201. *Researches on Residual Affinity and Co-ordination. Part XXXIV. 2 : 2′-Dipyridyl Platinum Salts.*

By Gilbert T. Morgan and Francis H. Burstall.

Recent researches on the co-ordination compounds of metallic salts containing 2 : 2′-dipyridyl have shown that this diamine furnishes a chelate group giving rise to compounds of remarkable stability and sometimes of exceptional colour (J., 1930, 2594; 1931, 2213; 1932, 20). It was anticipated, therefore, that platinum compounds in co-ordination with this base might supply additional evidence as to the chemical structure of chelated platinammines. The formation of two dissimilar platinous salts of the empirical formula [$PtCl_2$ dipy] has already been recorded by us (*J. Indian Chem. Soc.*, 1933, Rây No. 1) and later Rosenblatt and Schleede (*Annalen*, 1933, **505**, 51) prepared four complex compounds to which reference will be made at the appropriate place.

I. *Two Forms of* β*-2 : 2′-*Dipyridylplatinous Chloride.*—*Bis*-2 : 2′-*dipyridyl platinochloride*, $(2\text{dipy})H_2PtCl_4$, the first product from 2 : 2′-dipyridyl, hydrochloric acid, and potassium platinochloride, changes in boiling water to pale yellow β-2 : 2′-*dipyridylplatinous chloride* (I), which also exists in a deep red, crystalline modification. The latter form of dichloride is obtained by the action of hot concentrated hydrochloric acid on the mixed tetrammine (II) (*vide infra*) :

$$\underset{\substack{\text{(I.)}\\\text{Yellow form.}}}{[\mathrm{PtCl_2}\text{ dipy}]} \underset{\text{dil. HCl}}{\overset{\text{en}}{\rightleftarrows}} \underset{\text{(II.)}}{[\mathrm{Pt}\text{ dipy en}]\mathrm{Cl_2,2H_2O}} \underset{\text{en}}{\overset{\text{conc. HCl}}{\rightleftarrows}} \underset{\substack{\text{(I.)}\\\text{Red form.}}}{[\mathrm{PtCl_2}\text{ dipy}]}$$

The yellow and the red chloride give the same chemical reactions. They both dissolve in aqueous solutions of amines, giving the same mixed tetrammines; chlorine gives only one 2 : 2′-*dipyridylplatinic chloride* (III); silver nitrate reacts with both chlorides with formation of the same yellow 2 : 2′-*dipyridylplatinous nitrate* (IV), whereas with both the yellow and the red chloride moist silver oxide furnishes oxidisable solutions of the dihydroxide, but hydrochloric acid regenerates only the yellow form. Ethylene dimethyl disulphide dissolves both chlorides with the formation of the same mixed salt. Moreover, solvents such as chloroform and methylene dichloride convert the red into the yellow form. The foregoing facts suggest that difference in colour of the two chlorides denotes some modification in the arrangement of molecules in the crystal rather than a difference in chemical structure. Furthermore, the corresponding *bromide* (V) and *iodide* (VI) have so far been obtained each only in one form.

II. *Addition of Bases to* β-2 : 2′-*Dipyridylplatinous Chloride.*—(1) 2 : 2′-*Dipyridyl.* Solutions containing bis-2 : 2′-dipyridylplatinous chloride (VII) are obtained when (I) is dissolved in excess of aqueous 2 : 2′-dipyridyl, but evaporation leads to a viscid yellow

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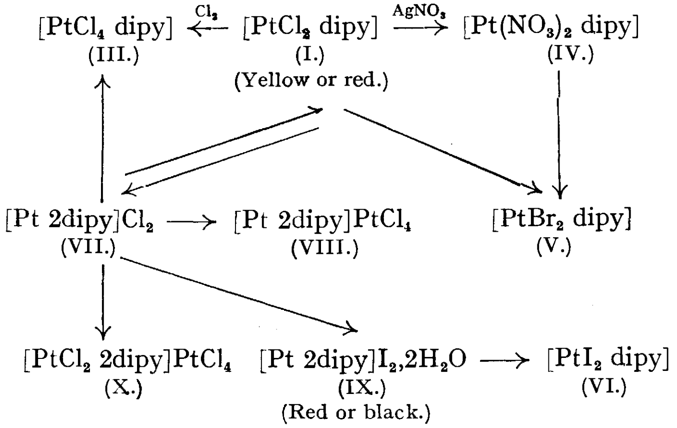
* The prefix β- refers to the *cis*-configuration, assuming a planar structure of 2 : 2′-dipyridyl and chlorine relative to the platinum atom (compare Drew, J., 1932, 2328, *et seq.*; Cox, Saenger, and Wardlaw, this vol., p. 182).

