XXIX.—*Researches on Residual Affinity and Co-ordination. Part XXIII. Interactions of Trimethylstibine and Platinic and Palladous Chlorides.*

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THE lower chlorides of platinum and palladium combine additively with ammonia, pyridine, thioethers, selenoethers and the trialkylphosphines and -arsines to give rise to co-ordination compounds of the general types $PtCl_2,2X$, $PtCl_2,4X$, $PdCl_2,2X$, and $PdCl_2,4X$.

In the case of the amine and pyridine derivatives of platinous chloride, there is considerable foundation for the belief that the compounds $PtCl_2,2X$ exist in *cis*- and *trans*-modifications, the four associating units and the central platinum atom being regarded as being in the same plane. A change of orientation from this coplanar arrangement to a tetrahedral configuration would, however, result in the disappearance of the above-mentioned *cis*- and *trans*-isomerism.

This change may occur with an increase in the atomic volume of the associating units and although coplanar arrangement may be the rule with amines it by no means follows that this configuration will persist in the additive compounds with phosphines and arsines.

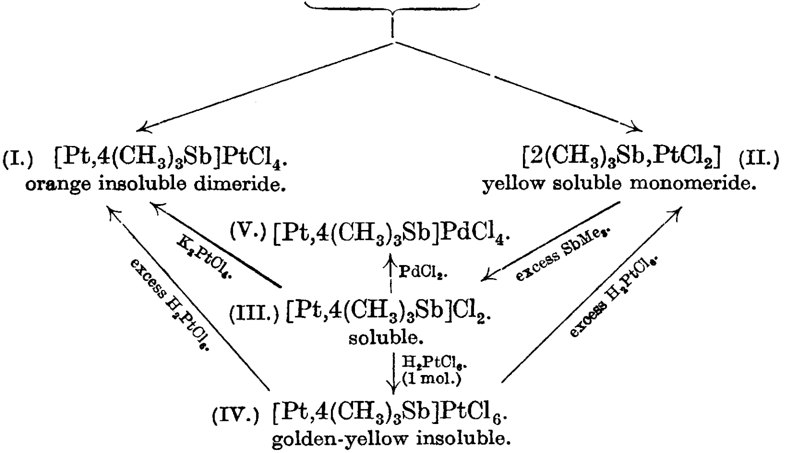
The compounds with trimethyl- and triethyl-phosphines were discovered by Cahours and Gal (*Compt. rend.*, 1870, **70**, 897; **71**, 208, 1381), who obtained two products of empirical formula $PtCl_2,2PR_3$, in each case, one white and the other yellow. Transformation of the latter to the former modification was noticed on heating, but no evidence was given, or has since been forthcoming, that the two substances have the same molecular complexity. These authors also obtained two isomeric arsenical derivatives, $PtCl_2,2As(C_2H_5)_3$, both of which were yellow but differed in solubility. But here again there is no evidence as to molecular complexity.

In the experiments described below, chloroplatinic acid and palladous chloride have been treated in turn with trimethylstibine. With the platinic compound reduction occurs giving rise to trimethylstibine dichloride, and the resulting platinous compound then interacts with more trimethylstibine forming one or two additive compounds according as to whether the reaction occurs in aqueous or alcoholic solution. In the former medium, an orange product is formed which is insoluble in water and organic solvents. In alcohol, this orange compound is precipitated, but a soluble substance is also formed which crystallises from organic media in pale yellow leaflets.

Analyses and molecular-weight determinations indicate that the soluble yellow product is *bistrimethylstibinedichloroplatinum* (II). The orange substance is evidently either isomeric or polymeric with this yellow compound, for it passes quantitatively into the latter at 60° or when left for several months at the ordinary temperature.

Owing to the insolubility of the orange compound in all neutral solvents, its molecular complexity cannot be determined by physical methods, but its structure has been ascertained by preparing it in two other ways.

$$H_2PtCl_6 + (CH_3)_3Sb = H_2PtCl_4 + (CH_3)_3SbCl_2.$$
$$PtCl_2 + Sb(CH_3)_3.$$



1. With excess of trimethylstibine, the yellow and orange compounds are both converted slowly into the soluble *tetrakistrimethylstibineplatinous chloride* (III), and this salt on treatment with cold aqueous potassium platinochloride gives rise to the orange compound, which is thereby shown to be *tetrakistrimethylstibineplatinous platinochloride* (I). With chloroplatinic acid or palladous

chloride tetrakistrimethylstibineplatinous chloride gives rise respectively to *tetrakistrimethylstibineplatinous platinichloride* (IV) or *tetrakistrimethylstibineplatinous palladochloride* (V).

