COMPOUNDS FORMED FROM COPPER SALTS AND TERTIARY ARSINES.

PART I.

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The tendency of arsenic to pass from the tervalent to the 4-covalent condition is well shown by the ease of formation and the stability of compounds of tertiary arsines with salts of platinum, gold and silver (Cahours and Gal, Jour. prakt. Chem., 1870, 110, 460; Mann and Pope, J.C.S., 121, 1758; Burrows and Parker, J.A.C.S., 1933, 55, 4133; Proc. Roy. Soc. N.S.W., 1934, 68, 39). The formation of addition compounds of tertiary arsines with the iodides of phosphorus, arsenic, antimony, tin and bismuth, and with compounds such as methyl diiodo arsine (Burrows and Turner, J.C.S., 1920, 117, 1373; 1921, 119, 1448) is to be attributed to the same tendency.

Ehrlich and Karrer (Ber., 1915, 48, 1634) obtained addition compounds of salvarsan with two molecules of cupric chloride. These authors concluded that in compounds formed by salvarsan and other arsenederivatives with metallic salts, the metal is attached to the arsenic atom, and is not coordinated with amino or hydroxyl groups.

The present communication contains a report on compounds obtained by acting on cuprous and cupric salts with phenyl dimethyl arsine and diphenyl methyl arsine. It was observed that cuprous iodide could be dissolved in a hot alcoholic solution of phenyl dimethyl arsine, and that on cooling the solution colourless prisms separated. Recrystallisation from acetone yielded two products, containing one and two molecules of arsine respectively to one of cuprous iodide. The other cuprous derivatives of this arsine that were isolated were bis-phenyl dimethyl arsine cuprous chloride and phenyl dimethyl arsine cuprous bromide; only in the case of cuprous iodide were
both types obtained. The cuprous chloride compound was obtained from cuprous chloride itself, and also from cupric chloride; presumably by reduction with excess of the arsine. The cuprous bromide compound was obtained from cupric bromide. No coordination compound corresponding to a cupric halide could be isolated. With diphenyl methyl arsine similar compounds were obtained from cupric chloride, cupric bromide, and also from cupric nitrate.

The three derivatives isolated are all cuprous derivatives with one molecule of arsine combined with one of the cuprous salt. When freshly prepared all of the above derivatives are white crystalline substances with characteristic melting points. On long standing in the atmosphere they slowly become light blue in colour. On treatment with sodium hydroxide they yield cuprous oxide, indicating that they are cuprous derivatives. They have a distinct odour of the arsine, and in most cases on boiling a solution of the compound for some considerable time it decomposes, with the separation of the cuprous halide. These facts led to the belief that these compounds were of the types [R.Cu]X and [R₂Cu]X, where R represents a molecule of the arsine and X an atom of halogen. On the other hand these derivatives are insoluble in water but soluble in alcohol, acetone, benzene, and chloroform, which would indicate that they are non-polar compounds rather than salts, and correctly formulated as \[ \text{Cu} \text{<}
\begin{cases} \text{R} & \text{X} \\ \text{Cu} \text{<}
\end{cases}\text{ and Cu<}
\begin{cases} \text{R₄} & \text{X} \\ \text{Cu} \text{<}
\end{cases}\text{ respectively. In solution in benzene they have molecular weights agreeing fairly closely with those calculated from the formulae, but their behaviour on heating or towards reagents can be attributed to the fact that they are not very stable in solution.}

In addition to the above, a third type of derivative has been isolated. If cupric chloride in alcoholic solution is treated with excess of arsine a cuprous chloride derivative rapidly separates as mentioned above. The filtrate on standing exposed to the air slowly deposited crystals, which on analysis were found to contain two atoms of copper, three of chlorine, and three molecules of arsine (Cu₂R₃Cl₃). In the case of phenyl dimethyl arsine the derivative was blue in colour, did not melt sharply, but could not be separated into two compounds. With diphenyl methyl arsine, however, a mixture of brown and blue crystals separated. Subsequently it was found
possible to prepare these derivatives separately by varying the conditions. Both the blue and the brown compound are crystalline, and have the same composition, Cu₂(Ph₂MeAs)₃Cl₃. They both melt at 245° C. to deep green liquids, and the melting point of a mixture is the same. Unfortunately they are almost insoluble in the ordinary solvents, being only slightly soluble in hot acetone and alcohol. It has not been possible to carry out a molecular weight determination. On treatment with sodium hydroxide the crystals appear to become coated with cuprous oxide. There is little doubt that these compounds are formed by the oxidation of the simple cuprous derivatives, \([Cu<^\text{R}\text{Cl}^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>\text{Cl}\text{]}\text{ , and valency considerations lead to the conclusion that one of the copper atoms is in the cuprous condition and the other in the cupric.}

