

8. *Studies in Co-ordination Chemistry. Part VII. Complexes of Univalent Copper with a (Ditertiary Arsine).*

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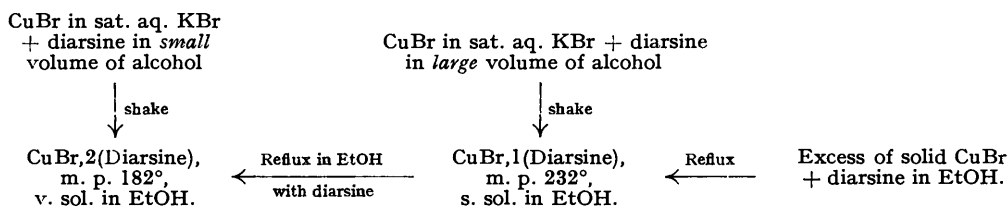
The complexes formed by univalent copper salts with the di(tertiary arsine) chelate group, *o*-phenylenebisdimethylarsine, have been investigated. Co-ordination compounds have been isolated of the empirical formulæ $\text{CuX}_2(\text{Diarsine})$ and $\text{CuX}(\text{Diarsine})$, where X = Cl, Br, and I. Compounds of the first type are more soluble in alcohol than those of the second type; they form electrolytically conducting solutions in nitrobenzene and give rise to a perchlorate of the formula $[\text{Cu}(\text{Diarsine})_2]\text{ClO}_4$; whence it is concluded that they are salts of four-covalent copper of the type $[\text{Cu}(\text{Diarsine})_2]\text{X}$. Compounds of the second type are considered to be salts also, with the formula $[\text{Cu}(\text{Diarsine})_2][\text{CuX}_2]$, and evidence in support of this formulation rather than a halogen-bridge structure is presented. All these cuprous complexes are diamagnetic. Attempts to prepare compounds in which the di(tertiary arsine) was co-ordinated to a cupric atom were unsuccessful.

IN earlier papers in this series (Nyholm, *J.*, 1950, 851, 857, 2061, 2071), the stereochemistry of the complex compounds formed by the chelate group *o*-phenylenebisdimethylarsine (I) with

iron, rhodium, nickel, and cobalt halides was investigated. Several of these showed marked stability, with strong covalent bonds, and since stabilisation of the higher valency state was observed in certain cases it was decided to study the behaviour of this chelate group with copper. Much work has been done on the complexes of copper with tertiary arsines but none has been reported on those with tertiary arsine chelate groups. Mann and Purdie (*J.*, 1936, 1503) described complexes of univalent copper with trialkyl-arsines and -phosphines and proved that tetramers of the type $[\text{CuI,AsEt}_3]_4$ were formed. The crystal structure of the triethylarsine compound was studied by Wells (*Z. Krist.*, 1937, **94**, 447), who showed that each cuprous atom was tetrahedrally co-ordinated; in addition to one covalently bound iodine atom, each copper atom was attached to two other iodine atoms, presumably by a co-ordinate link, and the triethylarsine molecule completed the four-fold co-ordination. The molecular weights of these compounds in various organic solvents showed four-fold association. Using methyldiphenylarsine and dimethylphenylarsine, Burrows and Sandford (*J. Proc. Roy. Soc. N.S.W.*, 1935, **69**, 182) isolated compounds with the formulæ $\text{CuX,AsR}_2\text{R}'$ and $\text{CuX}_2\text{AsR}_2\text{R}'$, where X = Cl, Br, I, and NO_3 . They found that several compounds of the type $\text{CuX,AsR}_2\text{R}'$ were monomeric in freezing benzene solution. These results suggest either that the compounds are tetramers which are considerably dissociated, or that the copper is two-covalent. The molecular complexity of the compounds with two molecules of arsine to each copper atom was not investigated. A co-ordination number of two for univalent copper is unusual but there is other evidence to show that univalent copper may behave like univalent silver and gold in this respect (Sidgwick, "The Chemical Elements," Oxford, 1950, p. 143 *et seq.*). However, apart from the X-ray crystal structure determination of cuprous oxide (Niggli, *Z. Krist.*, 1922, **57**, 253; see also Wells, "Structural Inorganic Chemistry," Oxford, 1945, p. 505), the evidence for a co-ordination number of two for univalent copper in crystalline compounds is slight.

