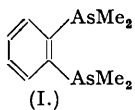


386. *Studies in Co-ordination Chemistry. Part VIII.* The Structure of the Blue and the Brown Cuprous-Cupric Complexes of Methyl-diphenylarsine.*

By R. S. NYHOLM.

The structure of the blue and the brown form of the cuprous-cupric complexes of methyl-diphenylarsine, formerly believed to be geometric isomers with the empirical formula $\text{Cu}_2\text{Cl}_3 \cdot 3\text{AsPh}_2\text{Me}$, has been investigated. The tertiary arsine is shown to be present as the arsine oxide and the empirical formula of the blue form is actually $\text{Cu}_3\text{Cl}_4 \cdot 4\text{AsPh}_2\text{MeO}$. This substance is an electrolyte in nitrobenzene solution, and the structural formula $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_2]_2$ is assigned to it on the basis of its physical and chemical properties. Confirmation of the existence of the complex cupric cation is afforded by the preparation of the compound $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{ClO}_4]_2$. The brown form is shown to contain a small amount of cupric chloride (5–10%), probably present as a polymerised $[\text{CuCl}_3]^-$ anion, which accounts for the difference in colour. The absorption spectra of the blue and the brown form and of the perchlorate complex in nitrobenzene solution have been examined and their similarity is apparent. Conversion of the spectrum of the blue into that of the brown was effected by addition of a trace of chlorine. Conversion of the blue into the brown solid occurs also in the crystalline state by treatment with chlorine. The magnetic susceptibilities of the various compounds have been measured and these support the structures proposed. The properties of the compounds are discussed, and the observations of previous workers interpreted.

In Part VII of this series (Kabesh and Nyholm, *J.*, 1951, 38) the complexes of copper salts with the chelate group *o*-phenylenebisdimethylarsine (I) were described. Salt-like cuprous complexes of the types $[\text{Cu}(\text{diarsine})_2]\text{X}$ and $[\text{Cu}(\text{diarsine})_2][\text{CuY}_2]$ ($\text{X} = \text{Br}, \text{I}, \text{ClO}_4$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}$) were described but all attempts to obtain compounds in which the ditertiary arsine was co-ordinated directly to a cupric atom were unsuccessful. Reduction always occurred to give a complex of univalent copper. Furthermore, no derivatives containing a

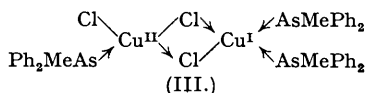
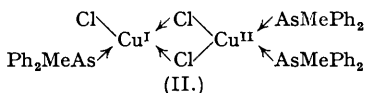


halogen bridge of the type $\text{>Cu} \begin{array}{c} \swarrow \text{Cl} \searrow \\ \nearrow \text{Cl} \nwarrow \end{array} \text{Cu} \text{<}$ could be isolated. These two

observations led to the reinvestigation of the structures of two cuprous-cupric complexes of methyl-diphenylarsine which had previously been formulated as non-electrolytes with structural formulæ involving both a chlorine bridge between a cuprous and a cupric atom and the co-ordination of the tertiary arsine directly to the cupric atom, as in (II) and (III) (Mellor, Burrows, and Morris, *Nature*, 1938, **141**, 414). In the light of the above work

* For Part VII, see *J.*, 1951, 38.

the physical properties of these compounds suggested salt-like structures rather than those shown in (II) and (III).



The compounds were isolated by Burrows and Sandford (*J. Proc. Roy. Soc. N.S.W.*, 1935, **69**, 182) when investigating the cuprous complexes of methyldiphenylarsine. They observed that the colourless solution obtained by the action of excess of arsine on a hot solution of cupric chloride gradually becomes blue when left exposed to the air for 24 hours, brown crystals being deposited. The addition of a little water to the clear solution immediately after reduction yielded blue crystals instead. The melting point of both forms was given as 245°, and on the basis of their analyses (Table I) the empirical formula $\text{Cu}_2\text{Cl}_3, 3\text{AsPh}_2\text{Me}$ was assigned to both. It was stated that both forms were practically insoluble in all solvents and were decomposed by mineral acids or sodium hydroxide solution. Salt-like structures such as $[\text{Cu}(\text{AsPh}_2\text{Me})_2][\text{CuCl}_3, \text{AsPh}_2\text{Me}]$ were suggested to account for the isomerism. A corresponding cuprous-cupric bromide was also described.

