) without losing its crystalline form. The chocolate colour changes at once to scarlet when the salt is moistened with water. The dried substance is not rehydrated in moist air. It is thus clear that hydration is incidental to, rather than a prime cause of, the high development of colour shown by these salts, so the special lattice theory can scarcely be supported. The above bromide is golden-yellow in aqueous solution. The crystalline *plati-bromide*, [Pt etn$_4$Br$_2$]Br$_2$, was found to be of this shade, and became green when rubbed with moist iron; when ground with moist [Pt etn$_4$]Cl$_2$ it became purple-black.

Reihlen and Flohr remarked, as a strong argument for the special lattice, that the ionised halogen atoms of Wolffram's red salt cannot be replaced by radicals which would alter the crystal lattice. This is probably due merely to the difficulty of preparing the salts and to differences in stability. The yellow *thiocyanate* [Pt etn$_4$Cl](NCS)$_2$, which is anhydrous, has now been obtained analytically pure, but as it is unstable in hot water, we have not been able to show that it retains the structure of Wolffram's salt. The pale yellow mono-hydroxy-compound, [Pt etn$_4$(OH)]Cl$_2$,2H$_2$O, was also obtained, but both its purity and its structure were uncertain. However, it was readily shown that two or all four of the ethylamine groups of Wolffram's salt may be replaced by propylamine, with the production of red salts which are analogous in properties, although they have not been isolated in the pure state. As this kind of substitution necessitates an alteration of lattice, it is clear that the special properties of salts of the type of Wolffram's salt are a consequence of chemical structure and not of crystal lattice.

The most probable structure for Wolffram's red salt is that of the simple derivative of tervalent platinum, [Pt etn$_4$Cl]Cl$_2$,2H$_2$O, which is to be regarded as intertransformable with the dimeric form, [Cl etn$_4$Pt·Pt etn$_4$Cl]Cl$_4$, in which platinum is formally quadrivalent. When the salt is dissolved in water, one or other of these forms enters into equilibrium with the kations, [Pt etn$_4$] and [Pt etn$_4$Cl$_2$], and chloride ions.

The literature already contains a number of substances in which platinum has been assigned the tervalent state, and all of them are coloured. The poorly-defined brown oxide and hydrated oxides of tervalent platinum, and the greenish-black chloride PtCl$_3$ being omitted, the following cases of crystalline substances may be cited :*

* Rây and Ghose's compound (*J. Indian Chem. Soc.*, 1934, **11**, 737), to which they ascribed the formula Pt(EtS·CH$_2$·CH$_2$·SEt)Cl$_3$, had already been described by Tschugaieff and Benevolensky (*Z. anorg. Chem.*, 1913, **82**, 420), who showed that it had the structure [Pt(EtS·CH$_2$·CH$_2$·SEt)$_2$][PtCl$_6$]. It is not therefore an example of a tervalent platinum compound.

(i) Blondel's acid and its salts (*Ann. Chim. Phys.*, 1905, **6**, 110; *Bull. Soc. chim.*, 1910, **7**, 99). The acid consists of orange prisms, $HPt(SO_4)_2,6H_2O$, which can be dried to a yellow dihydrate; the potassium salt, $KPt(SO_4)_2,H_2O$, forms yellow needles stable at 150°.

(ii) Jörgensen's reddish-brown α-$Pt(NH_3)etnBr_3$ and the analogous red α-$Pt(NH_3)pyCl_3$ (*J. pr. Chem.*, 1886, **33**, 489; J., 1932, 1013).
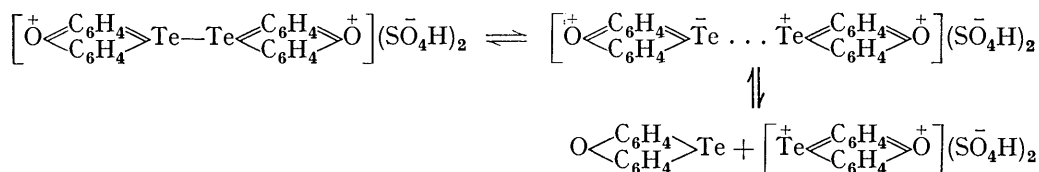
(iii) The compounds of Tschugaieff and Tscherniaeff (*Z. anorg. Chem.*, 1929, **182**, 159): β-$Pt(NH_3)_2(OH)Cl_2$, black needles; and the exceptionally well-defined red Pt $enCl_3$, which we later showed (unpublished work) to be preparable by grinding together a moist mixture of Pt $enCl_2$ and Pt $enCl_4$, in addition to the method of partial oxidation of Pt $enCl_2$ (see J., 1933, 1335). Head and one of us also observed (J., 1934, 224) that α-$[Pt(NH_3) etnCl_2]$ and α-$[Pt(NH_3) etnCl_4]$ form a red crystalline substance when mixed at 210°.

