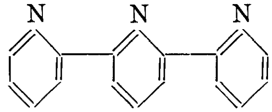
323. *Researches on Residual Affinity and Co-ordination. Part XXXV. 2 : 2′ : 2″-Tripyridylplatinum Salts.*

By Gilbert T. Morgan and Francis H. Burstall.

Co-ordination compounds of platinum with bases contributing three associating foci or tridentate groups have not received much attention, although the stereochemistry of such compounds presents many interesting features. It has been shown, however, by Mann (J., 1928, 890) that αβγ-triaminopropane furnishes either a chelate group with two adjacent amino-radicals co-ordinated to platinum or a tridentate system with its three amino-radicals all implicated. Later, Mann (this vol., p. 466) found that ββ′-diaminodiethylamine acts as a tridentate group with platinous salts.

Following on our researches with 2 : 2′-dipyridyl platinum compounds (this vol., p. 965) we now describe the results of investigating complex salts of platinum with 2 : 2′ : 2″-tripyridyl (2 : 6-di-2′-pyridylpyridine = trpy; I).



(I.)

$$\begin{tikzcd}
 & \begin{matrix}[\text{Pt trpy Cl}]_2\text{PtCl}_4\\ \text{(II.)}\end{matrix} \arrow[dl, shift right] \arrow[r] \arrow[dr] & \begin{matrix}[\text{Pt}_3\ 2\text{trpy Cl}_6]\\ \text{(III.)}\end{matrix} \\
\begin{matrix}[\text{Pt trpy Cl}]\text{Cl},3\text{H}_2\text{O}\\ \text{(red) (IV.)}\end{matrix} \arrow[ur, shift right] \arrow[r, shift left] \arrow[d] & \begin{matrix}[\text{Pt trpy NH}_3]\text{Cl}_2,\text{H}_2\text{O}\\ \text{(V.)}\end{matrix} \arrow[l, shift left] \arrow[r] & \begin{matrix}[\text{Pt trpy NH}_3]\text{PtCl}_4\\ \text{(VI.)}\end{matrix} \\
\begin{matrix}[\text{Pt trpy Cl}_3]\text{Cl},2\text{H}_2\text{O}\\ \text{(VII.)}\end{matrix} & \begin{matrix}\text{trpy H}_2\text{PtCl}_4\\ \text{(VIII.)}\end{matrix} \arrow[r] & \begin{matrix}[\text{Pt trpy Cl}]\text{Cl},3\text{H}_2\text{O}\\ \text{(IX.) (black)}\end{matrix} \arrow[ull]
\end{tikzcd}$$

Potassium platinochloride and 2 : 2′ : 2″-tripyridyl react slowly at 90° in an aqueous medium forming an orange, insoluble precipitate and an orange-yellow solution. The former is separated by hydrochloric acid into a red *platinochloride* (II) and a complex *bis*-2 : 2′ : 2″-*tripyridyltriplatinous hexachloride* (III). The filtrate contains the easily soluble deep red 2 : 2′ : 2″-*tripyridylplatinous chloride* (IV), which is obtainable as a *trihydrate* or a *dihydrate.* This salt (IV) gives the compound (II) with potassium platinochloride, whereas ammonia forms 2 : 2′ : 2″-*tripyridylamminoplatinous chloride hydrate* (V), which readily reverts to (IV) with loss of ammonia. With moist silver oxide, the complex salt (IV) readily yields a stable *hydroxide* [Pt trpy OH]OH,$2H_2O$, which with the respective halogen acids furnishes the *bromide* [Pt trpy Br]Br,$2H_2O$ and *iodide* [Pt trpy I]I,$2H_2O$. With chlorine, the tridentate complex salt (IV) is oxidised to an almost colourless *platinic* derivative (VII). Aqueous ammonia decomposes the platinochloride (II) in accordance with the scheme:

$$\underset{\text{(II.)}}{[\text{Pt trpy Cl}]_2\text{PtCl}_4} \xrightarrow{\text{NH}_3} \underset{\text{(VI.)}}{[\text{Pt trpy NH}_3]\text{PtCl}_4} + \underset{\text{(V.)}}{[\text{Pt trpy NH}_3]\text{Cl}_2}$$

The plato-salt (VI), which also arises from the interaction of (V) and potassium platinochloride, is black, recalling the intense colour of the green salt of Magnus.