TABLE I.

Analyses of blue and brown forms.

Ref.	Compound.	C, %.	H, %.	Cl, %.	Cu, %.	As, %.
Burrows and Sandford	Blue form	—	—	10·8	13·1	22·1
	Brown form	—	—	10·9	13·2	22·6
Mellor and Craig	Blue form (from aq. EtOH)	45·1	4·1	10·5	13·9	22·1
	Blue form (from PhNO_2)	44·7	4·0	10·5	13·8	22·0
This investigation	Brown form	44·9	3·9	10·6	13·9	22·3
	Blue form (mean of 5 analyses)	45·75	3·98	10·38	14·1	—
Calc. for	Brown form (mean of 4 analyses)	45·2	3·95	10·65	14·2	—
	$\text{Cu}_2\text{Cl}_3, 3\text{AsPh}_2\text{Me}$	48·8	4·0	10·9	13·1	23·3
Calc. for	$\text{Cu}_3\text{Cl}_4, 4\text{AsPh}_2\text{MeO}$	45·55	3·8	10·35	13·9	21·9

Later, Mellor, Burrows, and Morris (*loc. cit.*) showed that the molecular weights of the blue and the brown form in freezing nitrobenzene were 786 and 878 respectively (Calc. : 966). The low molecular weights were attributed to partial dissociation of the bridge in each case, but the attempted fission of the bridge with various co-ordinating agents such as pyridine gave inconclusive results. The structures which they suggested, (II) and (III), involve one square cupric atom and one tetrahedral cuprous atom in each case.

Mellor and Craig (*J. Proc. Roy. Soc. N.S.W.*, 1941, **75**, 27) showed that the magnetic moments of both forms were consistent with the assumption that part only of the copper was bivalent. They obtained a moment of 1·78 Bohr magnetons for the brown and between 1·5 and 1·8 B.M. for the blue, assuming only one cupric atom per molecule. Attention was drawn to the low moment of some blue specimens but no explanation could be advanced. Complete analyses were carried out on both forms, results being given in Table I. The low carbon values obtained were commented upon and the possible presence of methyldiphenylarsine oxide in both forms was considered but no evidence for its presence was obtained at that time. These workers concluded that further work was needed before structures (II) and (III) could be regarded as established.

Experience with other tertiary arsine complexes, notably the compound $[\text{FeCl}_2(\text{diarsine})_2][\text{FeCl}_4]$ (Part III, *J.*, 1950, 851) suggested that the properties of both the blue and the brown forms were more consistent with their formulation as salts rather than as non-electrolytes. Both forms are soluble in nitrobenzene and nitromethane but are quite insoluble in both benzene and chloroform. Although solubility in the first *per se* does not necessarily indicate a salt-like structure, yet it is highly significant when taken in conjunction with the insolubility of the compounds in chloroform and benzene. Also, the ready solubility of compounds such as $\text{CuCl}, 3\text{AsPh}_2\text{Me}$ (see p. 1772) in chloroform made it difficult to see why $\text{Cu}_2\text{Cl}_3, 3\text{AsPh}_2\text{Me}$, if a non-electrolyte, should not be at least slightly soluble in chloroform.

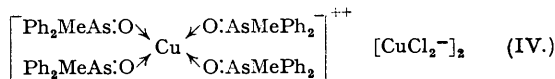
In view of some doubt as to the formula, several analyses have been carried out, the results being given in Table I. In general, these confirm Mellor and Craig's results. The analysis of the brown is almost the same as that of the blue compound except that the carbon is slightly lower and the chlorine slightly higher in the former. The significance of this is discussed later, but attention is directed first to the analysis of the blue form. Although the ratio $\text{Cl} : \text{AsPh}_2\text{Me}$ is

1 : 1, the ratio of Cl : Cu is 4 : 3 rather than 3 : 2 as originally proposed. Furthermore, all the carbon being assumed to be present as the tertiary arsine, the analyses add up to 95% only, the 5% difference being well outside experimental error; this suggested that oxygen was present in both forms. One oxygen atom for each arsine molecule gives the correct analysis for the blue form. This oxygen could be present either as water or as the compound methyldiphenylarsine oxide, AsPh_2MeO . The presence of water appears to be excluded partly by the hydrogen analyses but more especially by the work of Mellor and Craig (*loc. cit.*) who showed that the blue form did not change in weight when left over phosphoric oxide *in vacuo* for two weeks. Also, in this investigation it has been found that even if the blue form is melted and kept molten at 260° for several seconds the decrease in weight is only a fraction of the 5% deficiency.