No cupric complexes of tertiary arsines were described by Mann and his co-workers, but Burrows and Sandford (*loc. cit.*) described two isomeric cupric-cuprous complexes to which the formula $\text{Cu}_2\text{Cl}_3\cdot 3\text{AsPh}_2\text{Me}$ was ascribed. Halogen-bridge structures were suggested by Mellor, Burrows, and Morris (*Nature*, 1938, **141**, 414) to account for the isomerism, but the formulæ were difficult to establish with finality. As shown later, the ease with which bivalent copper is reduced by *tert.*-arsines makes it rather unlikely that the arsine is co-ordinated to the cupric atom and the latter is possibly present as a cuprichloride ion. The formulation of these isomers and the structures of other cuprous complexes of methyldiphenylarsine are being investigated. In the present investigation no cupric complexes with *o*-phenylenebisdimethylarsine were obtained; oxidation usually led to perhalides or complexes of indefinite composition.

The chelate group used here co-ordinated so readily with univalent copper that preparation of the compounds was carried out simply by shaking an aqueous solution of the cuprous halide, dissolved in excess of the corresponding potassium halide, with the required amount of the chelating compound dissolved in alcohol. The reaction was very much affected by the amount of alcohol used: a very small amount gave $\text{CuBr}_2(\text{Diarsine})$ and $\text{CuI}_2(\text{Diarsine})$, but a considerable amount afforded $\text{CuBr}(\text{Diarsine})$ and $\text{CuI}(\text{Diarsine})$. The chloride, $\text{CuCl}(\text{Diarsine})$, was prepared in like manner, but isolation of $\text{CuCl}_2(\text{Diarsine})$ was difficult owing to its high solubility in aqueous alcohol; furthermore, it decomposed readily when washed with alcohol or water, giving the di(tertiary arsine) and cuprous chloride. The preparation of a compound of the type $\text{CuX}(\text{Diarsine})$ (where X = halogen) may be effected also by refluxing an alcoholic solution of the di(tertiary arsine) with excess of the cuprous halide, the required compound crystallising out on cooling. This method of preparation was particularly suited to the preparation of the compound $\text{CuI}(\text{Diarsine})$. The relationships between the two types of compound are illustrated by reference to the two bromides:



The structural formulæ of these compounds were established by a combination of chemical and physical methods. It seemed likely that the compounds containing two molecules of

the chelate group were salts of the type $[\text{Cu}(\text{Diarsine})_2]\text{Br}$. Treatment of an aqueous-alcoholic or acetone solution of these compounds with silver nitrate gave a precipitate of silver bromide or iodide instantly, followed by a black precipitate of silver owing to reduction of excess of silver ion by the cuprous complex. This suggested that the halogen was ionised. Treatment of an aqueous-alcoholic solution of the complexes with perchloric acid gave a compound of the formula $[\text{Cu}(\text{Diarsine})_2]\text{ClO}_4$ at once. Confirmation of the salt-like character of these compounds is provided by their molecular weights and conductivities in nitrobenzene solution. The molecular weights observed are a little over half the formula weight, which is the result expected for almost complete dissociation into two ions. The molecular weights in benzene and chloroform will be discussed later. The conductivities of the bromide, iodide, and perchlorate in nitrobenzene solution were next measured, and these showed that ions were present. In the following table are shown the molecular conductivities (Λ) of several of the compounds investigated at concentrations of $m/100$ or less in nitrobenzene solution. For the bromide, iodide, and perchlorate the molecular conductivity is about 20–30 mho, and values similar to these have been observed by other workers for the molecular conductivities of uni-univalent electrolytes in nitrobenzene; *e.g.*, Foss and Gibson (*J.*, 1950, 3063) found that di-2-pyridyl-diethylgold(III) dibromodiethylaurate(III), *i.e.*, $[\text{dipy}, \text{AuEt}_2][\text{AuEt}_2\text{Br}_2]$, a uni-univalent electrolyte, had a molecular conductivity which varied between 26.7 and 24.6 mhos for concentrations between 0.0002 and 0.0028M.