(iv) In the palladium series there is the very crystalline black $Pd(NH_3)_2Cl_3$, obtained by chlorination of $Pd(NH_3)_2Cl_2$ (J., 1932, 1908). It may be noted also that the green-black compound produced by the action of sulphuric acid upon β-$Pt(NH_3)_2Cl_2$, to which the formula $H_2[(NH_3Cl)_2Pt \cdot O \cdot SO_2 \cdot O \cdot Pt(NH_3Cl)_2]$ has been assigned (J., 1934, 1790), may be formulated as a compound of tervalent platinum if the two platinum atoms are regarded as linked together.

It seems clear that several of the above compounds, particularly Pt $enCl_3$ and Jörgensen's two compounds, present close analogy with Wolffram's salt in respect of the valency state of their platinum atoms : all of these substances represent intermediate stages between the bi- and the quadri-valent state, or, as it may be expressed, the stage of half-oxidation. In a number of well-known cases of organo-metallic or -metalloidal and even of purely organic compounds, this stage of half-oxidation is represented by crystalline compounds showing much higher development of colour than the fully oxidised or the fully reduced compound : meriquinoid salts, complexes of the quinhydrone type, and in particular, the purple salts of the phenoxtellurylium series and their apparent analogues in the nitrogen, sulphur, selenium, and arsenic series, may be cited as instances. In each case, a choice has to be made between the assumption of an intermediate state of valency and that of a dimeric formula ; and in some of the instances (*e.g.*, the phenoxtellurylium complexes) the experimental results indicate the latter; but it is quite possible that in other cases there may be an equilibrium set up between the two forms, and this equilibrium may some-times be inclined almost entirely to the side of the monomeric substance of intermediate valency. Thus, the problem is really that of a choice between the dimeric and the " free radical " state, as, *e.g.*, in the case of triphenylmethyl and its analogues :

$$2CPh_3 \rightleftharpoons Ph_3C \cdot CPh_3 \rightleftharpoons Ph_3\overset{+}{C} + Ph_3\overset{-}{C}.$$
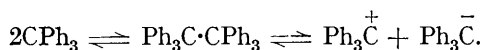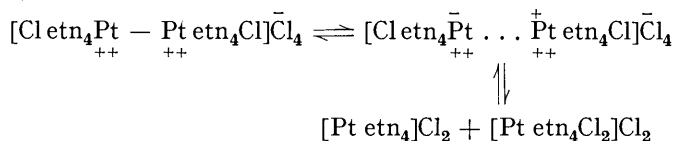
The assumption of a tendency towards ionisation of a dimeric substance associated with anions affords an explanation of the way in which it may become resolved, when in solution, into the ions of its fully reduced and fully oxidised component salts, *e.g.*, the purple salt shown below (on the left) is only pale yellow in hot acetic acid solution but is regenerated when the solution cools :

$$\left[\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}Te{-}Te{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{O}\right](S\bar{O}_4H)_2 \rightleftharpoons \left[\overset{+}{O}{<}^{C_6H_4}_{C_6H_4}{>}\bar{Te} \ldots \overset{+}{Te}{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{O}\right](S\bar{O}_4H)_2$$

$$\Updownarrow$$

$$O{<}^{C_6H_4}_{C_6H_4}{>}Te + \left[\overset{+}{Te}{<}^{C_6H_4}_{C_6H_4}{>}\overset{+}{O}\right](S\bar{O}_4H)_2$$

The hypothetical intermediate stage shows a substance in which the tellurium atoms are tending to develop opposite charges, and it will be clear that, as the tellurium atoms separate, the positive charges attract the negative acid radicals, the parent oxidised and reduced components of the purple complex being regenerated.