2. The former of those two salts when hydrolysed with excess of chloroplatinic acid furnishes *bistrimethylstibinedichloroplatinum* (II) and *tetrakistrimethylstibineplatinous platinochloride* (I), in the proportions of 17 : 1.

In the palladium series, trimethylstibine and palladous chloride interact at low temperatures to form an orange additive product, but this changes spontaneously on slight rise of temperature to a yellow substance, *bistrimethylstibinedichloropalladium* (VI). Excess of trimethylstibine converts this to the soluble orange *tetrakistrimethylstibinepalladous chloride* (VII), a soluble salt less stable than

(VI.) $[2(CH_3)_3Sb,PdCl_2]$. $[Pd,4(CH_3)_3Sb]Cl_2$ (VII.)

its platinum analogue, which did not give with palladous chloride an insoluble product corresponding with the orange dimeride of the platinous series.

Digested with dilute hydrochloric acid, the tetrakis compound is converted into a light yellow, crystalline substance, *trimethylstibinedichloropalladium hydrochloride* (VIII), $[(CH_3)_3Sb,PdCl_3]H$, which, unlike the other pallado-derivatives, is stable on keeping.

EXPERIMENTAL.

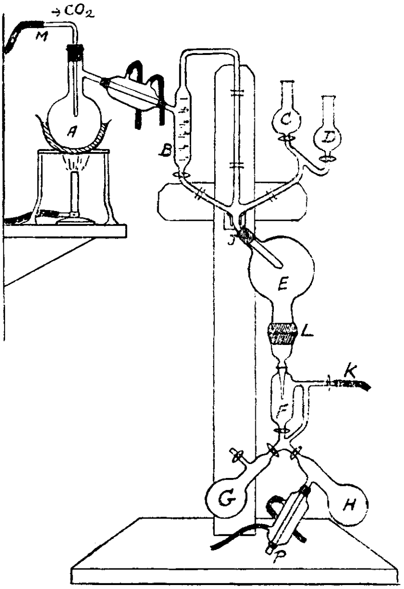
Trimethylstibine, being spontaneously inflammable in air, was manipulated in the apparatus shown in the accompanying figure. The base was prepared by the Grignard reaction (Hibbert, *Ber.*, 1906, **39**, 160) and converted into trimethylstibine dibromide by running its ethereal solution into bromine diluted with the same solvent.

Weighed quantities of the dibromide are introduced into flask A, together with a small quantity of water and the calculated amount of finely granulated zinc (Kahlbaum No. 1). The air in the apparatus having been previously expelled by a stream of carbon dioxide, the mixture is distilled and the trimethylstibine collected in the graduated receiver B. The reaction vessel E is turned through an angle of 120° by means of the movable rubber joint J, so that the filter disk, L, is raised above the reacting liquids. A slight excess of aqueous platinic or palladous chloride solution is delivered into E from the tap funnel, D, and to this is slowly added the calculated amount of trimethylstibine from the graduated receiver B. As the tertiary stibine is not miscible with aqueous solutions, the chemical combination is facilitated by shaking the vessel E and when the reaction is completed the apparatus is rotated so that the attachments of vessel E are now in the vertical position as shown by the diagram. By aspiration at K, the liquid contents of E are drawn through the filter, L, on which the insoluble product is collected. The precipitate is now washed with ether introduced through the tap funnel, C, and the ethereal washings are aspirated into the receiver F. Here the aqueous and ethereal filtrates are separated, the former being drawn off into the flask G, whilst the latter is collected in distilling flask, H, which is fitted with a condenser, P. On distilling off the solvent, a residue is obtained of the ether-soluble product, which is shown below to be trimethylstibine dichloride.

When alcoholic platinic chloride is employed the reaction is more vigorous because of the miscibility of trimethylstibine with this medium. The insoluble product is collected as before on filter L, whilst the alcoholic filtrate and washings are drawn into flask H. On removing the solvent, the residue contains trimethylstibine dichloride and bistrimethylstibinedichloroplatinum (or palladium).

The whole apparatus is so designed that these platinous and palladous derivatives of highly inflammable trimethylstibine can be prepared, collected and desiccated in an inert atmosphere and out of contact with air.

