SOME TETRA-COVALENT COMPOUNDS OF PLATINUM WITH TERTIARY ARSINES.

By G. J. Burrows, B.Sc.,
and R. H. Parker, M.Sc.

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INTRODUCTION.

Tetra-covalent platinous compounds have attracted considerable attention during recent years on account of the isomerism almost invariably observed in this type of derivative. The explanation originally advanced by Werner, that the occurrence of isomers in the case of diammine platinous chloride is due to the planar nature of the molecule permitting cis and trans arrangements of the chlorine atoms and ammonia groups around the platinum, was later challenged by Reihlen and Nestle (Ann., 1926, 447, 211, and 448, 1312). From molecular weight determinations (in liquid ammonia) these authors were led to conclude that one “isomer” was in reality a polymer of the other. Werner’s original view was still later supported by Hantzsch (Ber., 1926, 59, [B] 2761), who found that the molecular weights of the two bis-pyridine platinous chlorides in molten phenol were practically identical. More recently Angell, Drew and Wardlaw (Journ. Chem. Soc., 1930, 349), in discussing the isomeric bis-diethyl sulphide platinous halides, advanced the view that the differences observed in the properties of the two forms were capable of a quite different interpretation. They assigned to the chlorides, for example, the formulæ

\[ \begin{align*}
Et_2S&-\text{Pt} \quad \text{Cl} \\
Et_2S&-\text{Pt} \quad \text{Cl}
\end{align*} \]

\( \alpha \) dichloride. 

\[ \begin{align*}
\text{S}&-\text{Pt} \\
\text{Et}_2&-\text{Cl}
\end{align*} \]

\( \beta \) dichloride.
In a subsequent paper (Journ. Chem. Soc., 1932, 988) Drew, Pinkard, Wardlaw and Cox recorded the isolation of a third isomer of diammine platinous chloride, and assigned the following formulæ to the three isomers:

\[ \begin{align*}
\text{a} & : \text{Pt} & \text{NH}_3 & \text{NH}_3 & \text{Cl} \\
\text{b} & : \text{Pt} & \text{Cl} & \text{NH}_3 & \text{NH}_3 & \text{Cl} \\
\text{c} & : \text{Pt} & \text{Cl} & \text{NH}_3 \\
\end{align*} \]

Further evidence of the coplanar arrangement was supplied by Cox (Journ. Chem. Soc., 1931, 1089) from X-ray analysis of tetrammine platinous chloride. On the other hand, the resolution into optical enantiomers by Reihlen and Huhn (Ann., 1932, 499, 144) of bis-isobutylene diammine platinous chloride and of bis-2-amino-methyl-3-methyl-4-ethyl quinoline platinous chloride cannot be reconciled with a planar arrangement, and we are forced to believe that, in these compounds at least, the arrangement is tetrahedral.

Still more recently (Journ. Chem. Soc., 1934, 219) Drew and Head repeated the preparation of isobutylene diammine platinous chloride, and stated that their product was a mixture of two isomers with distinctly different solubilities in alcohol, a result to be expected for a coplanar arrangement of the two isobutylene diammine groups co-ordinated with the platinum. It is quite obvious that our knowledge of the stereochemistry of these compounds is still very obscure.

In view of the remarkable stability of the complex ions formed by silver with tertiary arsines (Burrows and Parker, Journ. Amer. Chem. Soc., 1933, 55, 4133), it was decided to prepare and examine the corresponding platinous compounds. Cahours and Gal (Journ. Prakt. Chem., 1870, 110, 460; Compt. Rend., 1870, 70, 897, 1380, and 71, 208) described compounds formed by trimethyl arsine and triethyl arsine with salts of platinum, palladium and gold. In particular they recorded the occurrence of isomeric bis-trimethyl platinous chlorides and bis-tributyl platinous chlorides having different solubilities in ether. Mann and Pope (Journ. Chem. Soc., 1922, 121, 1758) described platinum bis-chlorovinyl bis-
ββ′β‖-trichloro trivinyl arsine, which they apparently obtained in one form only.