Essentially, the same explanation may be invoked to show how Wolffram's salt may pass

into or separate from a colourless solution, and how the solution may contain the fully oxidised and fully reduced kations :

$$[Cl\,etn_4Pt - Pt\,etn_4Cl]\bar{C}l_4 \rightleftharpoons [Cl\,etn_4\bar{P}t \ldots \overset{+}{P}t\,etn_4Cl]\bar{C}l_4$$

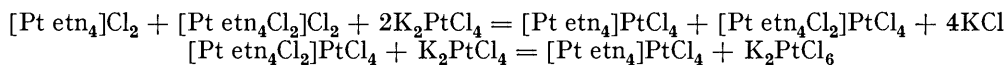$$[Pt\,etn_4]Cl_2 + [Pt\,etn_4Cl_2]Cl_2$$

The platinum atom which acquires the negative charge may be regarded as imparting it to the covalently attached chlorine atom, which thus becomes an ion; the scheme accounts for the fact that three of the four chloride ions of the original dimeric formula ultimately become associated with one of the component salts, whilst the other component salt attaches only one of the chloride ions. The positive charges of the original dimeric salt, although shown conventionally on the platinum atoms, are probably located upon the nitrogen atoms. Thus, when the ions reassemble in the solid, they might take up other positions than those shown above, and of the possibilities, the following seemed worthy of consideration :

$$[(\overset{+}{etn})_2(etn)_2Pt \ldots \overset{+}{P}t(Cl)(etn)_2(\overset{+}{etn})_2]\bar{C}l_5 \longrightarrow [Pt(etn)_2(etn)_2][\bar{P}tCl_2(etnCl)_4],$$ since it would indicate that the salt may be formulated conventionally as a plato-plati-ammine $[Pt\,etn_4][\bar{P}tCl_6etn_4]$, or the equivalent $[Pt\,etn_4][\bar{P}tCl_2(etn)_4](\bar{C}l)_4$. However, we failed to find evidence that $[Pt\,etn_4Cl_2]Cl_2$ could function like platinic chloride in combining with 2 mols. of hydrochloric acid or potassium chloride, and therefore this view was abandoned.

Reihlen and Flohr made the important discovery that Wolffram's red salt can be prepared by mixing $[Pt\,etn_4]Cl_2$ and $[Pt\,etn_4Cl_2]Cl_2$ in aqueous solution; and they also deduced that the ions of these component salts are regenerated when the red salt is dissolved in water. They tested the latter hypothesis by examining the action of cold aqueous sodium chloroplatinate on the red salt, which gave a brownish-yellow salt, $[Pt\,etn_4]PtCl_6$ or $[Pt\,etn_4Cl_2]PtCl_4$, together with a more soluble orange salt, $[Pt\,etn_4Cl_2]PtCl_6,2H_2O$. It is now found that, with chloroplatinic acid in the cold, an aqueous solution of Wolffram's salt gives the above two salts, the former of which, when crystallised from dilute hydrochloric acid, is rearranged as follows :

$$2[Pt\,etn_4]PtCl_6 = [Pt\,etn_4Cl_2]PtCl_6 + [Pt\,etn_4]PtCl_4.$$
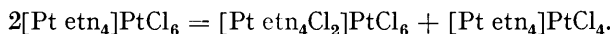
They found also that hot aqueous potassium chloroplatinite gave with the red salt a mixture of the insoluble violet-red salt, $[Pt\,etn_4]PtCl_4$, and potassium chloroplatinate, a reaction which was interpreted as a reduction :

$$[Pt\,etn_4]Cl_2 + [Pt\,etn_4Cl_2]Cl_2 + 2K_2PtCl_4 = [Pt\,etn_4]PtCl_4 + [Pt\,etn_4Cl_2]PtCl_4 + 4KCl$$
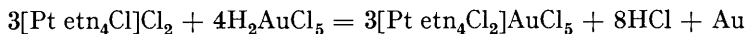$$[Pt\,etn_4Cl_2]PtCl_4 + K_2PtCl_4 = [Pt\,etn_4]PtCl_4 + K_2PtCl_6$$