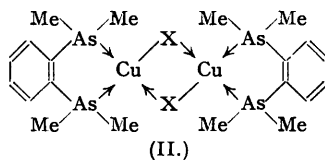
Molecular conductivities of cuprous complexes in nitrobenzene at 25°.

Compound.	M. p.	Concn., m.	Λ , mhos.
$[\text{Cu}(\text{Diarsine})_2]\text{I}$	189°	0.0092	23.3
$[\text{Cu}(\text{Diarsine})_2]\text{Br}$	182	0.0070	24.3
.....	—	0.00175	28.5
$[\text{Cu}(\text{Diarsine})_2][\text{ClO}_4]$	>300 *	0.0069	28.1
$[\text{Cu}(\text{Diarsine})_2][\text{CuCl}_2]$	266	0.00663	29.4
$[\text{Cu}(\text{Diarsine})_2][\text{CuBr}_2]$	232	0.00463	28.8
$[\text{Cu}(\text{Diarsine})_2][\text{CuI}_2]$	174	0.0054	17.9

* Decomposes.

It is evident, therefore, that these compounds are salts in which the four-covalent cuprous atom is co-ordinated to four arsenic atoms. The solubilities of the bromide and iodide, however, call for comment: both dissolved very easily in cold chloroform and are appreciably soluble in hot benzene. Their solubility must be ascribed to the presence of a very large cation containing many organic groups which apparently enables the compound to dissolve with the anion attached. These compounds are similar in this respect to the tetra-alkylammonium halides, certain of which are soluble in chloroform and benzene in which they must dissolve as ion-pairs. The molecular weights of both the iodide and the bromide were measured in boiling chloroform and values a little less than the formula weight were obtained. This also suggests the formation of ion-pairs.

Compounds of the type $\text{CuX}(\text{Diarsine})$ can be formulated in two obvious ways—as salts of the type $[\text{Cu}(\text{Diarsine})_2][\text{CuX}_2]$, or halogen-bridged dimers of type (II). The halogen-bridge hypothesis, although apparently favoured in view of the ease with which such association occurs in $[\text{CuI}, \text{AsEt}_3]_4$, was not supported by the properties of these compounds and was abandoned in favour



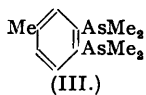
of the alternative structure for the following reasons. If these compounds had the bridged structure (II) one would expect to observe the following properties: (i) a molecular weight in suitable solvents corresponding to twice the formula weight of $\text{CuX}(\text{Diarsine})$; (ii) no electrolytic conductivity in nitrobenzene solution; (iii) it should be possible to split the bridge with a ligand like pyridine or *p*-toluidine to give a compound of the type $\text{CuX}(\text{Diarsine})\text{py}$. The molecular weight of the chloride was determined in both nitrobenzene and acetone and considerable dissociation was observed, but the solubility in benzene was too small to give an accurate molecular weight. This dissociation in acetone and nitrobenzene still might conceivably be due to splitting of the bridge by these solvents, but this is negated by the fact that treatment of a solution of the chloride with both pyridine and *p*-toluidine still gave the original compound on concentration. Most significant of all, however, is the conductivity of the nitrobenzene solution. Solutions of the chloride, bromide, and iodide in nitrobenzene at about 0.005M-concentration all showed molecular conductivities of about 20–30 mhos, indicating two ions (see table). It should be pointed out that the molecular-

weight measurements and the conductivity measurements on these compounds only indicate that in the solvent the solute is present as $[\text{Cu}(\text{Diarsine})_2][\text{CuX}_2]$ and do not establish with certainty that the compounds are not bridged in the solid state. However, it is considered improbable that a change from the bridged to the salt-like structure occurs on dissolution, as it would involve migration of a molecule of the chelate group. Furthermore, none of the properties of these substances suggests that the bridged structure is correct. It was observed that, in all solvents, compounds of the type $[\text{Cu}(\text{Diarsine})_2][\text{CuX}_2]$ were less soluble than those of the type $[\text{Cu}(\text{Diarsine})_2]\text{X}$, a phenomenon apparently associated with the larger anion. A chemical proof that the same action is present in both types of compound is provided by the fact that acetone solutions of both give the same perchlorate, $[\text{Cu}(\text{Diarsine})_2]\text{ClO}_4$, on treatment with perchloric acid. The bromide being taken as an example, the two compounds would be [di-(*o*-phenylenebisdimethylarsine)copper(II)] bromide and dibromocuprite(II).