Phenyl dimethyl arsine and diphenyl methyl arsine were selected for this investigation in view of their comparative stability and the ease of obtaining them in a pure condition. They were found to react readily with chloroplatinic acid* or with chloroplatinous acid, yielding fine crystalline compounds having characteristic melting-points. They are very soluble in cold chloroform, are appreciably soluble in acetone, and can be recrystallised from hot toluene. They are insoluble in methyl alcohol or ethyl alcohol and are regarded by us as being non-polar compounds of the type $R_2PtX_2$, in which $X$ is a molecule of the arsine. Quite early in the investigation we were led to believe that our products were mixtures of two forms—slight variations in colour were observed after crystallising from different solvents—but it was not found possible to effect a separation by employing different solvents. In this respect our experience was quite different from that of Cahours and Gal, who found that one form only of bis-triethyl arsine platinous chloride was soluble in ether or alcohol. Furthermore, only slight differences in melting-points were observed after recrystallising the various compounds from different solvents. It was observed, however, that where two different crops of crystals of any one product were obtained, one being paler than the other, the paler substance on heating appeared to change into the darker just before melting. Also, the final products appeared to be the same when prepared from the arsine by treatment with either chloroplatinic acid, potassium chloroplatinum or chloroplatinous acid. More definite evidence of the existence of isomers was obtained by examining the compounds many months after their preparation. A specimen of bis-diphenyl methyl arsine platinous dichloride, for example, melted at 214°C., appeared to be homogeneous when first prepared, and had a very pale yellow colour. The same specimen after eleven months appeared to be a mixture of two substances, one of which was bright yellow and the other almost colour-

* Portion of the arsine first reduces the chloroplatinic acid to the platinous condition; unchanged arsine then combines with the platinous chloride.
The product had originally been crystallised from hot toluene, in which solvent it was quite soluble. On heating the compound in toluene, eleven months after preparation, portion only was found to be soluble, and it was found possible to effect a separation with this solvent. Repeated extraction with toluene yielded:

(a) a solution from which a yellow crystalline form was obtained melting at 214°C; and

(b) a residue which crystallised from hot chloroform in pale-yellow needles, melting at 218°C.

Another specimen of bis-diphenyl methyl arsine platinous dichloride was recrystallised from toluene, melting at 214°C. It was then carefully heated just to its melting-point in a tube immersed in sulphuric acid. It resolidified on cooling to a yellow mass which was almost insoluble in toluene, but readily soluble in chloroform; the pale yellow product from this solvent melted at 218°C. After crystallisation from chloroform the compound was insoluble in toluene. No significance is attached to the difference in melting-points, but the behaviour towards toluene is considered to indicate that these compounds are capable of existence in isomeric forms. When first prepared the compounds are soluble in toluene, but they appear to change, slowly at the ordinary temperature and rapidly at the melting-point, into a form which is practically insoluble in that solvent. This behaviour has been observed in the case of the three compounds we have prepared, namely, bis-phenyl dimethyl arsine platinous chloride, bis-diphenyl methyl arsine platinous chloride, and bis-phenyl dimethyl arsine platinous bromide.

Unfortunately we have been unable to obtain accurate results for molecular weight determinations owing to the comparatively low solubilities of these large molecules in suitable solvents. The behaviour towards heat is not incompatible with Reihlen's results for bis-pyridine platinous chloride. It is quite possible that one form may be a polymer of the other and may depolymerise on long standing or on heating. Further work is at present in progress with other arsines, and it is hoped that by isolating more soluble compounds it will be possible to make accurate determinations of the molecular weights.
This compound was prepared from chloroplatinic acid, from chloroplatinous acid and from potassium chloroplatinite.