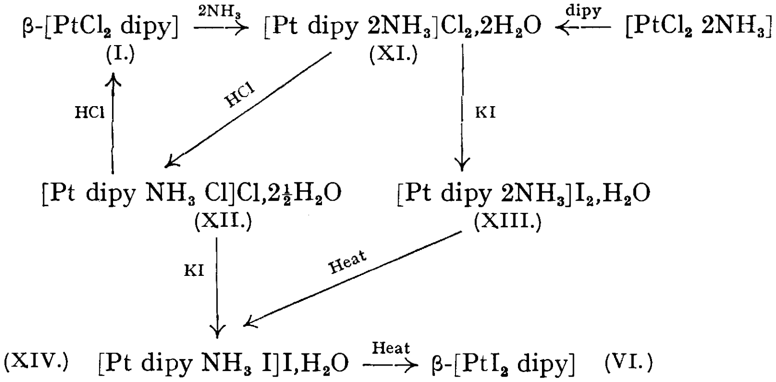
gum decomposing into its generators The presence of the complex (VII) is inferred by precipitation of the yellow *plato*-salt (VIII) and the *iodide* (IX). The foregoing plato-



salt is identical with the product obtained by heating potassium platinochloride and 2 : 2′-dipyridyl in aqueous medium, and Rosenblatt and Schleede (*loc. cit.*), who obtained it by the latter method, concluded without experimental support that it was the monomeric compound $[PtCl_2\ dipy]$. The iodide (IX) has been obtained in a red and a black form; the former passes into the latter on exposure of the dry salt. The black iodide, which probably has a binuclear structure, passes in turn into the simple iodide (VI) at 90°. Chlorine oxidises solutions of (VII), but the tetrachloride (III) is the only definite product obtainable from the viscid concentrate. Potassium platinochloride, however, furnishes the *plato*-salt (X) with the oxidised solution. Hydrochloric acid gives $[PtCl_2\ dipy]$ (yellow) in over 95% yield with a solution of (VII), and this is in marked contrast to the results obtained with the corresponding ethylenediamine and trimethylenediamine complex tetrammines, where a *trans*-elimination of co-ordinated addenda predominates (Drew, J., 1932, 2328; Drew and Tress, J., 1933, 1335).

(2) *Pyridine.* Solutions containing the tetrammine $[Pt\ dipy\ 2py]Cl_2$ or triamine $[Pt\ dipy\ py\ Cl]Cl$ or both are formed when the yellow and the red dichloride $[PtCl_2\ dipy]$ are dissolved in aqueous pyridine, but evaporation leads only to a viscid residue which gives red $[PtCl_2\ dipy]$ at 100°. Hydrochloric acid forms pyridine hydrochloride and yellow β-$[PtCl_2\ dipy]$, whereas potassium platinochloride precipitates the *plato*-salt $[Pt\ dipy\ 2py]PtCl_4$ or $[Pt\ dipy\ py\ Cl]_2PtCl_4$. Chlorine oxidises the foregoing solution, but only the triamine $[Pt\ dipy\ py\ Cl_3]Cl,2H_2O$ and the tetrachloride $[PtCl_4\ dipy]$ have been identified.

(3) *Ammonia.* 2 : 2′-*Dipyridyldiamminoplatinous chloride dihydrate* (XI) is formed by dissolving yellow or red $[PtCl_2\ dipy]$ in aqueous ammonia or when β-$[PtCl_2\ 2NH_3]$ is warmed with aqueous 2 : 2′-dipyridyl. A *monohydrate* has also been obtained.



