252. *Covalency, Co-ordination, and Chelation. Part II. Complex-formation by the Trimethylplatinic Group.*

By W. J. Lile and R. C. Menzies.

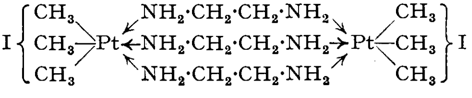
New compounds are described indicating that in its trimethyl compounds a co-ordination number of 6 is as characteristic a property of quadrivalent platinum as is a co-ordination number of 4 characteristic of tervalent gold (see Burawoy, Gibson, and Holt, *J.*, 1935, 1024).

In Part I (*J.*, 1933, 1290) it was pointed out that the alkylated derivatives of the elements 78 to 82—platinum to lead—only formed chelated compounds in those cases where the effective co-ordination number exceeded the normal valency. The dialkyls and alkyl halides of mercury, where the valency and co-ordination numbers are both two, and the tetra-alkyls and trialkyl halides of lead (both four) are unimolecular, and attempts to make their chelate derivatives failed. The halides of trimethylplatinum, dialkylgold, and dialkylthallium, on the other hand, are all associated in benzene solution, indicating that the effective co-ordination number is greater in each case than the normal valency functioning, and preparation of their chelate derivatives is easy (*J.*, 1928, 565, 1288; Gibson and Simonsen, *J.*, 1930, 2532; Brain and Gibson, *J.*, 1939, 766). The trimethylplatinum and dialkylgold halides are, however, difficult to make.

To such alkylated groups the name pseudo-atoms is often given and many of them resemble the atoms and, when charged, the ions of inorganic chemistry in their behaviour and compounds. According to Grimm (Geiger and Scheel's "Handbuch der Physik", Band XXIV, p. 519), similar atoms and pseudo-atoms are of such a nature that other atoms or groups brought into their neighbourhood are subjected to similar fields. The more obvious and earliest observed indications of such fields are acid or alkaline reaction, colour, melting point, solubility, and the formation or non-formation of ions. The atoms and ions of the alkali metals and of the alkaline-earth metals were thus soon recognised as two groups of similar atoms and two groups of similar derived ions. As regards organic and organometallic pseudo-atoms, Grimm's definition is a restatement of Berzelius's theory of compound radicals, of which a striking example was Bunsen's work on cacodyl (*Annalen*, 1841, **37**, 1). The ammonium and substituted-ammonium ions and the similar phosphonium and arsonium ions are examples of ions resembling those formed from the elements of Group I.

Less familiar is ethylboric acid (Khotinski and Melamid, *Ber.*, 1909, **42**, 3095), which resembles the compounds of the preceding element beryllium in having a sweet taste (Vauquelin, *Ann. Chim.*, 1798, **26**, 169, 173; Höber and Kiesow, *Z. Phys. Chem.*, 1898, **27**, 609). Ethylstannonic acid (Druce, *J.*, 1921, **119**, 758) is amphoteric and bears a strong resemblance to the hydroxides of aluminium, gallium, and indium. Diethylgold bromide (Pope and Gibson, *J.*, 1907, **91**, 2064) resembles the halides of univalent copper and silver in being colourless and insoluble in water, while monoethylgold dibromide resembles the salts of bivalent copper in being coloured and soluble in water and of bivalent silver in being coloured. The methyl-gold compounds as far as described are similar (Brain and Gibson, *J.*, 1939, 762). Penta-, tetra-, and tri-phenylchromium hydroxides are strong monoacid bases (Hein, *Ber.*, 1921, **54**, 1923; 1924, **57**, 8; Hein and Markert, *Ber.*, 1928, **61**, 2255), as is diphenyliodonium hydroxide.

Quite as striking as the above is the resemblance between some trimethylplatinic derivatives and those of silver. Trimethylplatinic nitrate (Pope and Peachey, *J.*, 1909, **95**, 571) is soluble in water, markedly deliquescent, and colourless. The chloride, also colourless, is insoluble in water. The iodide, obtained by Pope and Peachey as an orange sandy powder, was later obtained by Wiltshire (*J.*, 1933, 1294) as a white precipitate on adding potassium iodide to a solution in aqueous acetic acid of trimethylplatinic acetylacetone. Apart from the colour, both forms are similar under the microscope and are insoluble in water. Here again the derived pseudo-atom appears to belong to a lower group of the Periodic System than does the parent central atom. Trimethylplatinic iodide also resembles silver iodide in forming an addition compound with ammonia (Pope and Peachey, *loc. cit.*, p. 573), *viz.*, diamminotrimethylplatinic iodide, sparingly soluble in water, in which, as indicated by these authors, the metal is 6-covalent. This was again evident from the stable association of trimethylplatinic acetylacetone into double molecules in benzene (*J.*, 1933, 21) and is now further confirmed by the preparation of *dipyridinotrimethylplatinic iodide*, 2 : *2'-dipyridyltrimethylplatinic iodide*, *monoethylenediaminotrimethylplatinic iodide*, and *sesquiethylenediaminotrimethylplatinic iodide*, ethylenediamine being the only base from which two compounds were obtained. All four compounds are colourless except that the second, made from orange trimethylplatinic iodide, is pale yellow. The first two are insoluble, and the last two soluble in water, the mono-compound more readily. A possible structure for the last is shown in the inset: it is reminiscent of that of iron enneacarbonyl (Powell and Ewens, *J.*, 1939, 289). Both trimethylplatinic acetylacetone and the above dipyridyl compound are insoluble in water, but 2 : 2′-*dipyridyltrimethylplatinic acetylacetone* dissolves. In this compound there are seven potential co-ordinating addenda competing for six places, one nitrogen of the dipyridyl, or one oxygen of the acetylacetone gets left out, and, hanging loose, attaches itself to the solvent, conferring solubility on the whole molecule, as does a carbohydrate residue on a condensed system of aromatic rings.



