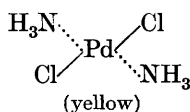
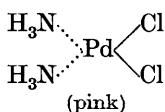


258. *The Supposed Isomerism among the Pallado-diammines.*

By HARRY DUGALD KEITH DREW, FREDERIC WILLIAM PINKARD,
GRAHAM HOLMES PRESTON, and WILLIAM WARDLAW.

A PINK and a yellow series of pallado-diammines, of general formula PdA_2X_2 , have long been known. Vauquelin (1813) discovered the first example by preparing the rose-pink compound $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, and Müller (*Ann. Pharm.*, 1853, 86, 341) obtained the corresponding yellow substance. Later workers have widely extended the series and have shown that the phenomenon is general in character.

The pink compounds are obtained by the direct action of the amine upon a palladous salt in aqueous solution; and the yellow, by dissolving the pink in excess of the amine and adding mineral acid. These methods are precisely those which in the case of platinum give rise, respectively, to the β -plato-diammines (plato-semidiammines) and the α -isomerides (platosammines); and hence it has been widely held that the pink and the yellow palladous compounds are isomeric substances which are the analogues of the β - and α -platodiammines. Their occurrence is therefore accounted for on the hypothesis of *cis*- and *trans*-planar isomerism due to Werner :



That conclusion is supported by the apparent monomeric character of the few palladous compounds of both series whose molecular weights have been observed; and, more recently, by an inference drawn from the results of Dickinson's X-ray crystal analysis of potassium and ammonium chloropalladites, which are tetragonal and contain the square-planar anion, PdCl_4'' (compare Lowry, *Nature*, 1929, 123, 548).

Our study of the plato-diammines (this vol., p. 988) led us to doubt the validity of this conclusion for several reasons; for example, whilst the pink palladous compounds change into the yellow on being heated alone or with water, the α - and β -plato-diammines cannot be intertransformed; again, there are no pink compounds among the many known plato-diammines. We have therefore carefully re-examined and extended some of the former work, and are now able to show beyond doubt (*a*) that the pink and yellow palladous diammines are not isomeric, (*b*) that the pink compounds are salts which contain each two palladium atoms in the molecule,

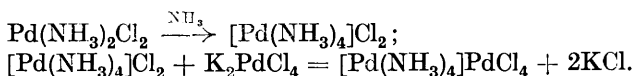
being the palladium analogues of Magnus's salts, and (c) that the yellow compounds are monomeric and correspond closely in behaviour with the α -platodiammines. Thus, for the derivatives of ammonia, the formulæ are :



The pink compounds were actually formulated in this manner long ago both by Kurnakow and by Gutbier, but their view has been rejected owing to the absence of any supporting evidence to be found either in the work of these or of later authors.

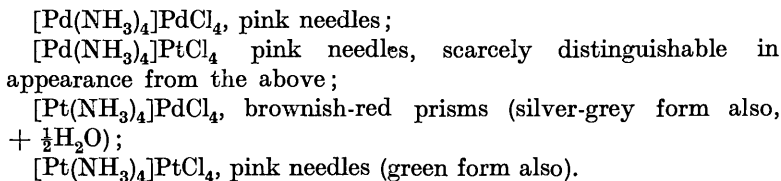
The evidence now brought forward may be grouped under the following heads :

(1) When the yellow diammine, $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, is dissolved in aqueous ammonia it gives the colourless tetrammine $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, the aqueous solution of which gives with potassium or ammonium chloropalladite a quantitative precipitate of the pink compound, shown by a number of reactions to be identical with that produced by the direct action of ammonia upon the aqueous potassium or ammonium salt. This cardinal fact, which seems, surprisingly, to have escaped previous attention, can only mean that the members of the pink series are pallado-salts :



The pink ethylenediamino-salt, $[\text{Pd en}_2]\text{PdCl}_4$, and the pyridino-analogue, $[\text{Pd py}_4]\text{PdCl}_4$, are similarly obtained each by the same two methods.

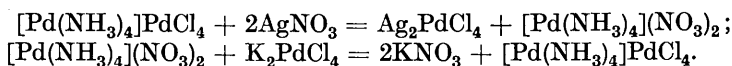
(2) Two new mixed plato-pallado-salts were prepared by combining a pallado- or plato-tetrammine with K_2PtCl_4 or K_2PdCl_4 . They fall into a series with the pink pallado-salt and the pink form of Magnus's salt :



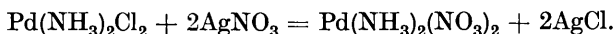
The analogy shows that the pink pallado-compounds must contain each two palladium atoms in the molecule. The salts behave with amines and with hydrochloric acid (see later) in a manner which confirms the above structures.