Hydrochloric acid converts (XI) into *2 : 2′-dipyridylamminoplatinous chloride* ($2\frac{1}{2}H_2O$) (XII) and finally into the yellow chloride (I). The foregoing tetrammine (XI) forms a *platinochloride* and in cold solution the *iodide* (XIII), which on warming with water readily loses ammonia, forming the *iodide* (XIV). This triammine on further heating gives the simple di-iodide (VI) with loss of ammonia.

(4) *Ethylenediamine.* *2 : 2′-Dipyridylethylenediaminoplatinous chloride dihydrate* (II) is formed when the yellow and the red dichloride [$PtCl_2$ dipy] (I) are dissolved in aqueous ethylenediamine or when β-[$PtCl_2$ en] is treated with aqueous 2 : 2′-dipyridyl. With concentrated hydrochloric acid the mixed tetrammine (II) gives the red form of the dichloride (I), whereas dilute acid precipitates the yellow form of (I). With intermediate strength of acid it is possible to induce the co-precipitation of both red and yellow 2 : 2′-dipyridylplatinous chlorides. Exhaustive action of hydrochloric acid furnishes a 95% yield of (I). The mixed tetrammine (II) also furnishes the corresponding *bromide* (XV) and iodide (XVI). Hydrobromic acid gives only the yellow form of β-2 : 2′-dipyridylplatinous bromide (V) with the tetrammine (XV).

$$\begin{tikzcd}
\underset{\text{(I.)}}{\beta\text{-}[PtCl_2\ dipy]} \arrow[r, shift left, "en"] & \underset{\text{(II.)}}{[Pt\ dipy\ en]Cl_2,2H_2O} \arrow[l, shift left, "HCl"] \arrow[dl, "KI"] \arrow[d, "Ag_2CO_3\ and\ HBr"] & \beta\text{-}[PtCl_2\ en] \arrow[l, "dipy"'] \\
\underset{\text{(XVI.)}}{[Pt\ dipy\ en]I_2,H_2O} & \underset{\text{(XV.)}}{[Pt\ dipy\ en]Br_2,2H_2O} \arrow[r, "HBr"] & \underset{\text{(V.)}}{\beta\text{-}[PtBr_2\ dipy]}
\end{tikzcd}$$

III. *Chlorination of Amminated 2 : 2′-Dipyridyl Platinous Salts.*—In *N*-hydrochloric acid solution the tetrammine [Pt dipy $2NH_3]Cl_2(1$ or $2H_2O)$ and the triammine [Pt dipy NH_3 Cl]Cl,$2\frac{1}{2}H_2O$ are oxidised by chlorine to the corresponding platinic compounds (XVII) and (XVIII). Both these salts react with a further quantity of chlorine in the absence of hydrochloric acid, forming orange-yellow explosive substances in which chlorine is partially substituted for the hydrogen atoms of the ammonia molecules. The complex chloroamine compound obtained from (XVII) appears to be a mixture of the two derivatives (XIX) and (XX) in equimolecular proportion, whereas (XVIII) forms a complex salt corresponding to (XX). In a similar manner, chlorine oxidises the bivalent platinum salt [Pt dipy en]Cl_2,$2H_2O$ to the platinic derivative (XXI), which is dehydrated to the *sesquihydrate* over sulphuric acid. Further reaction takes place in the absence of much hydrochloric acid and the orange chloroamine compound (XXII) is precipitated. The foregoing novel co-ordination compounds (XIX), (XX), and (XXII) evolve chlorine with hydrochloric acid and explode violently when heated or even when struck. The formulæ devised for their structure are advanced tentatively, since binuclear and more complex structures are possible. Their formation is probably to be associated with the presence of dipyridyl, since in the absence of this diamine such chloro-derivatives have not been recorded previously.

(XVII.) [Pt dipy $2NH_3\ Cl_2]Cl_2,2H_2O$

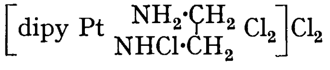
[Pt dipy $NH_3\ Cl_3]Cl,H_2O$ (XVIII.)

(XIX.)

$$\left[dipy\ Pt\ \begin{matrix}NH_3\\NHCl_2\end{matrix}\ Cl_2\right]Cl_2$$

[dipy Pt $NH_2Cl\ Cl_3]Cl$ (XX.)