FIG. 1.



I. *Platinum Series.*

Tetrakistrimethylstibineplatinous Platinochloride (I).—The addition of trimethylstibine to aqueous platinic chloride in the air-free apparatus resulted in the formation of an orange precipitate insoluble in water or in organic media, which was washed successively with water and ether and dried at the ordinary temperature: 0·2200 gave 0·0990 CO_2, 0·0639 H_2O, C = 12·24, H = 3·21; 0·1807 gave 0·0905 AgCl, Cl = 12·39; 0·0819 gave 0·0454 Sb_2S_3, Sb = 39·86; 0·2465 gave 0·0812 Pt, Pt = 32·94. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%.

When left for several months, or rapidly on heating at 65°, this substance undergoes depolymerisation to the pale yellow bistrimethylstibinedichloroplatinum. Both modifications are produced when the interaction of trimethylstibine and platinic chloride is effected in alcoholic solution; the orange dimeric compound is precipitated whereas the monomeric substance remains in solution.

Tetrakistrimethylstibineplatinous platinochloride was also obtained by the following methods, which throw light on its molecular complexity.

1. *From tetrakistrimethylstibineplatinous chloride* (III). A slight excess of aqueous potassium platinochloride was added to tetrakistrimethylstibineplatinous chloride, also dissolved in water, when the orange compound was precipitated quantitatively. This preparation was insoluble in organic solvents and changed at 60° into bistrimethylstibinedichloroplatinum.

2. *From tetrakistrimethylstibineplatinous platinichloride* (p. 189). When treated with a slight excess of aqueous chloroplatinic acid, this platinichloride gave a pale yellow deposit not entirely soluble in organic solvents and leaving in each instance a small amount of orange residue. The ratio of soluble to insoluble product was as 17 : 1. Moreover, when heated at 65°, the orange substance changed in the characteristic manner to the yellow soluble form separating from alcohol in pale yellow leaflets: 0·1139 gave 0·0553 AgCl, Cl = 12·00; 0·1133 gave 0·0653 Sb_2S_3, 0·0364 Pt, Sb = 41·1, Pt = 32·29. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%.

Bistrimethylstibinedichloroplatinum (II).—When trimethylstibine and platinic chloride interact in alcoholic solution, the preceding orange insoluble compound separates forthwith, leaving in solution *bistrimethylstibinedichloroplatinum* and trimethylstibine dichloride. After distilling off the solvent, the latter product is removed by ether, leaving the co-ordination compound in a state of purity: 0·1362 gave 0·0661 AgCl, Cl = 12·32. Molecular weight in chloroform gave $M = 605$. $C_6H_{18}Cl_2Sb_2Pt$ requires Cl = 11·9%; $M = 600$.

This monomeric compound was also prepared by heating its polymeride at 60° for several hours. The preparation crystallised from alcohol in pale yellow leaflets and did not yield the green salt of Magnus when treated with Reiset's chloride, $[Pt,4NH_3]Cl_2$: 0·1009 gave 0·0450 CO_2, 0·0303 H_2O, C = 12·12, H = 3·29; 0·1054 gave 0·0526 AgCl, Cl = 12·38; 0·1188 gave 0·0663 Sb_2S_3, Sb = 40·12; 0·1165 gave 0·0379 Pt, Pt = 32·54, M (in chloroform) = 634·7. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%; $M = 600$.

The by-product soluble in ether was identified as trimethylstibine dichloride by recrystallisation from this solvent, when it separated in colourless, six-sided crystals : 0·1271 gave 0·1664 AgCl, Cl = 30·02. $C_3H_9Cl_2Sb$ requires Cl = 30·03%. This dichloride is also formed on passing chlorine into an alcoholic solution of bistrimethylstibinedichloroplatinum.

When treated in alcoholic solution with hydroxylamine hydrochloride and sodium acetate, bistrimethylstibinedichloroplatinum was completely reduced. With excess of pyridine, the bistrimethylstibine derivative yields well-defined, colourless needles of tetrapyridineplatinous chloride, readily soluble in water or organic solvents. The pyridine was estimated by the method of Harvey and Sparks (*J. Soc. Chem. Ind.*, 1918, **31**, 41T) : 0·0495 gave Py = 55·0 ; 0·0434 gave 0·0215 AgCl, Cl = 12·25. $C_{20}H_{20}N_4PtCl_2$ requires Py = 54·3, Cl = 12·16%.