Chemical tests indicate that the arsine oxide rather than the arsine is present. It has been observed that complexes of univalent copper with methyldiphenylarsine, *e.g.*, $\text{CuCl}_3\text{AsPh}_2\text{Me}$, evolve the tertiary arsine readily when heated with sodium hydroxide solution. In contrast, however, no odour of methyldiphenylarsine was observed when either the blue form or the brown form was heated with this reagent. Attempts were then made to formulate the compound on the assumption that methyldiphenylarsine oxide was present, attention being directed first to the blue form since its analysis fits the formula $\text{Cu}_3\text{Cl}_4 \cdot 4\text{AsPh}_2\text{MeO}$ almost exactly.

Although co-ordination compounds of tertiary phosphine oxides have been described by Pickard and Kenyon (*Proc.*, 1906, 22, 42), *e.g.*, $\text{M}^{\text{II}}\text{X}_2 \cdot 2\text{R}_3\text{PO}$ where $\text{M}^{\text{II}}\text{X}_2 = \text{ZnCl}_2, \text{ZnI}_2, \text{CdI}_2, \text{HgCl}_2, \text{or CoCl}_2$, and the compound $\text{CuCl}_2 \cdot \text{PET}_3\text{O}$, yet no complexes of tertiary arsine oxides with metal salts have been described before. If the structures $\text{R}_3\text{P}=\text{O}$ and $\text{R}_3\text{As}=\text{O}$ be assumed to make a major contribution to the electronic formulæ of these substances (Hunter, Phillips, and Sutton, *J.*, 1945, 146) then a formal similarity to monoketones $\text{R}_2\text{C}=\text{O}$ is apparent. The latter form many co-ordination compounds such as $\text{SnCl}_4 \cdot 2\text{COR}_2$ with metallic salts (Sidgwick, "The Chemical Elements," Oxford, 1945, p. 614).

The tertiary arsine oxide might be co-ordinated to the cupric or the cuprous atom, the most likely structures in the two cases being $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_2]_2$ and $[\text{Cu}(\text{AsPh}_2\text{MeO})_2]_2[\text{CuCl}_4]$. In view of the reluctance of univalent copper to co-ordinate with oxygen, it is more likely that the arsine oxide would be attached to a cupric atom, which has a strong affinity for oxygen (Sidgwick, *op. cit.*, pp. 141, 168). Hence the first formula was considered more probable, the colour of the blue form lending some support to this idea. One might expect the complex cupric cation to be blue, whereas the $[\text{CuCl}_2]^-$ anion is colourless (see Part VII, *J.*, 1951, 38). Furthermore, the $[\text{CuCl}_4]^{--}$ anion is brownish-yellow and the blue colour would be difficult to account for if this ion were present (Sidgwick, *op. cit.*, p. 162). Experiments were then designed to confirm the formulation of the blue form shown in (IV).



The molecular conductivities of the blue and the brown form in nitrobenzene solution provide strong support for salt-like structures (see Table II). The molecular conductivity of

TABLE II.

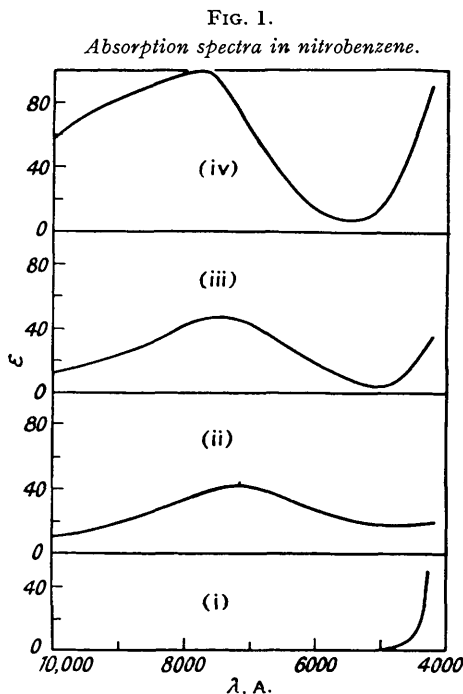
Molecular conductivity of various diphenylmethylarsine oxide complexes of copper. .
(Nitrobenzene solvent.)