It is interesting to note that Ritthausen (Journ. prakt. Chem., 1853, 59, 373) obtained a white crystalline compound of CuCl₃NH₃ by the action of a solution of ammonia on copper. This corresponds to the compounds of the type \([Cu<^\text{R}\text{Cl}^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>^>\text{Cl}\text{]}\text{ described in the present communication. This author also observed that a solution of this cuprous compound in aqueous ammonia, on standing exposed to the air, deposited blue crystals of a compound to which he assigned the formula Cu₂Cl₃NH₃.CuCl.NH₃.HO. From the analytical data actually published in that paper the atomic ratio Cu : Cl : NH₃ is 1 : 1.34 : 1.37, which would suggest the formula Cu₂Cl₃(NH₃)₃H₂O, one of the copper atoms being in the cuprous and the other in the cupric condition. Such a compound would be analogous to the arsine derivative Cu₂Cl₃(Ph₂MeAs)₃ isolated during the present investigation.

As regards the constitution of the two compounds Cu₂Cl₃(Ph₂MeAs)₃ it is possible that one may be a polymer of the other. As mentioned above, it has not been possible to decide this point by determining molecular weights, owing to the insolvability of the compounds. The very marked difference in colour cannot be attributed to the presence in one of a small quantity of impurity, as crystals of both substances separate together from the same solution, and very fine crystals of the blue form appeared to change very slowly to the brown when kept in specimen bottles for many months. Furthermore, the two forms
apparently become identical on heating to the melting point.

As pointed out above, valency considerations require that one of the copper atoms is cuprous and the other cupric, and the behaviour of the compounds towards reagents is consistent with this. Assuming that the compounds are monomolecular, three formulæ suggest themselves: (1) \[ \text{Cu}(\text{Ph}_2\text{MeAs})_2 \] \[ \text{Cu} \left( \text{Ph}_2\text{MeAs} \right)_3 \text{Cl}_3 \text{Cl}_2 \] and (3) \[ \text{Cu} \left( \text{Cu} \left( \text{Ph}_2\text{MeAs} \right)_3 \right) \text{Cl}_3 \text{Cl}_2 \] In the first the cuprous atom loses an electron to the cupric atom and is coordinated with two molecules of arsine, becoming a univalent positive ion, the cupric atom becoming a 4-covalent ion. In the second the cuprous atom loses one electron to the cuprous and at the same time is attached covalently to three molecules of arsine and one chlorine atom. In other words that compound may be regarded as a derivative of H[CuCl₂] in which the H is replaced by the complex 4-covalent cupric ion. In the third the cuprous atom becomes a simple cuprous ion, and the cupric atom is coordinated with the three molecules of arsine, passing into the 6-covalent state. In most complex cupric compounds the copper has a covalency of four, but several six-covalent derivatives have been described, such as [Cu₄Cl₆]. The six-covalent groups in such compounds would be arranged octahedrally, and Wahl (Acta. Soc. Sci. Fennica, 1928, 14, 1) prepared from cupric halides and ethylene diamine, compounds of the type [Cu₄(H₂O)₂]X₂. The tartrate of this complex ion was separated into two different optically active fractions, and these in turn were converted into active iodides.

The formula \[ \text{Cu} \left( \text{Cu} \left( \text{Ph}_2\text{MeAs} \right)_3 \right) \text{Cl}_3 \] is consistent with the insoluble nature of the compounds, and furthermore it would explain the isomerism. In one form the three arsine groups are in the 1, 2, 3 positions, whilst in the other they are in the 1, 2, 6. It is interesting to note that the isomeric cobalt triammines \[ \text{Co} \left( \text{NH}_3 \right)_3 \] usually show a marked difference in colour.