It is now found, however, that, when the reaction is carried out in the cold with equivalent solutions of the reactants, almost complete precipitation occurs of an apparently homogeneous *salt* having the median constitution as shown by analysis; the reaction could be expressed by the equation :

$$[Pt\,etn_4Cl]Cl_2 + K_2PtCl_4 = [Pt\,etn_4Cl]PtCl_4 + 2KCl$$
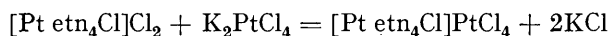
or the salt could be formulated as an equimolecular mixture or compound of Reihlen and Flohr's pair of salts, into which it is, in fact, resolved by crystallisation from hydrochloric acid, although the $[Pt\,etn_4]PtCl_6$ undergoes the subsequent change already given. Both Reihlen and Flohr's and our own experiments were thus ambiguous, but it was then found that if precipitation was conducted with successive half-equivalents of potassium chloroplatinite solution, a practically complete separation, successively, of the salts $[Pt\,etn_4]PtCl_4$ and $[Pt\,etn_4Cl_2]PtCl_4$ was obtained. It is therefore probable that the kations of these salts are actually present in an aqueous solution of Wolffram's salt, but it also remains probable that the plato-salts containing these kations are capable of uniting to form a complex.

The point was tested further by trying similar reactions with potassium chloropalladite, this salt being less liable to oxidation than the chloroplatinite owing to the instability of the palladic state. Here again, complete precipitation gave an apparently homogeneous salmon-pink salt, empirically [Pt etn$_4$Cl]PdCl$_4$, whereas fractional precipitation gave violet-pink [Pt etn$_4$]PdCl$_4$ and orange-yellow [Pt etn$_4$Cl$_2$]PdCl$_4$, in equimolecular proportion. The salmon-pink salt could be resolved into the above two salts by crystallisation from water or from hydrochloric acid.

The action of an excess of chloroauric acid, HAuCl$_4$, in presence of dilute hydrochloric acid, upon the red salt was also examined. The reagent, as has been recorded in other cases (*e.g.*, [Co(NH$_3$)$_5$Cl]AuCl$_5$), behaved as though it were H$_2$AuCl$_5$; but the gold chloride was, in part, reduced to metallic gold, the product being the yellow *aurichloride* of the plati-salt :

$$3[\text{Pt etn}_4\text{Cl}]\text{Cl}_2 + 4\text{H}_2\text{AuCl}_5 = 3[\text{Pt etn}_4\text{Cl}_2]\text{AuCl}_5 + 8\text{HCl} + \text{Au}$$

This reaction, like those of chloroplatinic acid and its sodium salt, throws little light on the structure of Wolffram's salt. The action of bases upon the red salt likewise gave little information, since it was either nil (as with pyridine) or reducing (as with ethylamine, which gave the tetrammine [Pt etn$_4$]Cl$_2$).

The following conclusions may be drawn regarding Wolffram's salt and its analogues : The anhydrous salts (the yellow chloride and thiocyanate, and the red bromide) are analogous in structure; they differ in structure from the dihydrates (the red chloride and the green bromide), which are analogous with one another. The aqueous solutions mainly contain the ions of the simple component salts, but there is probably an equilibrium with a form of the original salt. When the green bromide is dehydrated, it retains its original structure until mechanically disturbed, whereupon the structure changes almost completely into that of the red bromide; moistening with water completes the change. Reversal of the red to the green bromide only occurs when solution in water effects regeneration of the simple components, followed by their combination and rehydration. These facts seem best interpreted by assuming that the dihydrates have the simple structure with tervalent platinum, whilst the anhydrous forms have the dimeric structure.