Compound.	Molar concentration.	Molecular conductivity at 25° .
Blue form	2.57×10^{-3}	48.8 mho
Brown form	2.75×10^{-3}	44.7 mho
$[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{ClO}_4]_2$	4.17×10^{-3}	38.6 mho
$[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_3]_2$	3.63×10^{-3}	21.3 mho

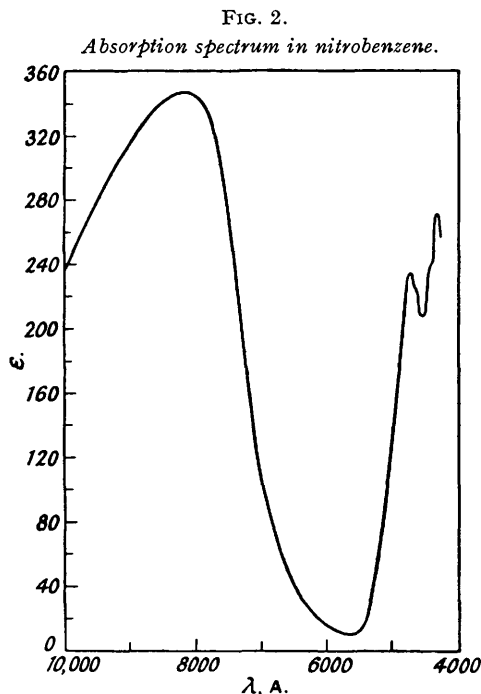
the blue form is considerably higher than that of uni-univalent electrolytes in nitrobenzene at about the same molar concentration; for the latter, values between 20 and 30 mho are found as a rule (see Part VII). Although it would be unwise to speculate too freely on the number of ions indicated by the molecular conductivity obtained, nevertheless it would appear that at least two and probably three are present. In dilute aqueous solution uni-univalent electrolytes have molecular conductivities of the order of 100—130 mho and the corresponding value for uni-bivalent electrolytes is about twice this figure. The high conductivity in nitrobenzene explains the molecular weight obtained by Mellor, Burrows, and Morris for the blue form (786); this arises from considerable ionisation of the compound $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_2]_2$, the molecular

weight of which is 1372.5. The limiting value of 454 would be expected only at very high dilutions.

Evidence for the existence of the cation $[\text{Cu}(\text{AsPh}_2\text{MeO})_4]^{++}$ was provided by the preparation of the blue compound tetrakis(methyldiphenylarsine oxide)copper(II) perchlorate, $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{ClO}_4]_2$. This crystallised from a solution containing the arsine oxide and copper sulphate to which perchloric acid had been added. The compound is a good conductor in nitrobenzene solution (see Table II). Like the blue and the brown form it is decomposed by hydrochloric acid.



- (i) $[\text{Cu}(\text{diarsine})_2][\text{CuCl}_2]$, $9.43 \times 10^{-3}\text{M}$.
 (ii) $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{ClO}_4]_2$, $7.15 \times 10^{-3}\text{M}$.
 (iii) Blue form, $8.0 \times 10^{-3}\text{M}$.
 (iv) Brown form, $7.4 \times 10^{-3}\text{M}$.



Chlorinated blue form, $8.0 \times 10^{-3}\text{M}$.

Results of magnetic susceptibility measurements on the blue and the brown form and on the perchlorate are given in Table III. Owing to the large diamagnetic correction the accuracy of the magnetic moments is limited but they show that the blue form contains one cupric atom per molecule. The moments of the blue form and of the perchlorate are practically identical. The

TABLE III.

Magnetic susceptibility measurements (20°).

Compound.	$\chi_g \times 10^{-6}$.	$\chi_M \times 10^{-6}$.	Diamag. correction.	$\chi_{\text{corr.}} \times 10^{-6}$.	μ (B.M.).
Brown form (Mean of 4 determinations) ...	0.92 ₆	1265	721	1986	2.1 ₇
Blue form (Mean of 3 determinations) ...	0.72 ₂	990	721	1711	2.0 ₇
$[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{ClO}_4]_2$	0.81 ₆	1060	705	1765	2.0 ₄
* $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_2]$	2.88	4170	761	4931	1.9 ₅

* This compound contains three cupric atoms per molecule, the others contain only one. The moment is calculated per cupric atom.

slightly higher moment of the brown form will be discussed later and it will be shown that this can be explained by the presence of a small amount of extra cupric chloride in the anion.