(3) (a) When the pink pallado-salt is treated with the equivalent of cold aqueous silver nitrate, it gives a precipitate of the brown

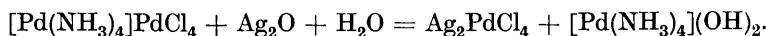
insoluble silver chloropalladite and a solution of the already known tetramminopallado-dinitrate, a colourless crystalline substance which readily dissolves in water giving a solution from which potassium chloropalladite reprecipitates the original pink compound :



On the other hand, the yellow compound gives only the corresponding diammino-dinitrate, as already shown by Müller (*loc. cit.*) :

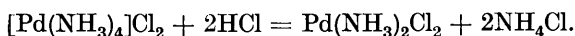


(b) When moist silver oxide is used instead of silver nitrate, the pink salt gives the almost colourless tetrammino-base which was isolated and analysed,



When cautiously neutralised with hydrochloric acid, this base gives the tetrammino-dichloride; whilst, when treated with aqueous potassium chloropalladite containing the equivalent of free hydrochloric acid, it gives back the original pink pallado-salt.

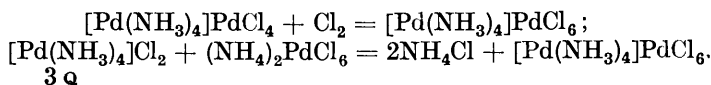
In contrast, the yellow diammine gives only the deep yellow diammino-base, $\text{Pd}(\text{NH}_3)_2(\text{OH})_2$, which with hydrochloric acid regenerates the yellow diammine. Naturally, when the tetrammino-base is treated with an *excess* of hydrochloric acid, the yellow diammine is precipitated, since this is the action of hydrochloric acid on the tetrammino-dichloride :



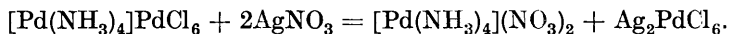
Müller (*loc. cit.*) prepared both of the above bases in an impure condition, but he obtained the tetrammino-base only from $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and does not appear to have examined the action of silver oxide on the pink salt.

The pink salts containing ethylenediamine or pyridine, instead of ammonia, behave like the foregoing pink salt, both with silver nitrate and with silver oxide; whilst the yellow diammines behave like yellow $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. The bases containing pyridine are, however, unstable and soon evolve pyridine.

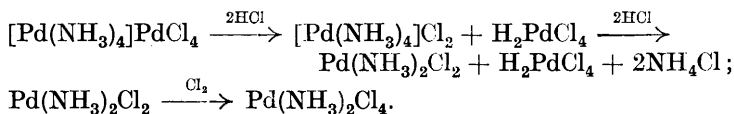
(4) When the pink ammine is suspended in water and treated with chlorine in the cold, it gives an orange-brown salt, identical with that obtained by treating the tetrammino-dichloride with a hydrochloric acid solution of ammonium chloropalladate; this salt is therefore the palladi-salt of the tetrammino-base :



Decomposition of the palladi-salt with aqueous silver nitrate was shown to give insoluble silver chloropalladate, and a solution of tetramminopalladous dinitrate, which gave again the original pink salt with aqueous K_2PdCl_4 :

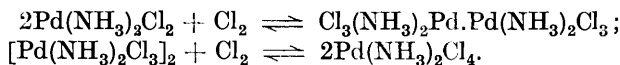


When the pink salt was treated with hydrogen peroxide and hydrochloric acid in the cold, however, it gave an orange solution containing H_2PdCl_4 and chlorine (or the unstable H_2PdCl_6) and an orange solid shown to be the rather unstable diammino-palladi-tetrachloride; this reaction is again in accord with what would be anticipated for the pallado-salt of a tetrammine in the presence of an acid and chlorine :



On being warmed with water, the tetrachloride readily decomposed into chlorine and the yellow diammine.

Chlorination of the corresponding pink ethylenediamino-compound gave parallel results. When, however, yellow $Pd(NH_3)_2Cl_2$ was treated with hydrogen peroxide and hydrochloric acid under the same conditions, it behaved quite differently from the pink salt, giving the almost black compound $[Pd(NH_3)_2Cl_3]_2$ in glistening rectangular needles. Chlorine in water or chloroform gave the same substance, but more energetic chlorination of the yellow diammine in carbon tetrachloride gave the foregoing tetrachloride, $Pd(NH_3)_2Cl_4$, which readily lost chlorine, reverting first to the black compound, and finally to the yellow $Pd(NH_3)_2Cl_2$.



Similar reactions are given by yellow $Pd enCl_2$ and $Pd py_2Cl_2$, but in these cases the orange diamminopalladi-tetrachlorides are more stable and can be isolated in a pure condition.

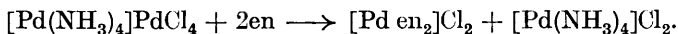
The black compound mentioned above is interesting, since it has two palladium atoms directly united together, a structure accompanied by great intensity of colour; we have already described an example of this class of substance in the platinum series (this vol., p. 1013). The black compound was discovered by St. Claire Deville and Debray in 1878 (*Compt. rend.*, **87**, 926), who assigned to it the correct empirical formula; Rosenheim and Maas (*Z. anorg. Chem.*, 1898, **18**, 331) erroneously stated that this substance was a mixture, chiefly of $(NH_4)_2PdCl_6$. Hofmann and others have confused the substance with the isomeric $[Pd(NH_3)_4]PdCl_6$.

(5) The action of aqueous solutions of amines on the pink and yellow pallado-diammines is complicated, owing to the looseness with which ammino-groups are held by the palladium as compared with the platinum atom; but the results are of value because they show clearly that the yellow pallado-diammines are akin to the α -plato-diammines.