Thus it seems that Wolffram's red salt and a number of other coloured platinum and palladium compounds afford distinct evidence of the occurrence of these elements in a tervalent or pseudo-tervalent state, presenting several features in common with the free radicals and with certain series of compounds containing carbon, tellurium, or other element in a lower valency, or pseudo-lower valency, state.

Apart from hypotheses regarding the shift of valency electrons from one shell to another, there appears to be little real distinction between the free radical and the state of the lower valency.

<div align="center">EXPERIMENTAL.</div>

[Pt etn$_4$]Cl$_2$,2H$_2$O was prepared, usually together with an explosive black by-product, from α- or β-Pt etn$_2$Cl$_2$ or from [Pt etn]PtCl$_4$ and warm aqueous ethylamine, as colourless, domed columns from water, m. p. 189°(Found, in air-dried sample : Cl, 14·1; H$_2$O, 7·5. Calc. for C$_8$H$_{32}$O$_2$N$_4$Cl$_2$Pt : Cl, 14·7; H$_2$O, 7·5%); it forms lustrous polyhedra from aqueous alcohol. It was also prepared from Wolffram's salt and ethylamine. Its chloroplatinite, [Pt etn$_4$]PtCl$_4$, forms violet-pink rectangular needles. Chloroauric acid oxidises it to yellow [Pt etn$_4$Cl$_2$]AuCl$_5$ (see p. 1251). The dihydrate gives the anhydrous salt when dried and this is rehydrated in moist air. The salt is transformed into Wolffram's red salt when moistened with aqueous hydrogen peroxide or sodium persulphate and then treated with hydrochloric acid. Sulphuric acid in place of hydrochloric acid produces no reddening.

α-*Di(ethylamino)di(propylamino)platinous chloride dihydrate*, similarly prepared from α-Pt etn$_2$Cl$_2$ and *n*-propylamine, formed colourless slender oblique needles from water, which could be dehydrated (Found, in air-dried sample : H$_2$O, 7·6. C$_{10}$H$_{36}$O$_2$N$_4$Cl$_2$Pt requires H$_2$O, 7·1%). The *tetra(propylamino)*-compound was prepared as a *dihydrate* from potassium chloroplatinite and an excess of *n*-propylamine as a very voluminous precipitate of colourless slender needles not very soluble in cold water; it could be dehydrated, the product not apparently becoming rehydrated in moist air (Found, in air-dried specimen : Pt, 35·6; H$_2$O, 7·4. C$_{12}$H$_{40}$N$_4$O$_2$Cl$_2$Pt requires Pt, 36·3; H$_2$O, 6·7%).

Dichlorotetra(ethylamino)platinic chloride was prepared by gently warming [Pt etn$_4$]Cl$_2$ with aqueous hydrogen peroxide, adding hydrochloric acid, and crystallising the precipitate from water. It formed anhydrous cream-white needles (Found : C, 18·4; H, 5·5; Pt, 37·2. Calc. for C$_8$H$_{28}$N$_4$Cl$_4$Pt : C, 18·6; H, 5·5; Pt, 37·7%), giving an almost colourless aqueous solution. With chloroauric acid, it gave yellow [Pt etn$_4$Cl$_2$]AuCl$_5$ (see p. 1251); with K[Pt(NH$_3$)Cl$_3$], it gave yellow crystals. The moistened substance was easily reduced to Wolffram's red salt when rubbed with a nickel strip, as described by Reihlen and Flohr, or with iron. Partial reduction occurred when the substance was boiled with aqueous alcohol or with a little aqueous ethylamine.

The *tetra(propylamino)*-compound was obtained similarly as an anhydrous white precipitate, very sparingly soluble in boiling water. It became red when moistened and rubbed with steel (Found : C, 25·0; H, 6·4; Pt, 34·7. C$_{12}$H$_{36}$N$_4$Cl$_4$Pt requires : C, 25·1; H, 6·3; Pt, 34·0%).