Detailed consideration of the structural formulæ of the compounds now described, as also of the trimethylplatinic derivatives of the halogens and β-diketones, is deferred until their molecular weights in solution have been determined. A quantitative examination by *X*-ray analysis of any found to give suitable crystals would also be welcome.

Trimethylplatinic chloride is the only compound for which both determinations have been attempted, it having been shown in Part I (*loc. cit.*, p. 1293) that its degree of association in benzene solution lies between 1·71 and 1·95, while Pauling ("Nature of the Chemical Bond," 1940, p. 102) points out that an incomplete structure of trimethylplatinic chloride indicates that tetramers $Pt_4(CH_3)_{12}Cl_4$ exist in the crystals, with each platinum atom forming six octahedral bonds.

Summarising, it may be said that in the case of platinum also combination with methyl groups alters the more obvious properties, on the basis of which classification of the elementary atoms and ions into groups was originally based, to those characteristic of a lower group, but that the less obvious but fundamental co-ordination number remains unchanged.

EXPERIMENTAL.

(Analyses marked with an asterisk are by Dr. Schoeller of Berlin.)

A theoretical yield (1·65 g.) of the white trimethylplatinic iodide used in some of the preparations described below was obtained by adding 5 g. of potassium iodide in 30 c.c. of water to a solution in hot dilute acetic acid of 1·65 g. of trimethylplatinic dipropionylmethane (*J.*, 1933, 22).

Dipyridinotrimethylplatinic iodide was obtained by heating 0·13 c.c. (excess) of pyridine with 0·1 g. of orange trimethylplatinic iodide in 10 c.c. of benzene. The almost colourless solution, after evaporation to about 2 c.c., was nucleated from long colourless prisms left on evaporating a drop on a slide and readily crystallised; m. p. 168° (without decomp.) (Found : N, 5·35. $C_3H_9PtI,2C_5H_5N$ requires N, 5·33%). No data were obtained for platinum, the compound decomposing explosively on heating.

2 : 2′-*Dipyridyltrimethylplatinic iodide* separated as colourless crystals (0·68 g., 95%) when the golden-yellow solution obtained from 0·212 g. (1 equiv.) of dipyridyl and 0·5 g. (1 equiv.) of colourless trimethylplatinic iodide in hot benzene was boiled for 1 min.; m. p. 273° (decomp.; darkening slowly above 225°) (Found : C, 30·0*; H, 3·30*; N, 5·40*; I, 24·8, 24·2; Pt, 37·2*. $C_3H_9IPt,C_{10}H_8N_2$ requires C, 29·8; H, 3·27; N, 5·35; I, 24·25; Pt, 37·3%). The iodine was determined by titrating an acetone solution with 0·1N-aqueous silver nitrate, potassium dichromate, which produces no precipitate with the dipyridyl compound, being used as internal indicator. From the acetone–water solution was obtained a bright yellow solid soluble in alcohol, acetone, and water; it crystallised from boiling alcohol in long, almost colourless needles, darkening above 220°, and fusing, with decomposition at 246°. This is believed to be dipyridyltrimethylplatinic nitrate, but analyses were not good.

The dipyridyl iodide after recrystallisation from acetone gave analytical figures high for C and H and low for N, indicating combination with the solvent, and its molecular weights in boiling chloroform decrease with increasing concentration, similarly indicating reaction with the solvent (cf. Biltz, *Annalen*, 1904, **331**, 334).

The precipitation of silver iodide from acetone solutions of this iodide further suggests the existence of some compound such as $[PtMe_3,dipy,COMe_2]I$.

On refluxing 0·2 g. of orange trimethylplatinic iodide with 0·17 g. (2 equivs.) of dipyridyl in an attempt to prepare a sesquidipyridyl compound similar to the ethylenediamine compound, the above iodide, m. p. 272° (Found : N, 5·1; Pt, 38·1%), was again obtained. This iodide is apparently unchanged on boiling with dilute acetic acid, hydrochloric acid, 2N-ammonia, or sodium hydroxide. It is, however, attacked by ethylenediamine (see p. 1170), and decomposed by boiling alcoholic potash.