Further experiments are in progress with other tertiary arsines, and it is hoped that they will enable us definitely to establish the constitution of these compounds.

M—December 4, 1935.
COMPOUNDS FORMED FROM COPPER SALTS.

Phenyl dimethyl arsine cuprous iodide: \[ \text{Cu}_1(\text{PhMe}_2\text{As}) \]
was obtained by boiling an alcoholic solution of phenyl dimethyl arsine with excess of cuprous iodide for about half an hour. After removing the excess of cuprous iodide, the filtrate was concentrated on the water bath until crystallisation commenced, a few c.c. of hot alcohol were added, and the solution allowed to crystallise in the air. Pale yellow crystals separated, and after drying in the air were found to melt at 127° C. The compound is readily soluble in cold alcohol, benzene, carbon tetrachloride and acetone, and sparingly soluble in ether. It could be crystallised (without change of the melting point) by dissolving in cold ether and allowing the cold solution to concentrate at the ordinary temperature. The solution, unless very dilute, was found to decompose on heating, with the precipitation of cuprous iodide and formation of bis-phenyl dimethyl arsine cuprous iodide.

Found: Cu=17·0, I=33·8 per cent.

C$_8$H$_{11}$AsCuI requires Cu=16·9, I=34·1 per cent.

Bis-phenyl dimethyl arsine cuprous iodide:

\[ \text{Cu}_1(\text{PhMe}_2\text{As})_2 \]
was prepared by digesting an alcoholic solution of the arsine with a slight excess of cuprous iodide on the water bath for a few minutes. The solution was decanted into a dish and allowed to crystallise. White prisms were obtained, and these were dried on porous plate and then recrystallised from acetone. The compound melts at 94° C. It is soluble in alcohol, benzene, ether, ethyl acetate, carbon tetrachloride, and acetone. After keeping for a few weeks a specimen had a strong odour of the arsine, but the melting point and composition remained unchanged after many months.

Found: Cu=11·5, I=22·7, As=27·0 per cent.

C$_{16}$H$_{22}$As$_2$CuI requires Cu=11·4, I=22·9, As=27·1 per cent.

Bis-phenyl dimethyl arsine cuprous chloride:

\[ \text{Cu}_1(\text{PhMe}_2\text{As})_2 \]
was prepared from the arsine and cuprous chloride in the same manner as the corresponding iodide. The cuprous chloride was freshly precipitated and was dried as quickly as possible by washing with alcohol and ether. The compound separated in white prisms, melting at 127° C. On keeping for a few days the colour changed
to a pale green, but on long standing it becomes definitely blue. It is soluble in methyl or ethyl alcohol, acetone, benzene, and chloroform, but decomposes on heating in solution.

\[
\text{Found: Cu}=13.6, \text{Cl}=7.9, \text{As}=32.0 \text{ per cent.}
\]

\[
\text{C}_{16}\text{H}_{22}\text{As}_{2}\text{CuCl} \text{ requires Cu}=13.5, \text{Cl}=7.8, \text{As}=32.4 \text{ per cent.}
\]

**Phenyl dimethyl arsine cuprous bromide:** \[
\text{[Cu}(\text{PhMe}_{2}\text{As})]\text{Br}
\]

When cupric bromide was treated in alcoholic solution with phenyl dimethyl arsine it underwent reduction, giving a cuprous derivative. For the preparation of this compound freshly prepared cupric bromide (1 mol) was dissolved in alcohol, and to the warm solution phenyl dimethyl arsine (2 mol) was added. The solution became colourless, and white prisms separated. The air-dried compound melted at 106° C. The compound appears to oxidise slowly on exposure to air, changing to blue, and ultimately to deep green. It is readily soluble in benzene and chloroform, and also in alcohol, but is insoluble in water.

\[
\text{Found: Cu}=19.8, \text{Br}=24.7, \text{As}=22.8 \text{ per cent.}
\]

\[
\text{C}_{8}\text{H}_{11}\text{AsBrCu} \text{ requires Cu}=19.4, \text{Br}=24.6, \text{As}=23.1 \text{ per cent.}
\]