(XXI.) [Pt dipy en $Cl_2]Cl_2,5H_2O$



$$\left[dipy\ Pt\ \begin{matrix}NH_2\cdot CH_2\\ |\\ NHCl\cdot CH_2\end{matrix}\ Cl_2\right]Cl_2$$

(XXII.)

IV. *Addition of Ethylene Dimethyl Disulphide to* β-[$PtCl_2$ dipy].—The disulphide $CH_3\cdot S\cdot C_2H_4\cdot S\cdot CH_3$ (ms) forms the unstable salt [Pt dipy ms]Cl_2 with both forms of β-[$PtCl_2$ dipy], and the same salt is also produced from β-[$PtCl_2$ ms] and 2 : 2′-dipyridyl in aqueous medium. The foregoing mixed salt easily loses co-ordinated addenda in the solid state. Under normal conditions both diamine and disulphide are liberated, but with 2*N*-hydrochloric acid only β-[$PtCl_2$ ms] and 2 : 2′-dipyridyl hydrochloride are formed. These reactions correspond with those of the mixed salt [Pt en es]Cl_2,H_2O (es = ethylene diethyl disulphide) previously examined by Drew and Wyatt (this vol., p. 56). The constitution of the mixed salt is inferred from the isolation of the stable [Pt dipy ms]$PtCl_4$.

EXPERIMENTAL.

I. *Preparation and Properties of the Two Forms of* β-2 : 2′-*Dipyridylplatinous Chloride.*—*Bis*-2 : 2′-*dipyridyl platinochloride,* $(dipy)_2H_2PtCl_4$, separated as a pale buff, crystalline precipitate when cold solutions of 2 : 2′-dipyridyl (1·5 g.), 2*N*-hydrochloric acid (50 c.c.), and potassium platinochloride (2·0 g.) were mixed (Found: Pt, 30·3, 30·3; Cl, 21·5; N, 8·8. $C_{20}H_{18}N_4Cl_4Pt$ requires Pt, 30·0; Cl, 21·8; N, 8·6%). An aqueous suspension of this salt decomposed on heating into the yellow form (I) and 2 : 2′-dipyridyl hydrochloride. Caustic and carbonated alkalis at once liberated the diamine, whereas ammonia gave the green salt of Magnus and 2 : 2′-dipyridyl.

β-2 : 2′-*Dipyridylplatinous chloride* (yellow form of I), formed by boiling the preceding compound in aqueous suspension, was best prepared as follows: potassium platinochloride (4·01 g.) in water (500 c.c.), 2 : 2′-dipyridyl (1·56 g.), and 2*N*-hydrochloric acid (20 c.c.) were heated to boiling; the liquid then became filled with a mass of filamentous yellow needles. A further quantity was obtained by evaporating the filtrate. The yield was nearly quantitative (Found: Pt, 46·1; Cl, 16·4; N, 6·4. $C_{10}H_8N_2Cl_2Pt$ requires Pt, 46·2; Cl, 16·8; N, 6·6%). This yellow form was sparingly soluble in chloroform and methylene dichloride.

β-2 : 2′-*Dipyridylplatinous chloride* (red form of I) separated from a briskly boiling solution of (II) (*vide infra*) (0·5 g.) in concentrated hydrochloric acid (10 c.c.) (Found: Pt, 46·4, 46·5; N, 6·3%). This red chloride was slightly soluble in chloroform and methylene dichloride, giving yellow solutions from which only the yellow dichloride crystallised. In addition, the red salt became yellow on long boiling with either of the foregoing solvents. It was not altered below 290°. The two forms of (I) dissolved at different rates in aqueous pyridine.

β-2 : 2′-*Dipyridylplatinic chloride* (III). The yellow form of (I) changed to a buff microcrystalline deposit when chlorine was passed into its aqueous suspension (Found: Pt, 39·9; Cl, 28·2; N, 5·95. $C_{10}H_8N_2Cl_4Pt$ requires Pt, 39·6; Cl, 28·7; N, 5·7%). The red variety speedily changed colour with chlorine, giving a precipitate indistinguishable from the product from (I) (yellow) (Found: Pt, 39·7%). The tetrachloride (III) was practically insoluble in organic media, but dissolved slowly in aqueous ammonia, pyridine, or ethylenediamine.