Monoethylenediaminotrimethylplatinic iodide was obtained by refluxing 1 g. of orange trimethylplatinic iodide with 0·08 c.c. (0·5 equiv.) of anhydrous ethylenediamine in 25 c.c. of benzene for 2 hours. The white solid (m. p. 204°) was separated from the pale yellow solution, and concentration of the filtrate to about one-third gave dull orange crystals, m. p. 206°. Recrystallised from water, in which it is more soluble than the sesqui-compound described below, the normal iodide was obtained as square plates and prisms; m. p. 204 (decomp.) (Found : Pt, 45·2; N, 6·9. $C_3H_9PtI,C_2H_8N_2$ requires Pt, 45·7; N, 6·7%). From the benzene mother-liquors more of this compound was recovered mixed with unchanged trimethylplatinic iodide. It is unchanged (m. p. and mixed m. p.) on boiling with dipyridyl in benzene.

Sesquiethylenediaminotrimethylplatinic iodide (0·63 g., white needles, darkening above 230° and melting at 273° with formation of a platinum mirror) was obtained from 0·73 g. of orange trimethylplatinic iodide and excess of ethylenediamine dissolved in benzene. Water was added and after evaporation of the benzene the product was recrystallised from water (Found : C, 16·05*; H, 4·58*; N, 8·5*; Pt, 42·5*. $2C_3H_9PtI,3C_2H_8N_2$ requires C, 15·76; H, 4·63; N, 9·2; Pt, 42·7%).

Action of ethylenediamine on dipyridyltrimethylplatinic iodide. 0·5 G. of the dipyridyl compound, from orange trimethylplatinic iodide, was dissolved in chloroform, 0·08 c.c. of ethylenediamine (1 equiv.) added to the hot solution, and the mixture heated under reflux. On standing, colourless crystals were produced. A drop of the clear solution, shaken with water and an aqueous solution of potassium mercuri-iodide, gave a white flocculent precipitate, indicating the presence of free dipyridyl. No such precipitate is produced by a solution of the dipyridyl compound. Rosettes and twinned needles of the sesqui-compound were obtained on recrystallisation from water; m. p. 266° (darkening above 240°) (Found : Pt, 41·9; N, 8·94%).

0·5 G. of the dipyridyl compound were then treated in cold chloroform with 0·06 c.c. of ethylenediamine, and the solution allowed to evaporate at room temperature. Pale yellow rhombic plates and a dark orange substance were deposited. These were separated into an acetone-soluble portion, yellow needles [m. p. 274° (decomp.) and mixed m. p. with the dipyridyl iodide 273°], and an acetone-insoluble portion. The latter after recrystallisation from water melted at 270° without decomposition. Mixed with the dipyridyl compound it melted at 246°, and mixed with the sesqui-compound at 271°. The presence of the monoethylenediamino-iodide was not observed.

Dipyridyltrimethylplatinic acetylacetone was obtained as pale yellow hexagonal plates and prisms on allowing to evaporate at room temperature the golden-yellow solution obtained by dissolving 0·17 g. of trimethylplatinic acetylacetone and 0·039 g. (0·5 equiv.) of dipyridyl in 10 c.c. of benzene. Crystallised from hexane–benzene, this gave dull orange needles, m. p. 143° (decomp.; darkening above 120°, with signs of softening) (Found : N, 5·5. $C_8H_{16}O_2Pt,C_{10}H_8N_2$ requires N, 5·6%). The same compound was also formed by heating the dipyridyl iodide (0·32 g.) and thallous acetylacetone (0·185 g.) under reflux in benzene, filtering and evaporating the solvent; crystals and a brown sticky mass were obtained, which was stirred with benzene and alcohol, and filtered from insoluble material. On evaporation, dull orange needles were obtained; m. p. 142° (decomp.; darkening above 115° with slight softening); mixed m. p. with the above acetylacetone compound 142—143° (decomp.). This compound is fairly soluble in water.

When the acetylacetone compound was dissolved in water, and a little acetic acid and excess of potassium iodide added, a white curdy precipitate was produced; after being washed and dried, this darkened slightly above 230° and had m. p. 268° (decomp.) and mixed m. p. with the dipyridyl iodide 270°. We thus have the following parallel pairs of reactions, all of which have been carried out :

$$\begin{tikzcd}
(CH_3)_3PtI \arrow[r, "\text{dipy}"] \arrow[d, shift right, "C_5H_7O_2Tl"'] & (CH_3)_3PtI,\text{dipy} \arrow[d, shift right, "C_5H_7O_2Tl"'] \\
(CH_3)_3Pt,C_5H_7O_2 \arrow[u, shift right, "KI"'] \arrow[r, "\text{dipy}"] & (CH_3)_3Pt,\text{dipy},C_5H_7O_2 \arrow[u, shift right, "KI"']
\end{tikzcd}$$

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UNIVERSITIES OF BRISTOL AND EDINBURGH.
MID-ESSEX TECHNICAL COLLEGE, CHELMSFORD.

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