(a) *Simple Tetrammines*.—The following colourless, crystalline substances result when either the pink or the yellow pallado-compound is treated with excess of the amine which it already contains: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$; $\text{Pd py}_4\text{Cl}_2 \cdot 3\text{H}_2\text{O}$; $\text{Pd en}_2\text{Cl}_2$ (anhydrous). The last two do not seem to have been analysed previously.

Of these, the *tetrapyridino-compound* is unstable in the solid state, and also in aqueous solution unless excess of pyridine be present. The tetrammino- is rather less stable than the *diethylenediamino-compound*. All three develop more or less free amine in aqueous solution, and all are decomposed even by very dilute hydrochloric acid in the cold (compare the plato-tetrammines, which are only decomposed when boiled with strong acid).

(b) *Mixed Tetrammines*.—Experiments showed that in aqueous solutions one amine may replace another in the tetrammines; thus, the nature of the final product depends on the nature of the free and combined amines and may also depend upon their concentrations. Nevertheless it is possible to prepare *mixed tetrammines*, e.g., by acting upon a yellow diammine with 2 mols. of an amine with less affinity for palladium than that already present. Thus, with the pair ammonia-ethylenediamine, free ethylenediamine tends to replace combined ammonia, so that the mixture $2\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + 2\text{en}$ gives $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 + [\text{Pd en}_2]\text{Cl}_2$; but $\text{Pd enCl}_2 + 2\text{NH}_3 \longrightarrow [\text{Pd en}(\text{NH}_3)_2]\text{Cl}_2$. So also, commencing with the pink salt:



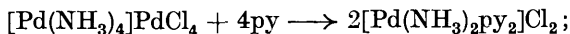
These results show that combined ethylenediamine has little tendency to replace combined ammonia, which could be anticipated from the fact that the tetrammines are fairly stable. On the other hand, if ammonia in large excess acts upon Pd enCl_2 , the product is chiefly $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$. An equimolecular mixture of $[\text{Pd en}_2]\text{Cl}_2$ and $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ in water remains substantially unchanged.

With the pair ammonia-pyridine, the results are somewhat different, because the following reaction is complete in dilute aqueous pyridine:

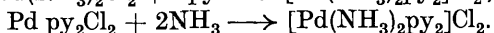
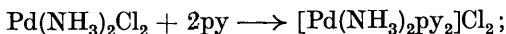


(in all reactions involving pallado-tetrammines containing pyridine, it is necessary to have present an excess of free pyridine, to prevent precipitation of diammine).

So also with the pink salt :

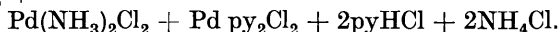
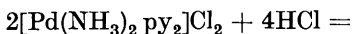


and with the yellow diammines :



If free ammonia be used in excess, it tends to replace pyridine, but free pyridine does not seem to replace combined ammonia. It will be seen that the tendency towards replacement of one amine by another, incipient in the plato-tetrammines, is a controlling influence in the palladium series.

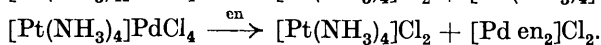
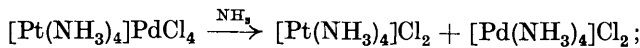
There is only one mixed pallado-tetrammine in each case, and this has a structure corresponding with that of an α -plato-tetrammine; for the product of decomposition with dilute hydrochloric acid was a mixture of the two simple α -diammines, *e.g.*:



The two diammines, produced in this case in almost equimolecular proportion, were quantitatively separable by means of cold chloroform, in which only the pyridino-compound dissolved. No trace of the mixed diammine, $\text{Pd}(\text{NH}_3)\text{pyCl}_2$, was present. Like the β -diammines, therefore, the β -tetrammines are absent in the palladium series.

When $[\text{Pd}(\text{NH}_3)_2\text{en}]\text{Cl}_2$ was decomposed with the equivalent of dilute hydrochloric acid, it gave a mixture of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and Pd enCl_2 , the latter being in great excess. The reaction was quantitative, and thus proves that the initial mixed tetrammine cannot be a molecular complex of the two simple tetrammines.

(6) The action of amines upon the mixed plato-pallado-salts is noteworthy. Magnus's salts are unaffected by cold aqueous ammonia or pyridine, and so also is the salt $[\text{Pd}(\text{NH}_3)_4]\text{PtCl}_4$; but the salt $[\text{Pt}(\text{NH}_3)_4]\text{PdCl}_4$, like the salts of the pink pallado-series, is dissolved by both amines, as well as by ethylenediamine, giving products easily identified :



Thus, the property of becoming disrupted in the presence of amines depends on the possession of the anion PdCl_4'' . This was confirmed by the fact that $[\text{Pd}(\text{NH}_3)_4]\text{PtCl}_4$, and not $[\text{Pt}(\text{NH}_3)_4]\text{PdCl}_4$, gives a

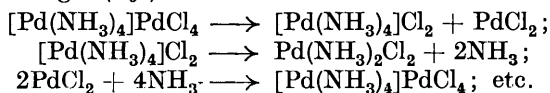
coloration with phenoxtellurine dibisulphate; for, whilst it has already been shown that Magnus's salts and alkali chloroplatinites invariably respond to that reagent, the pallado-salts do not, owing to the feeble tendency of palladium to become quadrivalent; even K_2PdCl_4 and $(NH_4)_2PdCl_4$ show only feeble colorations. These results incidentally confirm our interpretation of the phenox-tellurine dibisulphate reaction (*loc. cit.*).