The absorption spectra of the various compounds in nitrobenzene solution are shown in Figs. 1—3. The spectra of the blue form (curve iii) and the perchlorate complex (Curve ii) are very similar between 5000 and 10,000 A., but in addition the blue form begins to absorb again at

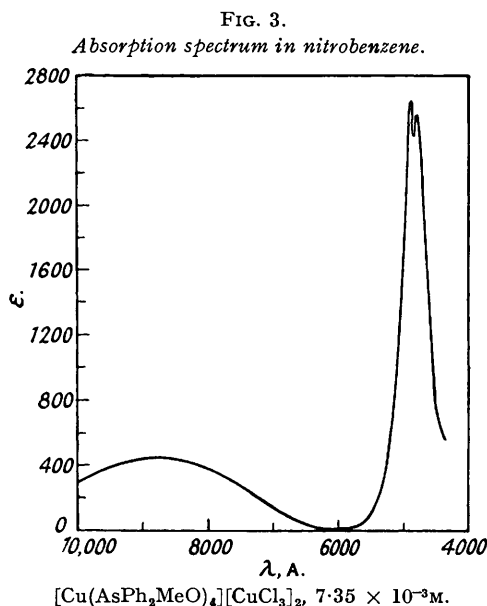
about 4500 Å. In order to compare these spectra with that of a compound containing the $[\text{CuCl}_2]^-$ anion, the spectrum of the complex $[\text{Cu}(\text{diarsine})_2][\text{CuCl}_2]$ (Curve i) was measured (see Part VII). Like the blue form, this substance begins to absorb at wave-lengths below 5000 Å.; presumably this could be attributed to the $[\text{CuCl}_2]^-$ anion. The solution of the blue form (Curve iii) was then treated with a bubble of chlorine; a yellow colour developed and the spectrum of the resulting solution is shown in Fig. 2. There is strong absorption near 8000 Å. and in the region 4000—5000 Å. These absorption bands are apparently due to cuprichloride anions of the types $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{--}$ since similar absorption bands were reported by Bjerrum (*Kgl. Danske Videnskab Selsk., Mat.-fys. Medd.*, 1946, 22, No. 18) for cuprichloride complexes in water. The absorption spectrum of the brown form is given in Curve iv, and comparison of this with Curve iii and Fig. 2 shows that the absorption spectrum of the brown form lies *inter-mediate*ly between these of the blue form and of its oxidation product, being in fact closer to the blue. The most obvious explanation for this is that the brown form contains the same cation as the blue but that the anion is not simply the $(\text{CuCl}_2)^-$ ion but has undergone partial oxidation; *i.e.*, there is a small excess of cupric chloride present probably as a (polymerised) $[\text{CuCl}_3]^-$ anion. This hypothesis provides a satisfactory explanation of the properties of the brown form and of its relationship with the blue. The absorption spectrum of the fully chlorinated compound, obtained by treatment of the solid blue form with chlorine gas, is shown in Curve v. This curve is very similar to Fig. 2 but the absorption is more marked in the 4500—5000 Å. region. It is noteworthy that the wave-lengths of the absorption maxima gradually increase as the concentration of the cuprichloride anion increases.

The intensity of colour of the brown form is remarkable in view of the fact that it is caused by less than 5% oxidation of the blue anion. Recent work (McConnell and Davidson, *J. Amer. Chem. Soc.*, 1950, 72, 3168) may be relevant. The absorption between 4000 and 6000 Å. of solutions of mixtures of cuprous and cupric chlorides is greater than that which might be predicted from Beer's law and the absorption of the individual components. The above workers propose a type of optical interaction in order to explain this; a similar phenomenon may occur here.

Without an X-ray crystallographic examination the manner in which the extra cupric chloride is present in the anion must remain uncertain. The presence of the $[\text{CuCl}_4]^{--}$ anion is excluded by the analysis required for the compound $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_4]$, and it is more likely that polymerised $[\text{CuCl}_3]^-$ anions are formed. Wells (*J.*, 1947, 1662) has shown that the garnet-red crystals of CsCuCl_3 actually contain spiral chains of CuCl_4 groups, some chlorine atoms being shared to complete the four-fold co-ordination. Prolonged treatment of the blue form with chlorine gives a reddish-brown compound, m. p. 127°, of the formula $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_3]_2$. This substance is readily soluble in nitrobenzene, in which it is an electrolyte (see Table II), and dissolves in water with decomposition. The gram susceptibility increases from 0.7 for the blue form to 2.88 and the magnetic moment per copper atom (1.95 B.M.) shows that all the copper is bivalent.