This and previous work emphasises that care must be taken before assigning halogen-bridged structures to co-ordination complexes. Mann and his co-workers (*J.*, 1936, 873; 1938, 702; 1940, 1209; see also *Ann. Reports*, 1938, 35, 148) have demonstrated conclusively that such bridges occur in the tertiary arsine and phosphine complexes of palladium, mercury, and cadmium, and Chatt (*J.*, 1950, 2301) has shown that bridges are present in platinum complexes of the type $[\text{PtX}_2, \text{PR}_3]_2$. Their use, however, with some other metals simply to complete the usual co-ordination number needs to be proved before being accepted. Recently, Foss and Gibson (*loc. cit.*) showed that certain gold complexes, for which bridged structures were originally proposed, were in fact salts. The presence of large organic groups in the molecules of tertiary arsines and phosphines frequently confers upon a complex solubility in organic solvents which may give the impression that it is a non-electrolyte. In particular, solubility in nitrobenzene must not be taken as indicating that the compound is a non-electrolyte; in Part III (*J.*, 1950, 851) it was shown that ferric complexes of the formula $\text{FeCl}_2(\text{Diarsine})_2$, which were initially thought to be halogen-bridged dimers of octahedrally co-ordinated ferric iron, were in fact salts of the type $[\text{FeCl}_2(\text{Diarsine})_2][\text{FeCl}_4]$. This compound was very soluble in nitrobenzene but was highly dissociated in it. Other reported cases where co-ordination complexes believed to be salts have been formulated as non-electrolytes on the basis of their solubility in organic solvents, are being investigated.

Attempts to obtain cupric complexes with this chelate group, either of the type $[\text{Cu}(\text{Diarsine})_2]\text{X}_2$ or $[\text{CuX}_2(\text{Diarsine})_2]$ (X = univalent anion) have been unsuccessful. When chlorine is added to the compound $[\text{Cu}(\text{Diarsine})_2][\text{CuCl}_2]$ in chloroform solution, the halogen is absorbed readily but the product is of indefinite composition and the manner in which it gradually undergoes change in moist air suggests partial oxidation of the diarsine initially. Addition of bromine to a solution of $(\text{Cu}(\text{Diarsine})_2)\text{Br}$ gave a purple compound which dissolved in both acetone and nitrobenzene to a green solution. It appeared to contain the cupribromide ion but again its indefinite composition made investigation unprofitable. Addition of iodine to the compound $[\text{Cu}(\text{Diarsine})_2]\text{I}$ in chloroform solution gave a yellow crystalline compound which, after recrystallisation from benzene, melted at 155° . Like the monoiodide, this compound was still diamagnetic, showing that bivalent copper was not present. Analysis showed this substance to be very roughly of composition $\text{Cu}(\text{Diarsine})_2\text{I}_3$ and it seemed probable that the two extra iodine atoms were present as an I_3^- ion or had been used to effect partial oxidation of the tertiary arsine. Of the two hypotheses, the former seemed the more likely, but since the compound obviously did not contain bivalent copper, the substance was not further investigated. Attempts to prepare the cupric compound $[\text{Cu}(\text{Diarsine})_2][\text{ClO}_4]_2$ were also unsuccessful. When a cold solution of copper sulphate in aqueous alcoholic perchloric acid was treated with a cold alcoholic solution of the di(tertiary arsine), a brown colour was observed at first but, within a second, spontaneous reduction occurred to give the white crystalline cuprous compound $[\text{Cu}(\text{Diarsine})_2]\text{ClO}_4$. Finally, treatment of the di(tertiary arsine) in alcoholic solution with cupric chloride directly failed to give a compound in which the arsine was co-ordinated to a cupric atom; especially on heating, reduction to form a cuprous complex occurred.