The mixed tetrammines gave *pallado-salts* which obviously belonged to the pink series; of these, the following were analysed: $[Pd(NH_3)_2en]PdCl_4$, pink needles; $[Pd(NH_3)_2py_2]PdCl_4$, pale salmon-pink needles.

(7) *Molecular Weights*.—Krauss and Brodkorb (*Z. anorg. Chem.*, 1927, **165**, 73) found that both the "pink" and the yellow pyridino-diammines" are monomeric in freezing phenol. They describe the "pink" compound as "red," whereas we find that it is orange-brown, and they prepared it "by the action of pyridine on H_2PdCl_6 in weak hydrochloric acid solution." We find that pure $[Pd py_4]PdCl_4$ changes with great ease into $Pd py_2Cl_2$, especially in contact with solvents. Like its analogues, $[Pd py_4]PdCl_4$ is insoluble in organic solvents, and it is difficult to see how it could dissolve in phenol without transformation into the soluble $Pd py_2Cl_2$. For this reason, and because the question of possible ionisation has not been considered, little reliance can be placed on Krauss and Brodkorb's result for the pink salt. On the other hand, we find that yellow $Pd py_2Cl_2$ is monomeric in boiling chloroform, in agreement with Krauss and Brodkorb's results for this substance in freezing phenol and for yellow $Pd(NH_3)_2Cl_2$ in boiling water.

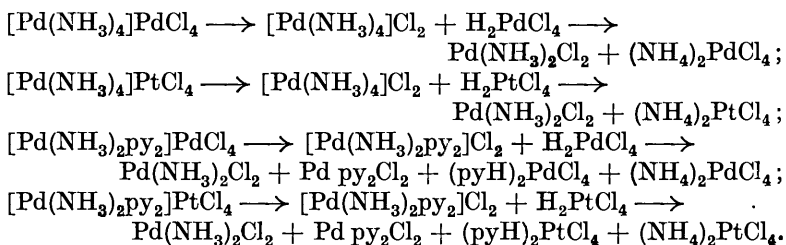
(8) Transformation of the pink to the yellow compounds is known to occur on heating in the dry state, on boiling with water or with hydrochloric acid, or even on long contact with water. We find that this last method is very slow in the case of $[Pd(NH_3)_4]PdCl_4$, whilst the presence of traces of hydrochloric acid renders it still slower. On the other hand, the pink compounds, when prepared by the action of 2 equivs. of the amines on aqueous K_2PdCl_4 , invariably contain small proportions of the yellow, and these are the larger the less the stability of the corresponding tetrammine. Moreover, the ease with which the change pink \rightarrow yellow form occurs seems to follow the same rule: thus $[Pd py_4]PdCl_4$ changes rapidly, and the tetrammine $[Pd py_4]Cl_2$ readily loses pyridine.

This suggests strongly that the transformation is due to the following changes (*e.g.*):

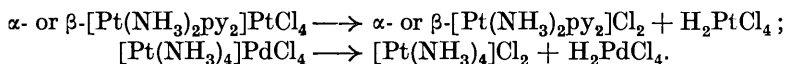


Alternatively, the first reaction (above) may result from the decomposition of the anion PdCl_4'' .

The decomposition of several pink salts by means of warm, dilute hydrochloric acid was examined in order to test this theory. In all cases the salts with palladium in the kation behaved as if they decomposed first into the pallado-tetrammine and the acid H_2PdCl_4 (or H_2PtCl_4), the tetrammines then further decomposing in the normal manner into pallado-diammines and free amines, which formed salts with H_2PdCl_4 or H_2PtCl_4 ; the pallado-diammines were themselves in part further changed by the hydrochloric acid into salts of H_2PdCl_4 , either of the normal or of Cossa's type, for the pallado-diammines are much less stable to acids than are even the β -plato-diammines. The following show the sense of the preliminary decompositions in typical cases studied :



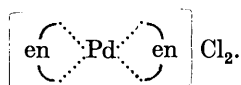
When, however, platinum is in the kation, the salts do not decompose into diammines because the plato-tetrammines are stable to dilute acid; however, the solutions still behave, *e.g.*, towards $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, as if they contained the disassociated salt (tetrammine and acid) :



The mechanism by which the pink salts are formed from K_2PdCl_4 and an aqueous amine is capable of several interpretations, but it may be remarked that if the formation be assumed of an intermediate pallado-diammine which reacts rapidly with further ammonia to give a tetrammine, sufficient unchanged K_2PdCl_4 may remain to interact with the tetrammine. This kind of change is, indeed, already seen in the action of amines on K_2PtCl_4 , where a little of the Magnus's salt invariably accompanies the main product (β -diammine). In both cases, tetrammines can be detected in the mother-liquors.