As mentioned previously, whereas the brown form is obtained from an alcoholic solution, water must be added to obtain the blue. Also, the addition of a few drops of concentrated hydrochloric acid favours the formation of the brown, even though some water is present. The addition of too much hydrochloric acid is to be avoided, otherwise no crystals appear at all, both forms being decomposed by mineral acid. In short, conditions which favour the formation of cuprichloride anions, *e.g.*, presence of hydrochloric acid or lithium chloride or the absence of water, favour the formation of the brown form. On the other hand, the opposite conditions favour the formation of the blue form since the equilibrium $[\text{CuCl}_3]^- + 4\text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{++} + 3\text{Cl}^-$ is thereby displaced to the right.

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Earlier workers have noted that on long storage the blue form becomes brown. On the formula proposed this could occur simply by partial oxidation of the $[\text{CuCl}_2]^-$ anion. In confirmation of this, it has been observed that when the solid blue form comes into contact with even a trace of chlorine it becomes brown instantly. Further chlorination gives the compound $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_3]_2$ discussed previously. The apparent "conversion" of the brown form into the blue brown is carried out by fractionally precipitating a solution of the former in nitrobenzene with light petroleum. The blue form separates first. In effect this is a separation of the blue form from a small amount of the cuprichloride complex, the latter being the more soluble.

Both the analyses and the magnetic measurements are consistent with the explanation advanced for the constitution of the brown form. As shown in Table I the brown form contains a slightly higher proportion of chlorine than the blue. From these chlorine analyses it may be calculated that the brown form contains about 5—10% more bivalent copper than the blue; the actual proportion is variable and will depend upon the conditions used during the preparation. The higher magnetic moment of the brown form follows as a direct consequence of the higher cupric content. The magnetic moment of 2.2 B.M. (see Table III) may be taken to mean that the cupric content is slightly higher than that calculated for the formula $\text{Cu}_3\text{Cl}_4 \cdot 4\text{AsPh}_2\text{MeO}$. Since the amount of excess cupric chloride is variable the magnetic susceptibility is variable also.

The melting points of these two forms are variable also, depending upon the composition. Generally speaking, as the chlorine content increases from 10.35%, so the melting point falls from 260° to about 245°. The highest melting point recorded was 260° for a recrystallised specimen of the blue form, and the lowest was 244° for an unrecrystallised specimen of the brown.

One puzzling observation by previous workers calls for comment. Mellor and Craig (*loc. cit.*) mention some unpublished experiments by Mellor and Morris dealing with the action of gaseous ammonia on the blue and the brown form. The latter stated that treatment of the residue from the ammonia treatment with methyl iodide yielded the methiodide of the tertiary arsine. Since it is not easy to see how methyl iodide could react with the arsine oxide, this observation is difficult to understand unless some reduction of the arsine oxide occurs during the ammonia treatment. Since a reducing agent, $[\text{Cu}(\text{NH}_3)_2]\text{Cl}$, can be formed during the reaction, it is suggested that this may reduce some of the arsine oxide to the tertiary arsine which then reacts with the methyl iodide to give the methiodide as stated.

Because it was at first thought that cations of the types $[\text{Cu}(\text{AsPh}_2\text{Me})_4]^+$ and $[\text{Cu}(\text{AsPh}_2\text{Me})_2]^+$ might be involved in the structures of these compounds, the cuprous complexes of methyl-diphenylarsine have been examined in more detail; the results of this investigation will be discussed in a later part of this series. Complexes containing 1, 2, 3, and 4 molecules of tertiary arsine to one molecule of cuprous halide have been isolated, and their structures investigated. The cation $[\text{Cu}(\text{AsPh}_2\text{Me})_4]^+$ occurs in compounds of the type $[\text{Cu}(\text{AsPh}_2\text{Me})_4]\text{X}$, where $\text{X} = \text{I}, \text{ClO}_4$. Compounds with the general formula $[\text{CuX}_3\text{AsPh}_2\text{Me}]^0$ are non-electrolytes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), and the structure of compounds containing 2 molecules of the tertiary arsine is still being examined. The demonstration here that the blue and the brown form involve co-ordination of the cupric atom with a tertiary arsine oxide and not with a tertiary arsine means that there are now no examples known which involve the co-ordination of a cupric atom directly to a tertiary arsine.