β-2 : 2′-*Dipyridylplatinous nitrate* (IV). A suspension of the yellow form of (I) in water was treated at 90° with rather less than the theoretical quantity of silver nitrate until free from soluble silver salt; the small yellow needles of (IV) which then crystallised from the cooled filtrate slowly decomposed (Found: Pt, 41·5; N, 10·8, 10·8. $C_{10}H_8O_6N_4Pt$ requires Pt, 41·1; N, 11·2%). The red variety became yellow with silver nitrate solution; the yellow filtrate then gave a nitrate similar to the previous preparation (Found: Pt, 41·3%). Both preparations gave the yellow dichloride with soluble chlorides.

β-2 : 2′-*Dipyridylplatinous bromide* (V) was precipitated in yellow needles when (IV) was treated with a soluble bromide, but was best prepared by heating a solution of [Pt dipy en]Br_2,$2H_2O$ (*vide infra*) with hydrobromic acid. Only the yellow form was obtained (Found: Pt, 37·9, 38·1. $C_{10}H_8N_2Br_2Pt$ requires Pt, 38·2%).

β-2 : 2′-*Dipyridylplatinous iodide* (VI) was formed when the tetrammine [Pt 2dipy]I_2,$2H_2O$ (*vide infra*) was boiled in aqueous suspension or heated at 90°. This iodide was practically insoluble in organic media, but dissolved in ethylenediamine (Found: Pt, 32·1. $C_{10}H_8N_2I_2Pt$ requires Pt, 32·3%). Only one form (yellow) was obtained.

2 : 2′-*Dipyridylplatinous hydroxide.* A deep brown solution containing this base was obtained when either the yellow or the red modification was heated in aqueous suspension with silver oxide in a stream of hydrogen. Hydrochloric, hydrobromic, or nitric acid gave only yellow chloride, bromide, or nitrate respectively with such solutions.

II. *Addition of Bases to* β-2 : 2′-*Dipyridylplatinous Chloride.*—(1) 2 : 2′-*Dipyridyl.* A solution containing bis-2 : 2′-dipyridylplatinous chloride (VII) resulted when the yellow variety was dissolved in excess (2 to 3 mols.) of aqueous 2 : 2′-dipyridyl, but a viscid gum, decomposing into its generators, was obtained on evaporation. Hydrochloric acid precipitated the yellow form, which sometimes possessed a red tint. In one experiment the yellow chloride (1·0 g.) and 2 : 2′-dipyridyl (1·0 g.) in water (50 c.c.) were heated; the filtrate from undissolved salt (0·04 g.) was then treated with concentrated hydrochloric acid (25 c.c.) at 90°. The yellow form recovered (0·936 g.) indicated a yield of 97·5%. 2 : 2′-Dipyridyl hydrochloride was the only other product identified in the residue. The red changed to the yellow variety when heated with warm aqueous 2 : 2′-dipyridyl; the yellow dichloride then dissolved.

Bis-2 : 2′-dipyridylplatinous iodide dihydrate (IX) separated in yellow leaflets when cold solutions of (VII) and potassium iodide were mixed. The yellow crystals reddened slowly and then remained unchanged in contact with cold water. After being washed with water, alcohol, and ether, this red iodide was analysed at once (Found : Pt, 24·1. $C_{20}H_{20}O_2N_4I_2Pt$ requires Pt, 24·5%). On exposure or gentle heating the red iodide became black (Found : Pt, 24·2%). Heating at 90° gave (VI).

Bis-2 : 2′-dipyridylplatinous platinochloride (VIII) was precipitated as a yellow microcrystalline salt when solutions of (VII) and potassium platinochloride were mixed or when potassium platinochloride (2·01 g.) and 2 : 2′-dipyridyl (0·8 g.) were boiled together in aqueous medium (Found : Pt, 46·6, 46·2; Cl, 16·2. $C_{20}H_{16}Cl_4Pt_2$ requires Pt, 46·2; Cl, 16·8%). This plato-salt possessed a deeper colour when prepared by the latter process than the product from direct synthesis. Both preparations became orange or red at 195—200° and gave the yellow form with hot hydrochloric acid. Phenoxtellurine di-bisulphate * produced an intense purple colour with this salt.