In acid solution, 2 : 2′ : 2″-tripyridyl and potassium platinochloride give 2 : 2′ : 2″-*tripyridyl platinochloride* (VIII), which is not changed by boiling water. When, however, this dry salt is heated at 240—260°, decomposition takes place with formation of an insoluble product of indefinite composition and a water-soluble black tridentate complex chloride (IX), which possesses the same empirical formula as the chloride (IV). This black chloride changes into the red isomeride in hot aqueous solution and forms a blue gelatinous *plato*-salt with potassium platinochloride. Although the relationship between (IV) and (IX) is not clear, the lower solubility and method of formation of (IX) indicate that it is a dimeride, whereas (IV) is the more stable monomeric variety. Apart from the foregoing considerations, it is not certain whether a tridentate salt such as (IV) is tetrahedral or planar in structure. There is no evidence at present to show whether the tridentate group of a triamine such as 2 : 2′ : 2″-tripyridyl, αβγ-triaminopropane, or ββ′-diaminodiethylamine can span the *trans* (α)-positions of the co-ordinated planar molecule.

EXPERIMENTAL.

2 : 2′ : 2″-*Tripyridylchloroplatinous Platinochloride* (II).—(*a*) Potassium platinochloride (4·0 g.) and 2 : 2′ : 2″-tripyridyl (2·3 g.) were digested with water at 90° for 6 hours, an orange-brown precipitate separating. This solid, after being washed with hot water and alcohol, was extracted with boiling 2*N*-hydrochloric acid until a sample of the residue no longer gave a black colour with warm aqueous ammonia. When the extract was cooled, the *platinochloride* crystallised in red plates (Found: Pt, 45·9; Cl, 16·7. $C_{30}H_{22}N_6Cl_6Pt_3$ requires Pt, 46·3; Cl, 16·8%).

(*b*) In cold aqueous solutions, 2 : 2′ : 2″-tripyridylplatinous chloride di- or tri-hydrate (IV) and potassium platinochloride produced a crimson gelatinous precipitate, which became red and granular on boiling. This plato-salt, which crystallised from hydrochloric acid (Found: Pt, 46·2%), reacted with aqueous amines and decomposed slowly into (III) (*vide infra*) in warm concentrated hydrochloric acid. With silver oxide it gave a solution of 2 : 2′ : 2″-tripyridylplatinous hydroxide (*vide infra*), but there was no colour reaction with phenoxtellurine dibisulphate.

Bis-2 : 2′ : 2″-*tripyridyltriplatinous Hexachloride* (III).—The yellow residue remaining after extraction of the foregoing plato-salt with hydrochloric acid was washed with water and alcohol (Found: Pt, 46·0; N, 6·7. $C_{30}H_{22}N_6Cl_6Pt_3$ requires Pt, 46·3; N, 6·6%). This highly complex *chloride* was insoluble in water and most organic solvents, but dissolved slowly in aqueous ammonia or pyridine.

2 : 2′ : 2″-*Tripyridylplatinous Chloride Trihydrate* (IV).—The aqueous filtrate obtained from the reaction between 2 : 2′ : 2″-tripyridyl and potassium platinochloride was evaporated, cooled, and treated with hydrochloric acid; the red chloride then separated as the dihydrate, whereas the *trihydrate* crystallised slowly from a cold aqueous solution and was air-dried (Found: Pt, 35·0, 35·7; N, 7·8; Cl, 13·0. $C_{15}H_{11}N_3Cl_2Pt,3H_2O$ requires Pt, 35·3; N, 7·6; Cl, 12·8%). The *dihydrate* was obtained from the trihydrate by desiccation over sulphuric

acid, by washing with alcohol, or by precipitating a warm solution with hydrochloric acid (Found : Pt, 36·6; N, 7·9. $C_{15}H_{11}N_3Cl_2Pt,2H_2O$ requires Pt, 36·5; N, 7·9%). This chloride was also formed by decomposing the chloride (IX) (*vide infra*) by hot water or acid, by the prolonged action of 2 : 2′ : 2″-tripyridyl on the plato-salt (II) or the complex salt (III) in aqueous medium, or by successive action of silver oxide and hydrochloric acid on (II). This complex platinous salt was not decomposed by boiling with concentrated hydrochloric acid, and was insoluble in most organic solvents.

2 : 2′ : 2″-*Tripyridylplatinous Hydroxide.*—A deep red solution of this base was formed when the foregoing chloride (IV) or the platinochloride (II) was warmed with freshly prepared silver oxide, the filtrate evaporated to small volume at 90°, and finally kept over sulphuric acid in a vacuum. The *hydroxide* was thus obtained as a very deep red (almost black) microcrystalline product (Found : Pt, 39·4. $C_{15}H_{13}N_3O_2Pt,2H_2O$ requires Pt, 39·2%). This slightly hygroscopic base was soluble in water or alcohol; its aqueous solution was stable on boiling. It dissolved in hydrochloric, hydrobromic, and hydriodic acid to give the corresponding salts.