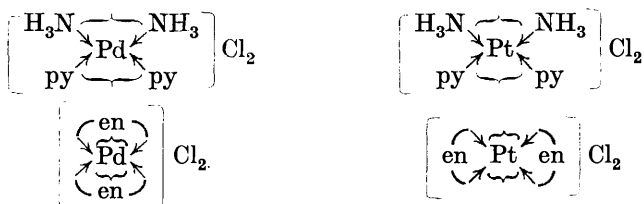
(9) Kurnakow and Gwosdarew (*Z. anorg. Chem.*, 1899, 22, 384) noticed that when $[\text{Pd en}_2]\text{Cl}_2$ is decomposed by hydrochloric acid it gives the yellow Pd enCl_2 . We find that the reaction is quantitative

if sufficient time be allowed and if the equivalent of dilute acid be used: $\text{Pd en}_2\text{Cl}_2 + 2\text{HCl} = \text{Pd enCl}_2 + \text{en}_2\text{HCl}$. It does not appear to have been remarked that this reaction creates a dilemma for Werner's planar hypothesis of the structure of pallado-ammines, since here the *trans*-elimination of groups which that theory requires cannot occur, for the theory postulates that the ethylenediamino-groups span *cis*-positions:



trans-Elimination would therefore leave both groupings still attached to palladium. Our own theory, however, readily accounts for the result, since the yellow pallado-diammines are all α -compounds, whereas in the platinum series the α -diammine containing ethylenediamine cannot exist.

Stereochemistry of the Palladous and Platinous Tetrammines.—It is clear from the results with the mixed tetrammines that the same pairing of valencies which we have postulated (this vol., p. 1006) in the case of platinum must also occur with palladium, *e.g.* :



Whilst in platinum, however, the linkings in β -positions (unbracketed) appear to be closer together than those in α -, in palladium there is no reason to assume this inequality. Our experiments throw no direct light upon the question as to whether the four groups in the tetrammines are situated in a plane or tetrahedrally around palladium; but they show that there is no longer any chemical evidence for assuming a planar configuration.

The absence of the structural analogues of the platinum β -diammines from the palladium series may be connected with the inferior attractive power of the less massive palladium atom for the valency electrons of nitrogen; the halogens attached to nitrogen might thus be able to ionise, and, combining with palladium, to destroy the β -structure, an electron passing to each nitrogen atom:



On the other hand, only the nature of the fine structure of the palladium atom can be held to account for the absence from it of β -positions corresponding stereochemically with those found in platinum.

EXPERIMENTAL.

Pallado-salts ("Pink Diammines").—*Preparation.* (a) A slight excess of the aqueous amine is added to a cold concentrated solution of K_2PdCl_4 [or with ammonia, of $(NH_4)_2PdCl_4$], and the pallado-salt at once filtered off (yield, about 80%). The filtrate contains tetrammine from which hydrochloric acid precipitates the yellow diammine; if too little amine be used, the filtrate may spontaneously deposit the latter. When the tetrammine is unstable the pink salt is liable to contain some of the diammine.

(b) A slight excess of cold aqueous K_2PdCl_4 is added to a freshly-made aqueous solution of the tetrammine, and the product filtered off after a few minutes (yield, quantitative).

The identity of the products of these two methods was proved by duplication of most of the chemical reactions hereinafter described, as well as from the physical properties and analysis.

Tetramminopalladium chloropalladite forms minute pink needles, stable when dry or for many months in cold very dilute hydrochloric acid, and partially changed to the diammine after several weeks in cold water, or at once in boiling water or in hot dilute hydrochloric acid [Found: Pd, 50.4. $Pd(NH_3)_4PdCl_4$ requires Pd, 50.4%].

Tetrapyridinopalladium chloropalladite forms light orange-brown microcrystals (yield, nearly quantitative); it easily changes to the diammine, slowly even when dry, more rapidly if moist or in contact with organic solvents or hot water; and is insoluble in water or chloroform. It can be prepared also from $(NH_4)_2PdCl_4$ and pyridine [Found: Pd, 31.6. $Pd(C_5H_5N)_4PdCl_4$ requires Pd, 31.8%].

Bisethylenediaminopalladium chloropalladite forms microscopic, pale pink needles, more stable than the foregoing salts, but changed to the diammine by hot water. It can be prepared also from $(NH_4)_2PdCl_4$ and ethylenediamine [Found: Pd, 44.8, 44.7. $Pd(C_2H_8N_2)_2PdCl_4$ requires Pd, 44.9%].

Diamminodipyridinopalladium chloropalladite (from the tetrammine and K_2PdCl_4) forms orange-yellow to salmon needles (Found: Pd, 38.7, 39.0. $C_{10}H_{16}N_4Cl_4Pd_2$ requires Pd, 39.0%), changed by hot water to a mixture (Found: Pd, 38.8%) of the two simple diammines.

The *diamminoethylenediamino-salt* (from the tetrammine and K_2PdCl_4) forms minute pale-pink needles (Found: Pd, 47.5. $C_2H_{14}N_4Cl_4Pd_2$ requires Pd, 47.5%).