Bis-2 : 2′-dipyridyldichloroplatinic platinochloride (X). Chlorine oxidised solutions of (VII), but the filtered solution gave only [$PtCl_4$ dipy] (Found : Pt, 39·1. Calc. : Pt, 39·6%). Addition of potassium platinochloride, however, precipitated (X) in buff needles (Found : Pt, 42·8. $C_{20}H_{16}N_4Cl_6Pt_2$ requires Pt, 42·7%).

(2) *Pyridine.* Pale yellow solutions were formed when the yellow or the red dichloride was heated with aqueous pyridine. At room temperature evaporation gave viscid yellow gums decomposing into the yellow form and pyridine, but at 90—100° the red form resulted, although the colour of the dichloride varied from orange to deep red in different preparations (Found : Pt, 46·5. Calc. : Pt, 46·2%). Solutions prepared as above gave the yellow variety with hydrochloric acid, whereas potassium platinochloride formed the yellow *plato*-salt [Pt dipy 2py]$PtCl_4$ or [Pt dipy py Cl]$_2PtCl_4$ (Found : Pt, 45·5. $C_{20}H_{18}N_4Cl_4Pt_2$ requires Pt, 46·1%. $C_{30}H_{26}N_6Cl_6Pt_3$ requires Pt, 46·2%).

2 : 2′-*Dipyridylpyridinotrichloroplatinic chloride dihydrate,* [Pt dipy py Cl_3]Cl,$2H_2O$. Chlorine was passed into a cold solution of the yellow or the red dichloride in aqueous pyridine from which any excess of pyridine had been previously removed by boiling. The filtered concentrate was cooled at 0°; the *triammine* then crystallised in pale yellow, filamentous threads and was air-dried (Found : Pt, 32·2, 31·7; Cl, 24·1; N, 6·4. $C_{15}H_{17}O_2N_3Cl_4Pt$ requires Pt, 32·0; Cl, 23·3; N, 6·9%). Aqueous or alcoholic solutions of this triammine slowly decomposed into [$PtCl_4$ dipy], pyridine, and water.

(3) *Ammonia.* 2 : 2′-*Dipyridyldiamminoplatinous chloride dihydrate* (XI) crystallised during the slow evaporation of a solution of the yellow dichloride in excess of aqueous ammonia. The pale yellow needles were recrystallised from water or dilute hydrochloric acid and air-dried (Found : Pt, 39·0; Cl, 14·5; N, 11·4. $C_{10}H_{14}N_4Cl_2Pt,2H_2O$ requires Pt, 39·65; Cl, 14·5; N, 11·4%). The red form became yellow with warm aqueous ammonia and then dissolved to a yellow solution, from which the foregoing salt was isolated (Found : Pt, 39·4%). On warming with excess of aqueous 2 : 2′-dipyridyl, β-[$PtCl_2$ $2NH_3$] dissolved completely, but some unchanged diammine crystallised when the filtered solution was cooled. Concentration with addition of ammonia gave the mixed tetrammine identical with the two previous preparations. A *monohydrate* was formed by addition of alcohol to a concentrated solution of dihydrate (Found : Pt, 40·9. $C_{10}H_{14}N_4Cl_2Pt,H_2O$ requires Pt, 41·1%). Potassium platinochloride gave a yellow plato-salt with a solution of the tetrammine, whereas hydrochloric acid finally precipitated the yellow form (0·5404 g. of [Pt dipy $2NH_3$]Cl_2,$2H_2O$ gave 0·4574 g. of [$PtCl_2$ dipy] = 98·7% theory).

2 : 2′-*Dipyridyldiamminoplatinous iodide hydrate* (XIII) separated in yellow crystals when cold solutions of (XI) and potassium iodide were mixed (Found : Pt, 29·5; N, 8·5. $C_{10}H_{16}ON_4I_2Pt$ requires Pt, 29·7; N, 8·5%). This iodide decomposed on heating into the triammine (XIV) (*vide infra*) and finally into [PtI_2 dipy].