The structure of the cuprous-cupric bromide complex described by Burrows and Sandford (*loc. cit.*) may also be understood. The compound was made by treating the colourless solution obtained by the action of methyl-diphenylarsine on an alcoholic solution of cupric bromide with excess of cupric bromide until a permanent brown colour was obtained; on storage, the solution deposited greenish-black crystals melting at 202°. Table IV gives the analysis obtained by the above workers together with those calculated for other possible compounds.

The deep green colour suggests the presence of some cupribromide anion, and since the experimental figures are clearly incompatible with the formula $\text{Cu}_2\text{Cl}_3 \cdot 3\text{AsPh}_2\text{Me}$, as judged by

TABLE IV.

Analyses of cuprous-cupric bromide complexes.

Compound.	Br, %.	Cu, %.	As, %.
$\text{Cu}_2\text{Cl}_3 \cdot 3\text{AsPh}_2\text{Me}$	21.9	11.5	20.5
$[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuBr}_2]_2$	20.65	12.35	19.35
$[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuBr}_3]_2$	23.1	11.0	17.3
$[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuBr}_4]$	21.5	8.5	20.2
Burrows and Sandford (Found)	21.5	11.5	19.1

value for arsenic, the compound appears to be a mixture of $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuBr}_2]_2$ and $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuBr}_3]_2$. For a mixture of 70% of the former and 30% of the latter the analysis is: Br, 21.4; Cu, 11.9; As, 19.3%, in fair agreement with the figures obtained. The compound is thus formally analogous with the brown chloride isomer.

The potentialities of the oxides of tertiary amines, phosphines, and arsines as ligands are being examined. Since in all cases co-ordination to the metal would be through the fairly electronegative oxygen atom, the elements most likely to co-ordinate are those with a strong affinity for oxygen, *e.g.*, chromium and aluminium. If it is assumed that the double bond structure is important in the cases of the tertiary phosphine and arsine oxides, then they may show a marked difference in behaviour from the tertiary amine oxides for which the single-bond structure only is possible. Tertiary amine oxides would form with metals structures of the type $\text{R}_3\text{N} \rightarrow \text{O} \rightarrow \text{M}$. In general, the donor capacity of an atom seems to diminish as the number of lone pairs of electrons available increases, *e.g.*, $\text{NH}_3 > \text{H}_2\text{O} > \text{HF}$; $\text{Et}_3\text{P} > \text{Et}_2\text{S} > \text{EtCl}$. In view of this, one might expect R_3PO and R_3AsO to be better ligands than R_3NO . However, the oxygen atom in R_3NO will be more negative than in the other two oxides and this may increase the donor capacity of the former. Experiments are being carried out to compare these oxides. It will also be of interest to examine the behaviour of the corresponding sulphides R_3PS and R_3AsS .

EXPERIMENTAL.

Preparation of the Blue and the Brown Compound.—Earlier workers have given details of the preparation of these compounds and the following experiments are recorded only to show the effect of different conditions upon the product isolated.

Effect of hydrochloric acid, water, and lithium chloride. Anhydrous cupric chloride (1.0 g.) was dissolved in alcohol (45 ml.), and the solution heated to boiling, filtered and treated whilst hot with methyl-diphenylarsine (1.8 g.) dissolved in alcohol (20 ml.), a colourless solution being obtained. This solution was divided into three equal parts A, B, and C. Part A was treated with 10*N*-hydrochloric acid (0.5 ml.) in alcohol (5 ml.), and the solution heated to boiling and left in a 100-ml. beaker freely exposed to the air; after 24 hours the solution had become blue but no crystals appeared, even on long storage. Part B was treated with distilled water (5 ml.) only, heated to boiling, and then set aside as above; after 24 hours blue crystals (0.4 g.), *m. p.* 256°, were found on the bottom of the beaker. Around the top of the solution, in that area from which a small amount of evaporation had occurred, were observed some very small brown crystals in addition. No doubt these arise from local concentration effects and the greater accessibility of air. Part C was treated with lithium chloride (0.5 g.) dissolved in alcohol-water (5 ml.; 1 : 1), and the solution heated to boiling and set aside. In spite of the presence of water and the absence of acid, brown crystals (0.33 g.) were obtained after 24 hours; these had *m. p.* 253°.