**Diphenyl methyl arsine cuprous nitrate:** \[
\text{[Cu}(\text{Ph}_{2}\text{MeAs})]\text{NO}_{3}
\]

was obtained in the form of white prisms melting at 107° C. by adding an alcoholic solution of the arsine (1 mol) to a concentrated aqueous solution of copper nitrate (1 mol) and recrystallising from alcohol. This compound is readily soluble in benzene and insoluble in water. The molecular weight in benzene, determined cryoscopically was found to be 378.

\[
\text{Found: Cu}=17.0, \text{As}=20.0 \text{ per cent.}
\]

\[
\text{C}_{13}\text{H}_{12}\text{O}_{3}\text{AsNCu} \text{ requires Cu}=17.2, \text{As}=20.3 \text{ per cent. M.wt., } 370.
\]

**Diphenyl methyl arsine cuprous bromide:** \[
\text{[Cu}(\text{Ph}_{2}\text{MeAs})]\text{Br}
\]

was prepared by adding excess of arsine (4 mol) to a hot alcoholic solution of cupric bromide (1 mol) and cooling, the compound separating in white prisms melting at 133° C. Like the corresponding nitrate, it is readily soluble in benzene and insoluble in water.

\[
\text{Found: Cu}=16.1, \text{As}=19.0, \text{Br}=20.4; \text{ m.wt. in benzene, } 399.
\]
C\textsubscript{13}H\textsubscript{13}AsBrCu requires Cu=16·4, As=19·4, Br=20·6 per cent. M.wt., 388.

Ter-diphenyl methyl arsine cuprous cupric bromide: \[
\left[ \text{Cu}_2\text{Br}_3\left(\text{Ph}_2\text{MeAs}\right)\right]
\]
was obtained by modifying the procedure adopted for the previous compounds. Cupric bromide was dissolved in alcohol and the arsine added drop by drop with stirring until the solution became colourless. More cupric bromide was then added to the solution (heated on the water bath) until a permanent brown colour was obtained. The liquid was filtered and the filtrate allowed to crystallise exposed to the air. After many hours the crystals which had separated were removed by filtration and air-dried. In the finely divided state the crystals were dark green, but large crystals appeared to be black. The substance melted at 202° C. It is very slightly soluble in hot acetone, but insoluble in all other liquids.

Found: Cu=11·5, As=19·1, Br=21·5 per cent.

C\textsubscript{39}H\textsubscript{39}As\textsubscript{3}Br\textsubscript{3}Cu\textsubscript{2} requires Cu=11·5, As=20·5, Br=21·9 per cent.

Blue Form. — The brown solution was prepared as before and allowed to stand for an hour. Water was then added until a green solution was obtained, which was allowed to stand overnight. The substance separated in the form of blue crystals having the same melting point as the brown form, and resembling it in its insolubility in all solvents.

Found: Cu=13·1, As=22·1, Cl=10·8 per cent.

C\textsubscript{39}H\textsubscript{39}As\textsubscript{3}Br\textsubscript{3}Cu\textsubscript{2} requires Cu=13·1, As=23·3, Cl=10·9 per cent.

A mixture of the two forms containing a trace of arsine was found to change slowly to the brown form on long standing.

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decomposed by mineral acids and by sodium hydroxide solution.

Found: Cu = 13.2, As = 22.6, Cl = 10.9 per cent.

$C_{39}H_{39}As_3Cl_3Cu_2$ requires Cu = 13.1, As = 23.3, Cl = 10.9 per cent.

**Blue Form.**—The brown solution was prepared as before and allowed to stand for an hour. Water was then added until a green solution was obtained, which was allowed to stand overnight. The substance separated in the form of blue crystals having the same melting point as the brown form, and resembling it in its insolubility in all solvents.

Found: Cu = 13.1, As = 22.1, Cl = 10.8 per cent.

$C_{39}H_{39}As_3Cl_3Cu_2$ requires Cu = 13.1, As = 23.3, Cl = 10.9 per cent.

A mixture of the two forms containing a trace of arsine was found to change slowly to the brown form on long standing.

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