2 : 2′-*Dipyridylamminoplatinous chloride* ($2\frac{1}{2}H_2O$) (XII) was formed (a) as a by-product from the preparation of (XI), (b) by long boiling of (XI) with water, and (c) by heating (XI) with 2*N*-hydrochloric acid until the dichloride [$PtCl_2$ dipy] began to separate. The reddish-yellow solution was filtered and cooled to 0°; the triamine then crystallised as an orange microcrystal-

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* We are indebted to Dr. H. D. K. Drew for a specimen of this substance.

line deposit. After recrystallisation this product was dried over sulphuric acid in a vacuum (Found : Pt, 40·3; N, 8·65. $C_{10}H_{11}N_3Cl_2Pt,2\frac{1}{2}H_2O$ requires Pt, 40·3; N, 8·7%). This triammine became crimson with cold water and then dissolved to an orange-yellow solution, from which, after long heating, hydrochloric acid precipitated the yellow dichloride, whereas potassium platinochloride gave a yellow plato-salt.

2 : 2′-*Dipyridylamminoplatinous iodide hydrate* (XIV) separated as an orange-yellow powder (a) when solutions of (XII) and potassium iodide were mixed, (b) from hot solutions of (XI) and potassium iodide, and (c) when (XIII) was warmed with water (Found : Pt, 30·5; N, 6·6. $C_{10}H_{11}N_3I_2Pt,H_2O$ requires Pt, 30·7; N, 6·5%). This iodide gave [PtI_2 dipy] on heating.

2 : 2′-*Dipyridyldiamminodichloroplatinic chloride dihydrate* (XVII) crystallised in almost white plates when chlorine was passed into a cold solution of (XI) in hydrochloric acid. A further quantity separated on addition of acetone to the filtrate. This preparation was air-dried (Found : Pt, 34·9. $C_{10}H_{14}N_4Cl_4Pt,2H_2O$ requires Pt, 34·65%). Over sulphuric acid in a vacuum the *monohydrate* was formed (Found : Pt, 35·7; loss of H_2O, 3·8. $C_{10}H_{14}N_4Cl_4Pt,H_2O$ requires Pt, 35·8; $1H_2O$, 3·2%).

2 : 2′-*Dipyridylamminotrichloroplatinic chloride hydrate* (XVIII) crystallised in flat greenish plates when chlorine was passed into a solution of (XII) in hydrochloric acid (Found : Pt, 37·4; N, 8·13. $C_{10}H_{11}N_3Cl_4Pt,H_2O$ requires Pt, 37·0; N, 7·95%).

The complex compounds (XIX) *and* (XX). When chlorine was passed into a neutral solution of (XVIII), the colour deepened and an orange-yellow explosive substance separated. The mixture was warmed and the solid was filtered off, washed with water, and dried [Found : Pt, 33·7, 33·9, 34·1; Cl, 34·2; N, 8·7. ($C_{10}H_{12}N_4Cl_6Pt + C_{10}H_{10}N_3Cl_5Pt$) requires Pt, 34·2; Cl, 34·0; N, 8·5%].

The foregoing data indicated that this orange substance was a mixture of the two derivatives (XIX) and (XX) in approximately equal proportion. In warm neutral solution the triammine (XVIII) reacted with a further quantity of chlorine, giving an orange product similar to the preceding preparation (Found : Pt, 35·5; N, 7·9. $C_{10}H_{10}N_3Cl_5Pt$ requires Pt, 35·8; N, 7·7%). It also dissolved in hot 2*N*-hydrochloric acid and gave (XVIII) with evolution of chlorine.