(a) Platinum (1 atom) was converted to chloroplatinic acid in the usual way, and to a concentrated aqueous solution an equal volume of alcohol was added. Diphenylmethyl arsine (3 molecules), dissolved in alcohol, was then added dropwise to this solution with vigorous stirring. The brown solution was then heated on the water-bath until the colour had almost disappeared. On standing a yellowish hard mass separated, and this was extracted with hot toluene, whereby the compound was obtained in short, thick, pale-yellow prisms melting at 207°C. A further extraction yielded a second crop of crystals of the same colour melting at 215°C, the total yield being 70 per cent. The extra molecule of arsine is used in reducing the chloroplatinic acid to platinous chloride. Bis-diphenylmethyl arsine platinous chloride is insoluble in water, ethyl and methyl alcohols, ether ligroin and ethyl acetate. It is only slightly soluble in hot benzene. It may be recrystallised from acetone, acetic acid, toluene or chloroform, being extremely soluble in the last. The melting-points after recrystallisation from acetone, chloroform, toluene and acetic acid were found to be 212°, 213°, 214° and 211°C. respectively.

Found Pt 25-8, Cl 9-2, As 19-6 per cent.

C_{26}H_{26}As_{2}Cl_{2}Pt requires Pt 25-9, Cl 9-4, As 19-9 per cent.

(b) Platinous chloride (1 atom), prepared according to the method of Nilson (Journ. Prakt. Chem., 1877, 123), was treated in aqueous alcohol with diphenylmethyl arsine (2 molecules). The platinum chloride, however, did not dissolve, and was recovered and converted into chloroplatinous acid with warm hydrochloric acid. An alcoholic solution of the arsine (2 molecules) was then added with stirring, and on warming a clear solution was obtained from which the compound separated in almost colourless needles on cooling, the yield being 80 per cent. This compound melted at 213°C. and resembled
that described under (a) as regards its solubility in different liquids.

(c) Potassium chloroplatinic (1 molecule), prepared from chloroplatinate and potassium oxalate and dissolved in 5 times its weight of hot water, was added to an alcoholic solution of diphenyl methyl arsine with continuous stirring. After some minutes a white precipitate began to separate. The stirring was continued for about two hours, when the precipitate was separated, washed with alcohol and ether and recrystallised from hot toluene. The product, pale-yellow needles, melted at 214°C, and was found to contain 25-6 per cent. of platinum. It was identical with the product obtained by the other methods.

As Angell, Drew and Wardlaw (Journ. Chem. Soc., 1930, 349) had found that only one form of bis-diethyl sulphide platinous chloride reacted readily with moist silver oxide, it was decided to apply the same treatment to the arsine derivative. For this purpose an excess of freshly-prepared moist silver oxide was rubbed with the arsine in a glass mortar for about twenty minutes, after which hot water was added and the resulting suspension filtered. The filtrate on treatment with hydrochloric acid remained clear, but on evaporation yielded a very small amount of yellowish solid which on recrystallisation from chloroform melted at 214°C. The residue from the above filtration was repeatedly extracted with small quantities of absolute alcohol, and the extract on evaporation in vacuo over phosphorus pentoxide yielded a product melting at 200°C. This was not analysed, but was considered to be bis-diphenyl methyl arsine platinous hydroxide \((\text{Ph}_2\text{MeAs})_2\text{Pt(OH)}_2\). It was converted to the chloride by treatment with hydrochloric acid, and this product after drying and recrystallising from chloroform melted at 214°C.

Reference has already been made in the introduction to the change which takes place in the compound after a long period at the ordinary temperature or on melting. Heating to the melting-point converts the compound into a form which, although no longer soluble in toluene, is readily soluble in chloroform and can be recrystallised from this solvent in the form of pale-yellow needles melting at 218°C and containing 25-7 per cent. of
platinum. A specimen, originally crystallised from toluene, after eleven months was found to have changed into a mixture, portion of which was soluble in toluene from which it crystallised in yellow needles (m.p. 214°C, Pt 25·6 per cent., As 19·5 per cent). The remaining portion, insoluble in toluene, was crystallised from chloroform, also in yellow needles (m.p. 218°C, Pt 25·6 per cent., As 19·5 per cent.).

Bis-phenyl Dimethyl Arsine Platinous Bromide

(PhMe₂As)₂PtBr₂.