This investigation shows that, whereas iron, cobalt, and nickel were stabilised in their higher valency states with this chelate group, copper on the other hand co-ordinates only in its lower valency state. In this respect, arsenic is somewhat similar to sulphur which also seems preferentially to stabilise the univalent state. The investigation produced no evidence concerning the stereochemistry of these complexes. No doubt the copper atom is tetrahedral, and the diamagnetism is consistent with the use of sp^3 tetrahedral bonds, but this has not been proved for these compounds. It is noteworthy that no case has yet been reported of the resolution of a complex



of univalent copper. The stability of the compounds of the type $[\text{Cu}(\text{Diarsine})_2]\text{Br}$ (or I), suggests that by using an unsymmetrical chelate group such as (III), it might be possible to achieve the optical resolution of a tetrahedral cuprous complex. This is being further examined.

EXPERIMENTAL.

[Di(o-phenylenebisdimethylarsine)copper(I)] Dichlorocuprite(I).—Cuprous chloride (1.5 g.) was dissolved in saturated aqueous potassium chloride solution (50 ml.) containing 1 drop of 10N-hydrochloric acid and the solution was filtered. The filtrate was treated with *o*-phenylenebisdimethylarsine (4.0 g.) in absolute alcohol (6 ml.) and well shaken for 10 minutes in a stoppered flask. A white crystalline precipitate was formed at once and after $\frac{1}{2}$ hour and occasional shaking the solution was filtered and the compound washed many times with saturated potassium chloride solution and dried at the pump. (Washing with water or alcohol at this stage was liable to cause decomposition.) The dry mixture of the complex and potassium chloride was extracted with chloroform in small amounts (total volume 150 ml.), and the chloroform solution filtered and treated with excess of light petroleum (b. p. 60–80°). The white crystalline compound was filtered off and well washed with light petroleum (4.4 g.). After recrystallisation from either acetone or alcohol the *salt* melted at 266° [Found: C, 31.4; H, 4.3; Cl, 9.2%; *M* (ebullioscopic in acetone; 2.73% solution), 405; (cryoscopic in nitrobenzene, 2.03% solution, 448; (4.64% solution), 454). $\text{C}_{20}\text{H}_{32}\text{Cl}_2\text{As}_4\text{Cu}_2$ requires: C, 31.2; H, 4.16; Cl, 9.2%; *M*, 770]. The compound was very soluble in chloroform, bromoform, and nitrobenzene, soluble in acetone and hot alcohol, and slightly soluble in benzene; it was insoluble in water and light petroleum. Treatment of an acetone solution of the complex with aqueous silver nitrate gave a precipitate of silver chloride at once, followed by reduction of excess of silver nitrate to silver. In powder form, the compound was diamagnetic with $\chi = -0.43 \times 10^{-6}$ at 16.5°. For conductivity in nitrobenzene, see the table. When treated with excess of 30% aqueous perchloric acid, an acetone solution of the compound afforded a precipitate of the perchlorate $[\text{Cu}(\text{Diarsine})_2]\text{ClO}_4$.

[Di(o-phenylenebisdimethylarsine)copper(I)] Bromide.—Cuprous bromide (1.5 g.) was dissolved in a saturated aqueous solution of potassium bromide (30 ml.) containing concentrated hydrobromic acid (1 drop), and the solution filtered at once into a stoppered flask. To this was added *o*-phenylenebisdimethylarsine (2.9 g.) dissolved in alcohol (10 ml.). A white precipitate was formed immediately and after the mixture had been shaken for $\frac{1}{2}$ hour was filtered off and washed three times with saturated potassium bromide solution and thrice with distilled water. The *bromide* was too soluble in alcohol to permit of recrystallisation from this solvent, so it was purified by recrystallisation from a mixture of chloroform and light petroleum and obtained as a white crystalline powder (2.7 g.), m. p. 182° [Found: C, 33.6; H, 4.7; Br, 11.2%; *M* (ebullioscopic in acetone; 3.5% solution), 410; (4.2% solution), 430; (in chloroform; 2.5% solution), 632; (cryoscopic in nitrobenzene, 2.92% solution), 435; (4.95% solution), 452. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{BrCu}$ requires C, 33.6; H, 4.48; Br, 11.2%; *M*, 715.5]. The compound was very soluble in chloroform, bromoform, nitrobenzene, alcohol, and acetone, and slightly soluble in benzene, but insoluble in water. An alcoholic solution reacted instantly with silver nitrate solution to give a precipitate of silver bromide followed by silver. In powder form, the compound was diamagnetic with $\chi = -0.50 \times 10^{-6}$ at 23°. For conductivity in nitrobenzene, see table.