(4) *Ethylenediamine.* 2 : 2′-*Dipyridylethylenediaminoplatinous chloride dihydrate* (II) crystallised in pale yellow needles (a) when the yellow dichloride in aqueous ethylenediamine was evaporated and cooled (Found : Pt, 37·8; Cl, 13·9; N, 10·95. $C_{12}H_{16}N_4Cl_2Pt,2H_2O$ requires Pt, 37·65; Cl, 13·7; N, 10·8%). (b) The red dichloride became yellow with warm aqueous ethylenediamine and then dissolved; the tetrammine separated on addition of alcohol and was identical with preparation (a) (Found : Pt, 37·6%). (c) The compound β-[$PtCl_2$ en], made by the action of ethylenediamine on aqueous potassium platinochloride (Drew, *loc. cit.*), dissolved slowly (4—5 hours) in aqueous 2 : 2′-dipyridyl at 90°. The hot filtrate deposited some unchanged β-[$PtCl_2$ en] on cooling (Found : Pt, 59·6. Calc., 59·85%); (II) then separated on addition of alcohol and was identical with preparations from (a) and (b) (Found : Pt, 37·4%). The alcoholic residues furnished a little [$PtCl_2$ dipy] (yellow). Potassium platinochloride gave a yellow plato-salt with this mixed tetrammine, whereas hydrochloric acid precipitated the yellow or the red form of (I) according to the dilution of the acid; (1) 0·03 g. of (II) in 10 c.c. of *N*-hydrochloric acid at 100° gave yellow [$PtCl_2$ dipy]; (2) 0·03 g. of (II) in 1 c.c. of concentrated hydrochloric acid at 100° gave red [$PtCl_2$ dipy]; (3) 0·03 g. of (II) in 4 c.c. of 2*N*-hydrochloric acid usually gave a mixture of the red and the yellow dichloride. Exhaustive action of hydrochloric acid gave a 95·3% yield of yellow dichloride [0·5368 g. of (II) gave 0·4132 g. of (I)]. Ethylenediamine hydrochloride was the only definite compound identified in the residue.

2 : 2′-*Dipyridylethylenediaminoplatinous bromide dihydrate* (XV), prepared by successive action of silver carbonate and hydrobromic acid on a solution of (II), separated in pale yellow needles which gave yellow [$PtBr_2$ dipy] with hydrobromic acid (Found : Pt, 32·5; N, 9·3. $C_{12}H_{16}N_4Br_2Pt,2H_2O$ requires Pt, 32·2; N, 9·2%).

2 : 2′-Dipyridylethylenediaminoplatinous iodide hydrate (XVI) crystallised in yellow needles when an aqueous solution containing (II) and potassium iodide was cooled (Found : Pt, 28·4. Calc. : Pt, 28·6%) (compare Rosenblatt and Schleede, *loc. cit.*).

2 : 2′-*Dipyridylethylenediaminodichloroplatinic chloride pentahydrate* (XXI) crystallised in almost white, glistening leaflets when chlorine was passed into a concentrated solution of (II) in *N*-hydrochloric acid. A further quantity was obtained from the filtrate by addition of acetone. The product was air-dried (Found : Pt, 30·3, 30·0. $C_{12}H_{16}N_4Cl_4Pt,5H_2O$ requires Pt, 30·35%). This pentahydrate lost $3\frac{1}{2}$ molecules of its combined water over sulphuric acid in a vacuum (Found : loss, 10·1. Calc. for $3\frac{1}{2}H_2O$, 9·8%).

The compound (XXII). When chlorine was passed into a warm neutral solution of the foregoing platinic salt, an orange-yellow insoluble product separated. This was washed with warm water and alcohol (Found : Pt, 34·1; N, 9·5; Cl, 30·7. $C_{12}H_{15}N_4Cl_5Pt$ requires Pt, 33·2; N, 9·6; Cl, 30·2%). This product liberated chlorine with hydrochloric acid, but was otherwise more stable than the corresponding ammonia compounds (XIX) and (XX).

IV. *Addition of Ethylene Dimethyl Disulphide to* [$PtCl_2$ dipy].—2 : 2′-*Dipyridylethylenedimethyldisulphineplatinous chloride* was formed in solution when the yellow dichloride was dissolved in the aqueous disulphide. The red dichloride became yellow with the sulphur compound and then dissolved. The dichloride β-[$PtCl_2$ ms], prepared from potassium platinochloride and ethylene dimethyl disulphide, was dissolved in aqueous 2 : 2′-dipyridyl. Acetone precipitated the mixed salt, but the product was too unstable to be analysed. Potassium platinochloride furnished the *plato*-salt [Pt dipy ms]$PtCl_4$ (Found : Pt, 47·8. $C_{14}H_{18}N_2Cl_4S_2Pt$ requires Pt, 48·2%).

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