This was prepared from bromoplatinic acid and excess of the arsine in alcoholic solution. The solution was heated on the water-bath for several hours, the colour becoming considerably brighter, and a yellow crystalline precipitate separated. This was removed by filtration, washed with alcohol and ether and air-dried. The compound resembled the corresponding chloride in solubilities. Portion was recrystallised from chloroform in yellow needles melting at 196°C.

Found Pt 23·0, Br 18·8 per cent.*

C₂₆H₂₆As₂Br₂Pt requires Pt 23·1, Br 19·0 per cent.

A sample of this product from chloroform was found to change on prolonged exposure to light to a reddish product melting at 144°C. and containing 22·1 per cent of platinum. This has not been investigated further.

Another portion was recrystallised from toluene in yellow plates melting at 193°C. Found Pt 23·3, Br 18·7 per cent. On heating to the melting-point this compound was rendered insoluble in toluene, although it could be recrystallised from chloroform, yielding a compound containing 23·1 per cent, platinum and melting at 196°C.

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* In the analysis platinum was estimated by ignition. For the estimation of bromine, 0·1 gramme of the compound was heated with a few c.c. of concentrated nitric acid in the presence of silver nitrate, giving silver bromide and platinum, the latter being removed by filtration. The filtrate was treated with zinc dust and then with a little nitric acid to dissolve any silver precipitated. The resulting platinum was added to the first residue and, after weighing, the amount of platinum was subtracted, giving the silver bromide.
AN X-RAY STUDY OF OPALS.

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(Read before the Royal Society of New South Wales, August 1, 1934.)

The presence of crystalline material in opals has been noted by Levin and Ott (J. Am. Chem. Soc., 1932, 54, 828), (Z. Krist., 1933, 85, 305), and ourselves (This Journal, 1932, 66, 378). Collected data from all three sources indicate that opals may contain crystallites of either a- (high) cristobalite, a- (low) cristobalite, or a- (low) quartz.

The presence in opals of a-cristobalite, which has presumably existed through geological ages, is so interesting as to warrant a study of the manner of its origin. In this connexion the Australian opals afford excellent material, since it is possible to obtain specimens which have been formed under the most diverse geological conditions.* Of particular interest are those opals formed in association with groundwaters, as at Lightning Eidge, Coober Pedy and White Cliffs. This type of occurrence is probably unique.

**Experimental Results.**

Employing the usual Debye-Scherrer technique, the authors obtained powder photographs of two types:

1. Those showing the lines of a-cristobalite or a-quartz,
2. Those showing a broad band in the position of the most intense line of either a- or a-cristobalite.

The demarcation between the two types of pattern was not sharp. There occurred a gradual variation from lines of excellent sharpness to the broad lines characteristic of colloidal crystal dimensions, and finally to a broad diffuse band.

*The authors wish to thank Professor W. R. Browne for geological data, and also Dr. Ida A. Brown and the Curator of the Mining Museum, Mr. M. Morrison, for specimens of opal.

Bis-diphenyl Methyl Arsine Platinous Bromide (Ph₂AsMe)₂PtBr₂.

This was prepared from bromoplatinic acid and excess of the arsine in alcoholic solution. The solution was heated on the water-bath for several hours, the colour becoming considerably brighter, and a yellow crystalline precipitate separated. This was removed by filtration, washed with alcohol and ether and air-dried. The compound resembled the corresponding chloride in solubilities. Portion was recrystallised from chloroform in yellow needles melting at 196°C.

Found Pt 23·0, Br 18·8 per cent.*

C₅₆H₅₆As₂Br₂Pt requires Pt 23·1, Br 19·0 per cent.

A sample of this product from chloroform was found to change on prolonged exposure to light to a reddish product melting at 144°C. and containing 22·1 per cent. of platinum. This has not been investigated further. Another portion was recrystallised from toluene in yellow plates melting at 193°C. Found Pt 23·3, Br. 18·7 per cent. On heating to the melting-point this compound was rendered insoluble in toluene, although it could be recrystallised from chloroform, yielding a compound containing 23·1 per cent. platinum and melting at 196°C.

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