[Di(o-phenylenebisdimethylarsine)copper(I)] Dibromocuprite(I).—By a procedure similar to the foregoing $[\text{CuBr}$ (1.0 g.), warm saturated aqueous KBr (30 ml.), hydrobromic acid (1 drop), *o*-phenylenebisdimethylarsine (1.5 g.), alcohol (90 ml.)] a white precipitate was obtained immediately, and after $\frac{1}{2}$ hour's shaking and standing overnight, the *dibromocuprite* was collected, washed once with aqueous alcohol (50%) then with saturated aqueous potassium bromide solution, and finally with water to remove potassium bromide. After recrystallisation from alcohol the compound (1.8 g.) melted at 232° (Found: C, 28.1; H, 3.8; Br, 18.7. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{Br}_2\text{Cu}_2$ requires C, 27.9; H, 3.7; Br, 18.6%); it was very soluble in chloroform, bromoform, and nitrobenzene, and dissolved in acetone and hot alcohol, but was only slightly soluble in benzene. It was insoluble in water and light petroleum. It was diamagnetic, but the exact susceptibility was not determined. For electrolytic conductivity in nitrobenzene solution, see table.

[Di(o-phenylenebisdimethylarsine)copper(I)] Iodide.—By the foregoing procedure $[\text{CuI}$ (1.9 g.), saturated aqueous KI solution (50 ml.), *o*-phenylenebisdimethylarsine (2.8 g.) in absolute alcohol (5 ml.)], a white precipitate was formed at once, and after 5 minutes' shaking and $\frac{1}{2}$ hour's standing, the *iodide* was collected and well washed with saturated potassium iodide solution followed by distilled water and finally with aqueous alcohol. It was then recrystallised from alcohol and dried in a vacuum desiccator; yield 2.0 g., m. p. 189° [Found: C, 31.8; H, 4.3; I, 16.6; Cu, 8.6%; *M* (ebullioscopic in benzene; 3.1% solution), 660; (in chloroform; 2.5% solution), 750. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{ICu}$ requires C, 31.4; H, 4.2; I, 16.6; Cu, 8.3%; *M*, 762.6]. The compound was very soluble in chloroform, soluble in acetone, and moderately soluble in alcohol, and dissolved in hot benzene. On treatment with silver nitrate, it behaved analogously to the bromide. In powder form the compound was diamagnetic with $\chi = -0.53 \times 10^{-6}$ at 20.6°. For conductivity in nitrobenzene, see table.

[Di(o-phenylenebisdimethylarsine)copper(I)] Di-iodocuprite(I).—Cuprous iodide (0.7 g.) was heated under reflux with alcohol (50 ml.) containing *o*-phenylenebisdimethylarsine (1.0 g.) for about $\frac{3}{4}$ hour. Most of the cuprous iodide, which was present in excess, dissolved, but a dark suspension gradually formed, presumably owing to partial reduction of the cuprous iodide by the tertiary arsine. The solution was then filtered hot, and the clear filtrate on cooling gave sparkling plates of the *di-iodocuprite* (0.9 g.), m. p. 174° (Found: C, 25.5; H, 3.4; I, 26.7; Cu, 13.5. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{I}_2\text{Cu}_2$ requires C, 25.2; H, 3.36; I, 26.7; Cu, 13.34%). The compound had solubilities similar to those of its chloro- and bromo-analogues, and its behaviour with silver nitrate was similar. In spite of the fair solubility in

benzene at room temperature, the low solubility at the freezing point vitiated attempts to determine the molecular weight cryoscopically. For conductivity in nitrobenzene, see table. This compound may also be obtained by treatment of a solution of cuprous iodide in saturated aqueous potassium iodide with an alcoholic solution of the di(tertiary arsine). The product contains some of the monoiodide which must be separated by treatment with hot alcohol, in which it is more soluble than the required product. The method given above is, however, preferable.