2 : 2′ : 2″-*Tripyridylplatinous bromide dihydrate*, also formed on mixing solutions of the chloride (IV) and a soluble bromide, crystallised in yellow needles (Found : Pt, 31·1. $C_{15}H_{11}N_3Br_2Pt,2H_2O$ requires Pt, 31·3%). The *iodide dihydrate*, similarly prepared from hot solutions of (IV), crystallised from hot water in orange-yellow needles (Found : Pt, 27·0; N, 6·0. $C_{15}H_{11}N_3I_2Pt,2H_2O$ requires Pt, 27·2; N, 5·8%). In cold solution the chloride (IV) and a soluble iodide precipitated a crimson gelatinous iodide which became yellow and granular on heating.

2 : 2′ : 2″-*Tripyridyltrichloroplatinic Chloride Dihydrate* (VII).—When chlorine was passed into a warm solution of the chloride (IV), the colour faded to a very pale yellow, and on cooling the concentrated filtrate the platinic chloride crystallised in almost white needles or plates (Found : Pt, 32·2; N, 7·0. $C_{15}H_{11}N_3Cl_4Pt,2H_2O$ requires Pt, 32·2; N, 6·9%). This air-dried *dihydrate* when desiccated over sulphuric acid passed into a *monohydrate* (Found : Pt, 32·95. $C_{15}H_{11}N_3Cl_4Pt,H_2O$ requires Pt, 33·2%). On exposure, this platinic derivative decomposed slowly, regenerating the corresponding chloride of bivalent platinum (IV).

2 : 2′ : 2″-*Tripyridylamminoplatinous chloride hydrate* (V) separated as a yellow microcrystalline precipitate on addition of alcohol to a concentrated solution of (IV) in aqueous ammonia. This tetrammine was washed successively with ammoniacal alcohol and ether and analysed at once (Found : Pt, 36·4. $C_{15}H_{14}N_4Cl_2Pt,H_2O$ requires Pt, 36·5%); it speedily lost ammonia on exposure or in solution, regenerating compound (IV).

2 : 2′ : 2″-*Tripyridylamminoplatinous Platinochloride* (VI).—(*a*) This plato-salt, which separated as a blue flocculent precipitate on mixing solutions of (V) and potassium platinochloride, was washed with water and alcohol (Found : Pt, 49·5. $C_{15}H_{14}N_4Cl_4Pt_2$ requires Pt, 49·9%).

(*b*) The plato-salt (II) was heated and stirred with concentrated aqueous ammonia; the plato-salt (VI) was then formed as a black microcrystalline deposit, which was washed with water and alcohol (Found : Pt, 49·7%). The filtrate from this preparation gave (IV) with hydrochloric acid. Both samples (*a*) and (*b*) generated the red plato-salt (II) with warm hydrochloric acid.

2 : 2′ : 2″-*Tripyridyl platinochloride* (VIII) separated in golden-yellow needles on mixing hot solutions of 2 : 2′ : 2″-tripyridyl in 2*N*-hydrochloric acid (40 c.c.) and potassium platinochloride (4·0 g.) in 300 c.c. of water (Found : Pt, 34·0; N, 7·3. $C_{15}H_{13}N_3Cl_4Pt$ requires Pt, 34·0; N, 7·3%). Aqueous amines and caustic and carbonated alkalis eliminated 2 : 2′ : 2″-tripyridyl, but boiling with water did not alter this platinochloride.

2 : 2′ : 2″-*Tripyridylplatinous Chloride Trihydrate* (*black form*) (IX).—On heating the foregoing platinochloride (4·5 g.) at 230—260° for 5 hours, a little hydrogen chloride was evolved and some 2 : 2′ : 2″-tripyridyl hydrochloride sublimed. The cold brown residue (4·1 g.) was extracted successively with alcohol and water at 40°. As soon as the mixture was moistened it became black and partially dissolved to a deep red solution, leaving a yellow-brown insoluble residue. The red filtrate was treated with aqueous ammonium chloride, and the precipitate recrystallised on cooling from the minimum quantity of warm water (40°). The small black plates of the *trihydrate* were air-dried (Found: Pt, 35·5; Cl, 12·5; N, 7·7. $C_{15}H_{11}N_3Cl_2Pt,3H_2O$ requires Pt, 35·3; Cl, 12·8; N, 7·6%). This chloride was rapidly decomposed by hot 2*N*-hydrochloric acid, and more slowly by boiling water, into the red compound (IV). Potassium platinochloride gave with a solution of this chloride a blue gelatinous precipitate drying to a reddish-purple powder, which retained water very tenaciously (Found : Pt, 44·35%) and gave the red plato-salt (II) with hydrochloric acid.

CHEMICAL RESEARCH LABORATORY, TEDDINGTON, MIDDLESEX. [*Received, August 23rd,* 1934.]