Wolffram's red salt, [Pt etn$_4$Cl]Cl$_2$,2H$_2$O, was obtained at once by slowly adding concentrated hydrochloric acid to a strong aqueous solution of [Pt etn$_4$]Cl$_2$ containing hydrogen peroxide (about twice the theoretical quantity). It formed brilliant, slender, pleochroic needles from hot water, having a red-brown colour when slowly separated, but a scarlet colour with bluish-green reflex on rapid separation; the powdered salt was intensely red; it melted and decomposed at 180°; with further hydrogen peroxide and hydrochloric acid it gave [Pt etn$_4$Cl$_2$]Cl$_2$. In the presence of dilute sulphuric acid, it was oxidised quantitatively by potassium permanganate to the platinic state. In a stream of dry air at 100°, it was dehydrated in a few minutes (with phosphoric oxide, in some hours) to yellow pseudomorphs of the anhydride; these were rehydrated very rapidly in moist air to the scarlet salt. The action of excess of aqueous silver nitrate was examined quantitatively : in the cold, two-thirds of the chlorine was precipitated at once as silver chloride, whereas the remaining one-third was only incompletely precipitated even by prolonged boiling of the filtrate in presence of nitric acid; the whole of the chlorine was obtained by the Carius method (J., 1934, 1787) [Found, in air-dried salt : C, 18·5; H, 6·3; Cl (total), 20·3; Cl (ionised), 14·1; Pt, 37·3; H$_2$O, 6·8. Calc. for dihydrate : C, 18·5; H, 6·2; Cl (total), 20·4; Cl (ionised), 13·7; Pt, 37·7; H$_2$O, 7·0%]. With aqueous sodium nitrite, the salt gave yellow needles; with sodium phenylacetate, minute white needles; with potassium iodide, iodine and a dark crystalline precipitate. When heated with excess of aqueous ethylamine, it was reduced almost quantitatively to [Pt etn$_4$]Cl$_2$, the base being changed probably into an *N*-chloroethylamine; the same reaction took place slowly in the cold. With pyridine, instead, the salt was recovered unchanged; whilst, with ammonia, a colourless substance was obtained which again became scarlet when moistened with hydrochloric acid.

Analogues of Wolffram's Chloride.—(i) *Analogues containing ethylamine. Bromotetra-(ethylamino)platinum bromide*, [Pt etn$_4$Br]Br$_2$,2H$_2$O, was obtained by adding excess of potassium bromide to a lukewarm concentrated aqueous solution of Wolffram's salt; it separated as slender green needles, which suddenly became red at 85° and melted with decomposition at 182° (Found : Br, 36·2; Pt, 30·1; H$_2$O, 5·6. C$_8$H$_{28}$N$_4$Br$_3$Pt,2H$_2$O requires Br, 36·8; Pt, 30·0; H$_2$O, 5·5%). It remained green when dried at 100°, but suddenly changed to a reddish-chocolate form of the *anhydrous* salt (Found : C, 15·8; H, 4·8; Pt, 32·35. C$_8$H$_{28}$N$_4$Br$_3$Pt requires C, 15·6; H, 4·55; Pt, 31·75%); it did not reabsorb water from moist air, but when moistened with water it at once became scarlet. When the green dihydrate was crystallised from water, it separated from the warm solution as bright red rectangular needles with steel-blue reflex, which were anhydrous (Found : C, 15·7; H, 4·9; Pt, 32·0%), but from the cold solution it again separated as the green dihydrate. This, when warmed or left for some days with a little water, changed to the red compound without dissolving. The red and the chocolate form of this bromide melted suddenly with decomposition at 182°, the latter having first become red. The *thiocyanate* of the analogous chloro-compound was obtained similarly in the cold by use of potassium thiocyanate, forming minute yellow crystals, unstable to boiling water (Found : C, 22·1; H, 5·1; Cl, 7·2; Pt, 36·85. C$_{10}$H$_{28}$N$_6$ClS$_2$Pt requires C, 22·8; H, 5·3; Cl, 6·7; Pt, 37·0%. The monohydrate requires C, 22·05; H, 5·5; Cl, 6·5; Pt, 35·8%). [Pt etn$_4$(OH)]Cl$_2$,2H$_2$O was prepared as light yellow columns with oblique ends by a few seconds' boiling of an aqueous solution of Wolffram's salt containing about four times the theoretical amount of hydrogen peroxide; its identity is not established, however, for the chlorine content was high. If the time of heating was too long, an alkaline, colourless, very soluble platinic tetrammine, probably [Pt etn$_4$(OH)$_2$]Cl$_2$, was produced; this substance gave with hydrochloric acid almost colourless needles of [Pt etn$_4$Cl$_2$]Cl$_2$. The monohydroxy-compound was immediately changed into Wolffram's red salt by hydrochloric acid, and into green needles (presumably of [Pt etn$_4$Br]Br$_2$,2H$_2$O) by hydrobromic