[*Di(o-phenylenebisdimethylarsine)copper(I)*] *Perchlorate*.—(i) The monobromide (0.6 g.), dissolved in absolute alcohol (50 ml.), was treated with 60% perchloric acid (10 ml.), and the solution well stirred; a white precipitate was obtained immediately, and was filtered off and washed many times with alcohol and dried in a vacuum desiccator; yield 0.4 g. It decomposed explosively when heated to 310° (Found: C, 32.6; H, 4.5; Cu, 8.5. $C_{20}H_{32}O_4ClAs_4Cu$ requires C, 32.7; H, 4.4; Cu, 8.6%). When it was heated with silver nitrate and nitric acid no silver chloride was formed, showing that all the halogen was present as perchlorate. The compound was insoluble in water and in organic solvents other than nitrobenzene.

(ii) Copper sulphate pentahydrate (0.65 g.) was dissolved in distilled water (17 ml.) containing 60% perchloric acid (5 ml.), and the solution filtered. To the cold solution was added *o*-phenylenebisdimethylarsine (1.45 g.) dissolved in alcohol (40 ml.). A red brown colour was observed momentarily on mixing but this quickly gave place to a white precipitate. The mixture was well shaken for $\frac{1}{2}$ hour, then filtered, and the compound well washed with alcohol. The *perchlorate* (1.3 g.) was obtained as pearly white plates [Found: C, 33.0; H, 4.0; Cl (by Carius method), 5.2. $C_{20}H_{32}O_4ClAs_4Cu$ requires C, 32.7; H, 4.4; Cl, 4.8%], having properties identical with those of the compound prepared as in (i). In powder form, the compound was diamagnetic, with $\chi = -0.46 \times 10^{-6}$ at 17°. For conductivity in nitrobenzene, see table.

Action of Iodine on the Iodide.—The monoiodide [$Cu(Diarsine)_2$]I (1.9 g.) was dissolved in chloroform (15 ml.), and iodine (0.5 g.) dissolved in chloroform (10 ml.) added. The solution became brownish-purple and the chloroform was then removed at the pump, giving a yellowish-brown residue which when recrystallised rapidly from alcohol, gave a brownish-yellow compound (1.36 g.), m. p. 152° (Found: C, 24.5; H, 3.2; I, 32.0. Calc. for $C_{20}H_{32}As_4I_3Cu$: C, 23.7; H, 3.16; I, 37.6%). This compound was diamagnetic ($\chi = -0.42 \times 10^{-6}$ at 15°) and hence did not contain bivalent copper. The mother-liquors from the above recrystallisation deposited excess of the monoiodide. The compound was then recrystallised from benzene and obtained as sparkling golden-brown plates (0.5 g.), m. p. 155° (Found: C, 24.6; H, 3.9; I, 34.7%). The analysis is still not that of the tri-iodide, [$Cu(Diarsine)_2$]I₃ as above, probably owing to contamination with the monoiodide. Since oxidation to bivalent copper has not occurred, the extra iodine has apparently either oxidised part of the arsenic or is present as a tri-iodide ion.

Electrolytic Conductivities in Nitrobenzene.—The nitrobenzene was purified by fractional crystallisation, followed by drying (P_2O_5) and distillation under reduced pressure. Its specific conductivity was 0.73×10^{-6} mho/cm.³. A dip-type conductivity cell was used, of constant 0.515. The electrodes were of bright platinum and unplated. All measurements were carried out at 25° in a thermostat.

Analysis.—Microanalyses for carbon and hydrogen, also chlorine by the Carius method, were carried out by Messrs Weiler and Strauss, Oxford. For halogen and copper, about 0.2 g. of the compound was treated with excess of silver nitrate (20 ml. of *m*/20-solution), distilled water (20 ml.), and 15*N*-nitric acid (30 ml.), and the mixture heated on the water-bath. The black precipitate of silver dissolved rapidly, and heating was then continued until decomposition was complete (about 3 hours). The silver halide was then filtered off and weighed in a sintered Gooch crucible in the usual manner. The filtrate was used for the copper determination. Excess of silver ion was precipitated as chloride, coagulated, and filtered off. The solution was then made alkaline with sodium hydroxide, just acidified with acetic acid, cooled, and treated with a slight excess of salicylaldoxime solution (1 g. in 5 ml. of absolute alcohol + 95 ml. of distilled water). The precipitated copper complex was filtered off after $\frac{1}{2}$ hour, dried at 105°, and weighed. The copper determination was checked by carrying out a Kjeldahl decomposition with concentrated sulphuric acid and potassium sulphate on one of the compounds, and the reliability of the above procedure was established.

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