Pallado-plato-salts.—Prepared from the tetrammine and aqueous K_2PdCl_4 or K_2PtCl_4 :

Tetramminopalladium chloroplatinite: short, slender, pink needles; blackened by boiling water; with hot dilute hydrochloric acid gives $Pd(NH_3)_2Cl_2$ and ammonium salts of H_2PtCl_4 (Found: Pd + Pt, 59.15. $H_{12}N_4Cl_4PdPt$ requires Pd + Pt, 59.0%); with phenoxtellurine dibisulphate it gives a dark red coloration.

Tetramminoplatinum chloropalladite: lilac-grey needles (silver-grey when dry), which contain $\frac{1}{2}H_2O$ even after being dried over phosphoric oxide (Found: Pd + Pt, 58.3, 58.05, 58.25. $H_{12}N_4Cl_4PdPt, \frac{1}{2}H_2O$ requires Pd + Pt, 58.0%); is not changed by warming with dilute hydrochloric acid, but if boiled with stronger acid it changes to a stable red-brown *anhydrous* modification, separating in small square plates (Found: Pd + Pt, 59.4, 58.7. $H_{12}N_4Cl_4PdPt$ requires Pd + Pt, 59.0%). With phenoxtellurine dibisulphate, the grey form gives no apparent colour change.

Diamminodipyridinopalladium chloroplatinite: very pale salmon-pink micro-crystals (Found: Pd + Pt, 47.15. $C_{10}H_{16}N_4Cl_4PdPt$ requires Pd + Pt, 47.5%); with phenoxtellurine dibisulphate it gives an intense dark red coloration; boiled with very dilute hydrochloric acid, it gave an almost equimolecular mixture (Found: Pd, 39.9, 38.8. Calc.: Pd, 39.0%) of $Pd(NH_3)_2Cl_2$ and $Pd py_2Cl_2$, together with soluble salts of H_2PtCl_4 .

Pallado-diammines (Yellow Series).—These are prepared from the aqueous tetrammines by treatment with a slight excess of dilute hydrochloric acid, followed by standing; also, by boiling the aqueous tetrammines, or by treating the pink pallado-salts with hot water or hot dilute acid as already indicated.

Diamminopalladous chloride: dendritic clusters of orange-yellow to yellow prismatic needles, rather soluble in boiling water, but not without some decomposition; insoluble in chloroform [Found: Pd, 50.45, 50.45. Calc. for $Pd(NH_3)_2Cl_2$: Pd, 50.4%].

Dipyridinopalladous chloride: light yellow, pointed crystals; insoluble in water, but readily soluble in chloroform [Found: Pd, 31.5, 31.4, 31.8; *M* (ebullioscopic in chloroform), 332. Calc. for $Pd(C_5H_5N)_2Cl_2$: Pd, 31.8%; *M*, 336].

Ethylenediaminopalladous chloride: well-defined, orange-yellow to yellow, rectangular needles; soluble in hot water without decomposition; insoluble in chloroform (Found: Pd, 44.9. Calc. for $C_2H_8N_2Cl_2Pd$: Pd, 44.9%).

All of these diammines dissolve in warm hydrochloric acid to give solutions of salts of H_2PdCl_4 , which, on repeated evaporation and solution, decompose with regeneration of the diammines. Diamminopalladous nitrate, prepared from the corresponding yellow

dichloride and silver nitrate, forms a yellowish-brown crystalline powder, soluble in water; it is unstable in the presence of alcohol and is difficult to purify; with aqueous sodium chloride it gives a yellow precipitate of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ [Found: Pd, 39.7. Calc. for $\text{Pd}(\text{NH}_3)_2(\text{NO}_3)_2$: Pd, 40.3%].

Tetrammines.—These are prepared by the action of aqueous amines on the pink salts or on the yellow diammines. All decompose when their solutions are evaporated in the laboratory atmosphere, but they are stable for varying periods in cold water; they are decomposed by acids. Most of them are best isolated from aqueous solution by slow precipitation with alcohol, a little ether being added if necessary. The simple tetrammines are best recrystallised from warm aqueous alcohol containing a little of the free amine. They are all colourless, transparent, and readily soluble in cold water.

Tetramminopalladous chloride monohydrate: long needles, ends sometimes square and sometimes pointed [Found: Pd, 40.8, 40.6. Calc. for $\text{Pd}(\text{NH}_3)_4\text{Cl}_2\cdot\text{H}_2\text{O}$: Pd, 40.45%]; it becomes faintly yellow if kept in a desiccator. The *tetrapyridino*-analogue forms large cubes often with facets, sometimes yellowish; stable in aqueous solution only for a short time, except in presence of free pyridine; decomposes if dried [Found: Pd, 19.7. $\text{Pd}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2\cdot 3\text{H}_2\text{O}$ requires Pd, 19.5%].

The *bisethylenediamino-chloride* forms large prisms, showing square and sometimes hexagonal faces; relatively stable (Found: Pd, 36.1. $\text{C}_4\text{H}_{16}\text{N}_4\text{Cl}_2\text{Pd}$ requires Pd, 35.85%).