Chlorination of the blue form. Chlorine was passed for several hours over the finely powdered blue isomer (0.207 g.), the colour changing to a deep reddish-brown. After drying in a vacuum desiccator the increase in weight was 5.0%; that calculated for complete oxidation to $[\text{Cu}(\text{AsPh}_2\text{MeO})_4][\text{CuCl}_3]_2$ is 5.2%. This salt contained C, 43.2; H, 3.7; Cl, 14.9 ($\text{C}_{52}\text{H}_{52}\text{O}_4\text{Cl}_6\text{As}_4\text{Cu}_3$ requires C, 43.2; H, 3.6; Cl, 14.75%).

Tetrakis(methyldiphenylarsine oxide)copper(II) Perchlorate.—This was prepared both by the action of hydrogen peroxide on the tertiary arsine and also by chlorine oxidation of the latter. (a) Copper sulphate pentahydrate (0.25 g.), dissolved in distilled water (20 ml.), was treated with methyldiphenylarsine (1.0 g.) in alcohol (20 ml.), and the solution heated on the water-bath with constant addition of 30% hydrogen peroxide. After 3 hours' heating, excess of sodium perchlorate solution and hydrogen peroxide were added, and the mixture left for 24 hours. Blue crystals (1.0 g.) of the required perchlorate were obtained which were filtered off, washed with alcohol, and dried *in vacuo* [Found: C, 47.7; H, 4.2; Cl (Carius), 4.7. $\text{C}_{52}\text{H}_{52}\text{As}_4\text{O}_{12}\text{Cl}_4\text{Cu}$ requires C, 47.7; H, 4.0; Cl, 5.4; Cu, 5.05%]. No precipitate is obtained when the compound is heated with nitric acid and silver nitrate solution, or with nitric acid and barium chloride solution, showing that both chloride ion and sulphate ion are absent. On treatment with sodium hydroxide solution a blue precipitate is formed first, being readily soluble in excess of the alkali to a blue solution, probably owing to the formation of a salt in which the tertiary arsine oxide behaves as a dibasic acid, *i.e.*, $\text{Na}_2[\text{Cu}(\text{O} \rightarrow \text{AsMePh}_2)_2]$. However, the nature of this solution was not investigated further.

(b) Methyldiphenylarsine (2.0 g.), dissolved in alcohol (50 ml.), was treated with excess of chlorine gas, the solution evaporated to dryness, and the residue boiled with sodium hydroxide to effect hydrolysis of the arsine dichloride. The solution was then treated with a little excess of chlorine to ensure that oxidation was complete. After evaporation to dryness, the residue was dissolved in distilled water, and copper sulphate pentahydrate (0.5 g.) added. Owing to the alkalinity, a black precipitate of copper oxide was formed but this dissolved on the addition of excess of perchloric acid. A little chlorine was evolved at this stage and then on heating on the water-bath a pale blue precipitate appeared. After 3 hours' heating, the compound (2.1 g.) was filtered off, well washed with alcohol and water, and dried *in vacuo* (Found: C, 47.4; H, 4.4; Cu, 4.9%). For magnetic susceptibility see Table III. On heating, the compound decomposed explosively above 200°.

Oxidation of the Blue Form with Potassium Dichromate.—By dissolving the blue form in 4*N*-hydrochloric acid and titrating it potentiometrically with *N*/20-potassium dichromate, it is possible to establish

that two-thirds of the copper is present in the cuprous state. Owing to the ease with which the compound HCuCl_2 in solution absorbs oxygen, carbon dioxide must be passed throughout the titration. The blue isomer (0.4606 g.) was dissolved in hot, air-free 4*N*-hydrochloric acid (70 ml.), carbon dioxide being passed into the solution. *N*/20-Potassium dichromate (20 ml.) was added to the warm solution, followed by solid ferrous ammonium sulphate (0.4034 g.). The excess of the latter was then titrated potentiometrically with *N*/20-potassium dichromate, a titre of 13.0 ml. being obtained. The calculated titre, it being assumed that the formula of the blue substance is $[\text{Cu}(\text{Ph}_2\text{MeAsO})_4][\text{CuCl}_2]_2$, is 13.4 ml.

Magnetic Susceptibility Measurements.—The Gouy method was used. For details see Part III (*J.*, 1950, 851).

Absorption spectra were determined with a Unicam Spectrophotometer, 1-cm. glass cells being used.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

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