Tetrakistrimethylstibineplatinous Chloride (III).—An attempt to prepare this compound by adding excess of trimethylstibine to platinous chloride resulted in the formation of the orange polymeride. This product, when treated with more trimethylstibine, dissolved and the solution gave immediately a dark orange-brown precipitate readily soluble in water or organic solvents, separating from the latter in orange-brown crystals. These are somewhat plastic and difficult to purify, and hence the compound was characterised by conversion into its *chloroplatinate*. For this purpose, the calculated amount of chloroplatinic acid in aqueous solution was mixed with the tetrakis compound, when a golden-yellow deposit was obtained : 0·0802 gave 0·247 Pt, Pt = 30·81. $C_{12}H_{36}Cl_6Sb_4Pt_2$ requires Pt = 30·80%.

Tetrakistrimethylstibineplatinous palladochloride (V), prepared by adding aqueous palladous chloride to an alcoholic solution of the tetrakis compound, crystallised from alcohol in brown leaflets which were very unstable, being decomposed completely on exposure to air for 24 hours : 0·0339 gave 0·0210 Sb_2S_3, 0·0056 Pt, 0·0032 Pd ; Sb = 43·9, Pt = 17·08, Pd = 9·46. $C_{12}H_{36}Cl_4SbPtPd$ requires Sb = 43·6, Pt = 17·52, Pd = 9·59%.

*Bistri-*n*-butylstibinedichloroplatinum*, $[2(C_4H_9)_3Sb\cdot PtCl_2]$.—Attempts to prepare the higher homologues of trimethylstibinedichloroplatinum by adding triethylstibine and tri-*n*-butylstibine to aqueous solutions of platinic chloride led to very unstable, ill-defined products, from which crystalline bistrialkylstibinedichloroplatinums could not be isolated in a state of purity. Analysis of the higher homologue showed that the product had undergone extensive decomposition.

II. *Palladium Series.*

Bistrimethylstibinedichloropalladium (VI).—On adding trimethylstibine to an aqueous solution of palladous chloride cooled in a freezing mixture, an orange-yellow deposit separated, the colour of which persisted at the low temperature. As the temperature rose to normal the product became lemon-yellow and retained this colour on drying. The product was soluble in alcohol or chloro, form, but insoluble in water or ether. On prolonged warming, it decomposed without melting, liberating metallic palladium: 0·1059 gave 0·0570 CO_2, 0·0352 H_2O, C = 14·60, H = 3·69; 0·0568 gave 0·0256 PdSb, 0·0323 AgCl, Pd = 21·09, Cl = 14·01; *M* in chloroform = 515. $C_6H_{18}Cl_2Sb_2Pd$ requires C = 14·2, H = 3·58, Pd = 21·0, Cl = 13·95%; *M* = 508.

Tetrakistrimethylstibinepalladous Chloride (VII).—The more soluble tetrakis compound formed in the preceding preparation separated from the aqueous filtrate in well-defined, golden-orange needles contaminated with trimethylstibine dichloride, the latter being removed by ether. The tetrakis compound was readily soluble in water, but was decomposed by boiling, although it was more stable than the bis compound: 0·0957 gave 0·0595 CO_2, 0·0292 H_2O, C = 17·00, H = 3·42; 0·0616 gave 0·0079 Pd, Pd = 12·80. $C_{12}H_{36}Cl_2Sb_4Pd$ requires C = 17·05, H = 4·28, Pd = 12·6%.

This tetrakis compound was also obtained by the action of excess of trimethylstibine on bistrimethylstibinedichloropalladium, although the yield was diminished by reduction of a portion of the palladium present in the latter reagent. The stability of the resulting product was increased materially by keeping it in the dark throughout its preparation and separation. When boiled for some time with dilute hydrochloric acid or a large excess of chloroform, this tetrakis derivative was converted into a lemon-yellow substance (VIII) soluble in water or organic media and distinctly acidic to bromophenol-blue. Unlike the other pallado-derivatives (VI and VII), this product was stable on keeping in the air and gave a light brown precipitate with cæsium hydroxide: 0·1121 gave 0·0490 Sb_2S_3 and 0·0321 Pd, Sb = 31·1, Pd = 28·6. $C_3H_{10}Cl_3SbPd$ requires Sb = 32·03, Pd = 28·07%.

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