The *diamminodipyridino*-salt forms stellate clusters of minute needles; it can be kept in a desiccator, but decomposes in cold water unless excess of pyridine is present (Found, for anhydrous tetrammine prepared by three methods: Pd, 28.5, 28.9, 29.1, 28.9, 29.0, 28.6, 28.75, 28.0, 28.45, 28.3, 29.0. $\text{C}_{10}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Pd}$ requires Pd, 28.85%). Fractionation from aqueous alcohol containing pyridine, followed by analysis of the crops, showed that this substance was a true compound. It appears also to form a *monohydrate*, minute rectangular needles (Found: Pd, 27.8, 27.9. $\text{C}_{10}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Pd}\cdot\text{H}_2\text{O}$ requires Pd, 27.5%). This tetrammine results (1) when $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pd py}_4]\text{Cl}_2$ are mixed in molecular proportion in water containing pyridine; (2) when $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ or $[\text{Pd}(\text{NH}_3)_4]\text{PdCl}_4$ is acted upon by an excess of aqueous pyridine; (3) when $\text{Pd py}_2\text{Cl}_2$ or $[\text{Pd py}_4]\text{Cl}_4$ is acted upon by the calculated quantity of ammonia; if ammonia be in excess, it replaces pyridine. When decomposed by dilute hydrochloric acid in the cold, the mixed tetrammine gives approximately equimolecular proportions (e.g., Found: Pd, 40.3, 38.9, 41.4, 41.1. Calc.: Pd, 39.0%) of

$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Pd py}_2\text{Cl}_2$, completely separated by means of chloroform (*e.g.*, Found for former : Pd, 50.2, 50.4; for latter : Pd, 31.4, 31.5. Calc. : Pd, 50.4; Pd, 31.8%).

Diamminoethylenediaminopalladous chloride forms nacreous thin plates, or long colourless needles, very easily soluble in cold water; it is stable when dry or in solution (Found : Pd, 39.2, 39.1. $\text{C}_2\text{H}_{14}\text{N}_4\text{Cl}_2\text{Pd}$ requires Pd, 39.25%). This tetrammine was obtained only by the action of ammonia on Pd enCl_2 , the alternative methods (above) giving mixtures of the two simple tetrammines. When the mixed tetrammine was treated with the calculated quantity of diluted hydrochloric acid in the cold, it gave quantitatively a mixture of Pd enCl_2 and $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in the molar proportion 4 : 1 (Found, in mixture : Pd, 45.8. Calc.: Pd, 45.9%).

Dipyridinoethylenediaminopalladous chloride, white needles, probably of the dihydrate (Found : Pd, 24.7. $\text{C}_{12}\text{H}_{18}\text{N}_4\text{Cl}_2\text{Pd}\cdot 2\text{H}_2\text{O}$ requires Pd, 24.7%), was prepared only from pyridine and Pd enCl_2 , since ethylenediamine displaced pyridine from $\text{Pd py}_2\text{Cl}_2$ and gave a mixture of the two simple tetrammines. The mixed tetrammine gave with cold dilute hydrochloric acid a mixture of the two simple diammines.

Tetramminopalladous nitrate : prepared by the action of cold aqueous silver nitrate upon $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ or $[\text{Pd}(\text{NH}_3)_4]\text{PdCl}_4$; the latter method is complicated by side reactions. The dinitrate crystallises readily from water in long, colourless, flat, hexagonal or rectangular needles (Found : Pd, 35.8, 36.1. $\text{H}_{12}\text{O}_6\text{N}_6\text{Pd}$ requires Pd, 35.7%); it gives no precipitate with aqueous sodium chloride; with cold dilute nitric acid, it gives a yellow solution of the diammine dinitrate.

Bases.—Entirely different bases were obtained by treating (1) the pink and (2) the yellow pallado-diammines with excess of moist silver oxide in the cold, filtering, and evaporating the filtrate in a vacuum. The bases were all readily soluble in water and strongly alkaline to litmus; they rapidly absorbed carbon dioxide, and neutralised hydrochloric acid to give the dichlorides—in (1) of the pallado-tetrammines, but in (2) of the diammines. Owing to their avidity for carbon dioxide, it was not possible to obtain the bases analytically pure.

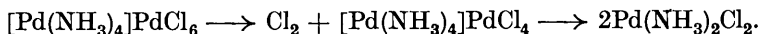
Tetramminopalladous hydroxide formed a transparent, pale yellow glass, which could not be further purified (Found : Pd, 50.1, 50.2. $\text{H}_{14}\text{O}_2\text{N}_4\text{Pd}$ requires Pd, 51.1%). Identical bases were prepared by using samples of the pink salt prepared (*a*) from ammonia and $(\text{NH}_4)_2\text{PdCl}_4$, and (*b*) from $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and $(\text{NH}_4)_2\text{PdCl}_4$; but repeated experiments indicated that the base becomes progressively less pure after isolation.

The tetrapyridino-hydroxide was similarly prepared from $[\text{Pd py}_4]\text{PdCl}_4$, but it so rapidly lost pyridine that it could not be isolated. On evaporation yellow needles (Found: Pd, 35.9%), possibly of $\text{Pd py}_2(\text{OH})_2$, were obtained; with hydrochloric acid, this substance gave $\text{Pd py}_2\text{Cl}_2$.