acid. With aqueous potassium bromide, it gave slender orange needles of, presumably, [Pt etn$_4$(OH)]Br$_2$. The anhydrous *hydroxy-salt* consisted of pale yellow pseudomorphs, which were soon converted into the *dihydrate* in moist air (Found, in dihydrate : C, 19·1; H, 6·5; Pt, 39·0; H$_2$O, 7·2. C$_8$H$_{33}$O$_3$N$_4$Cl$_2$Pt requires C, 19·2; H, 6·6; Pt, 39·1; H$_2$O, 7·2%. Found, in anhydrous substance : C, 20·1; H, 5·9; Pt, 42·0. C$_8$H$_{29}$ON$_4$Cl$_2$Pt requires C, 20·7; H, 6·3; Pt, 42·1%).

(ii) *Analogues containing* n-*propylamine* (pn). It was found that [Pt pn$_4$]Cl$_2$,2H$_2$O, and more especially α-[Pt etn$_2$ pn$_2$]Cl$_2$,2H$_2$O, were reddened when moistened with hydrogen peroxide and hydrochloric acid. So also, a mixture (*a*) of [Pt etn$_4$]Cl$_2$,2H$_2$O and [Pt pn$_4$Cl$_2$]Cl$_2$ and (*b*) of [Pt pn$_4$]Cl$_2$,2H$_2$O and [Pt pn$_4$Cl$_2$]Cl$_2$ gave in each case a red colour when ground between glass surfaces.

A solution of α-[Pt etn$_2$ pn$_2$]Cl$_2$,2H$_2$O in excess of aqueous hydrogen peroxide gave with hydrochloric acid a dark reddish-brown precipitate, with intensely red streak (m. p. 187°). A similar red precipitate was obtained from [Pt pn$_4$]Cl$_2$,2H$_2$O in the same manner. Unfortunately, although each of these substances was obtained in good crystals, neither could be prepared free from unchanged plato-tetrammine dichloride, but it is evident that analogues of Wolffram's salt exist when propylamine is substituted for ethylamine; titration with acid permanganate and also chlorine analyses confirmed this, although in each case the figures were inexact.

Complex Salts derived from Wolffram's Salt.—In all cases, the red salt was completely dissolved in cold water and treated with a clear solution of the reagent.

(*a*) With chloroplatinic acid in hydrochloric acid, glistening, golden, hexagonal tables of [Pt etn$_4$]PtCl$_6$ separated slowly (Found : C, 12·15; H, 3·6. Calc. for C$_8$H$_{28}$N$_4$Cl$_6$Pt$_2$: C, 12·25; H, 3·55%); the mother-liquor gave square yellow plates of [Pt etn$_4$Cl$_2$]PtCl$_6$,2H$_2$O, as described by Reihlen and Flohr.

The original precipitate of plato-plati-chloride (above), when recrystallised from hydrochloric acid, was resolved into a mixture of violet-pink rectangular needles of [Pt etn$_4$]PtCl$_4$ and massive yellow rectangular prisms of [Pt etn$_4$Cl$_2$]PtCl$_6$,2H$_2$O. By the action of potassium chloroplatinite on [Pt etn$_4$Cl$_2$]Cl$_2$, a yellow *salt* having the composition [Pt etn$_4$Cl$_2$]PtCl$_4$ was obtained (Found : C, 11·9; H, 3·6; Pt, 50·5. C$_8$H$_{28}$N$_4$Cl$_6$Pt$_2$ requires C, 12·25; H, 3·6; Pt, 49·85%). This substance appeared to differ in crystalline form from the isomeride [Pt etn$_4$]PtCl$_6$, above.

(*b*) With a strictly molecular proportion of potassium chloroplatinite, Wolffram's salt gave an almost quantitative precipitate of slender, light, salmon-pink needles, having the composition of *chlorotetra(ethylamino)platinous chloroplatinite*, [Pt etn$_4$Cl]PtCl$_4$ (Found : C, 12·5; H, 3·9; Pt, 52·4. C$_8$H$_{28}$N$_4$Cl$_5$Pt$_2$ requires C, 12·85; H, 3·75; Pt, 52·2%).

When a half-molecular proportion of the chloroplatinite was used, the violet-pink *salt* [Pt etn$_4$]PtCl$_4$ separated quantitatively as slender needles (Found : C, 13·3; H, 4·2. C$_8$H$_{28}$N$_4$Cl$_4$Pt$_2$ requires C, 13·5; H, 3·95%); the filtrate from this, when precipitated with another equal proportion of potassium chloroplatinite, gave almost quantitatively yellow prisms of [Pt etn$_4$Cl$_2$]PtCl$_4$ [see (*a*) above. (Found : C, 12·1; H, 3·7; Pt, 50·2%)].

(*c*) With a molecular proportion of potassium chloropalladite, the red salt gave an almost quantitative precipitate of salmon-pink needles (Found : C, 14·6; H, 4·6; Cl, 27·6; Pd + Pt, 46·3. [Pt etn$_4$Cl]PdCl$_4$ requires : C, 14·55; H, 4·25; Cl, 26·9; Pd + Pt, 45·8%); this *salt* colours the wash waters yellow, the more soluble [Pt etn$_4$Cl$_2$]PdCl$_4$ dissolving, and a corresponding excess of [Pt etn$_4$]PdCl$_4$ being left. Successive precipitations with two half-molecular proportions of potassium chloropalladite gave : (i) slender violet-pink needles of the sparingly soluble *chloropalladite*, [Pt etn$_4$]PdCl$_4$ (Found : C, 15·5, 15·55; H, 4·9, 4·5; Pd + Pt, 48·9. C$_8$H$_{28}$N$_4$Cl$_4$PdPt requires C, 15·4; H, 4·5; Pd + Pt, 48·4%), and (ii) golden-yellow square plates (octahedral when fully developed) of the more soluble [Pt etn$_4$Cl$_2$]PdCl$_4$ (Found : C, 14·1; H, 4·4; Pd + Pt, 43·4. C$_8$H$_{28}$N$_4$Cl$_6$PdPt requires C, 13·8; H, 4·05; Pd + Pt, 43·4%); this *salt*, like several other plati-ammines, separates only slowly and incompletely from its solution in hydrochloric acid, whereas the plato-analogue separates rapidly and almost completely.

[Pt etn$_4$Cl$_2$]PdCl$_4$ was also prepared directly from potassium chloropalladite and [Pt etn$_4$Cl$_2$]Cl$_2$ (Found : C, 13·9; H, 4·3; Pd + Pt, 42·8%).

(*d*) With an excess of chloroauric acid in hydrochloric acid, a yellow precipitate of flat hexagonal prisms, sometimes containing particles of free gold, slowly separated (Found : C, 11·95; H, 3·55; Cl, 28·8; Au + Pt, 47·3%). This was dissolved in hot dilute hydrochloric acid and filtered from any gold, brilliant hexagonal plates, somewhat sensitive to light, separating (Found : C, 11·9; H, 3·45; Cl, 30·1; Au + Pt, 47·0, 47·5. C$_8$H$_{28}$N$_4$Cl$_7$AuPt requires C, 11·7;

H, 3·4; Cl, 30·2; Au + Pt, 47·8%). Evidently, the salt first precipitated is *dichlorotetra-(ethylamino)platinous chloroaurate*, [Pt etn$_4$Cl$_2$]AuCl$_5$, which is merely purified on recrystallisation.

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