Diamminopalladous hydroxide formed an orange solution in water; when concentrated in a vacuum, the solution left an orange glass (Found: Pd, 61.85. $\text{H}_8\text{O}_2\text{N}_2\text{Pd}$ requires Pd, 61.1%); the base absorbed carbon dioxide from the air, giving the carbonate (Found: Pd, 55.9. Calc.: Pd, 53.1%), which, however, was not obtained pure.

Dipyridinopalladous hydroxide formed a yellow solution in water, which, however, had the odour of pyridine; on evaporation in a vacuum, yellow needles were obtained (Found: Pd, 32.3, 32.2. $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{Pd}$ requires Pd, 35.7%). Although with hydrochloric acid this substance gave $\text{Pd py}_2\text{Cl}_2$, it was obviously not pure and had possibly become transformed into the carbonate, $\text{Pd py}_2\text{CO}_3$ (Calc.: Pd, 32.85%).

Chlorination Products of the Pink and Yellow Pallado-diammines.—*Tetramminopalladous chloropalladate*, prepared by chlorination in water of samples of the pink salt obtained by both of the methods previously given, was a brownish-orange powder (Found: Pd, 42.7, 42.6. $\text{H}_{12}\text{N}_4\text{Cl}_6\text{Pd}_2$ requires Pd, 43.15%). The same substance was obtained by combining together $(\text{NH}_4)_2\text{PdCl}_6$ and $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ (Found: Pd, 43.0%). When mixed with aqueous silver nitrate and filtered, all three samples of $[\text{Pd}(\text{NH}_3)_4]\text{PdCl}_6$ gave a solution which produced the original pink compound when treated with aqueous $(\text{NH}_4)_2\text{PdCl}_4$. When heated with water, the pallad-salt loses chlorine and gives yellow $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$:



Diamminopalladic chloride: orange powder, prepared (1) by chlorinating the pink salt in the cold with hydrochloric acid and hydrogen peroxide, (2) by chlorinating the yellow diammine suspended in carbon tetrachloride [Found: Pd, 37.0. Calc. for $\text{Pd}(\text{NH}_3)_2\text{Cl}_4$: Pd, 37.75%]; it gradually became black on being left under water; when heated with water, it gave chlorine and $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$.

$[\text{Pd}(\text{NH}_3)_2\text{Cl}_3]_2$: shimmering black rectangular needles; prepared by chlorinating the yellow diammine in the cold with hydrochloric acid and hydrogen peroxide, or with chlorine in aqueous or chloroform suspension (Found: Pd, 43.3, 42.7, 42.8. Calc.: Pd, 43.15%). It was stable in air, but when heated with water it gave chlorine and $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$.

Dipyridinopalladic chloride: reddish-orange powder, prepared by

chlorination of the yellow diammine in chloroform solution, or in suspension in water or carbon tetrachloride [Found: Pd, 26.6. Calc. for $\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$: Pd, 26.2%]; insoluble in cold chloroform.

Bisethylenediaminopalladous chloropalladate: dark brown powder, prepared (a) by chlorinating the pink salt, obtained by either method, in water, and (b) by treating $[\text{Pd en}_2]\text{Cl}_2$ with $(\text{NH}_4)_2\text{PdCl}_6$ (Found: Pd, 39.4, 39.1, 39.2. $\text{C}_4\text{H}_{16}\text{N}_4\text{Cl}_6\text{Pd}_2$ requires Pd, 39.05%).

Ethylenediaminopalladic chloride: brown powder, prepared by the action of chlorine on Pd enCl_2 in chloroform or carbon tetrachloride (Found: Pd, 34.9. $\text{C}_2\text{H}_8\text{N}_2\text{Cl}_4\text{Pd}$ requires Pd, 34.55%).

Decomposition of $[\text{Pd en}_2]\text{Cl}_2$ with Hydrochloric Acid.—Although, with the calculated quantity of cold dilute acid, the tetrammine gives a quantitative yield of yellow Pd enCl_2 , yet the intermediate stage must be the production of a triammine. This can be obtained by using stronger acid, in which the *triammine hydrochloride* is sparingly soluble and therefore separates, although it is difficultly purified. It is a pale lemon-yellow crystalline substance, readily soluble in water (Found: Pd, 29.9, 29.55. $\text{C}_4\text{H}_{17}\text{N}_4\text{Cl}_3\text{Pd}, \text{H}_2\text{O}$ requires Pd, 30.3%). Its aqueous solution slowly loses ethylenediamine hydrochloride and changes into Pd enCl_2 ; heating brings about the change at once. The substance forms a brown, crystalline *pallado-salt* $[\text{Pd en}(\text{enH})\text{Cl}]\text{PdCl}_4$ (Found: Pd, 41.25. $\text{C}_4\text{H}_{17}\text{N}_4\text{Pd}_2\text{Cl}_5$ requires Pd, 41.7%). These substances are of novel type. Their examination is only in a preliminary stage.

Summary.

(1) It is shown by means of many reactions that the pink palladous compounds are not isomeric with the yellow.

(2) The pink are dimeric substances, and are the analogues of Magnus's salts; the yellow are monomeric, and are allied to the platinous α -diammines.

(3) The β -series of platinous diammines and tetrammines has no counterpart in the compounds of palladium.

(4) There are no longer any chemical grounds for assuming *cis*- and *trans*-planar isomerism among palladium compounds.

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