

227. *Studies in Co-ordination Chemistry. Part XI.* New Types of Cuprous-Tertiary Arsine Complexes.*

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A series of cuprous complexes of methyldiphenylarsine has been prepared and their structures have been investigated. Four types, containing 1, 2, 3, and 4 molecules of the tertiary arsine to each molecule of cuprous halide have been isolated; examples of the last two types have not been reported previously. Complexes with the empirical formula $\text{CuX}_2\text{AsMePh}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are tetrameric, as earlier workers reported for the corresponding trialkylarsine derivatives. The structure of compounds with the empirical formula $\text{CuX}_2\text{As}_2\text{MePh}_2$ cannot be decided with certainty without an X-ray crystallographic examination because on dissolution they undergo dissociation. From the method of preparation the structure in the solid state is probably $[\text{Cu}(\text{AsMePh}_2)_4][\text{CuX}_2]$, but the conductivity in nitrobenzene and molecular-weight measurements in benzene and nitrobenzene indicate that chiefly non-electrolytes are formed in solution. The new class of compounds with the empirical formula $\text{CuX}_2\text{As}_3\text{MePh}_2$ are non-electrolytes containing four-covalent copper; these also dissociate in solution. Finally, compounds with the empirical formula $\text{CuX}_2\text{As}_4\text{MePh}_2$ ($\text{X} = \text{I}, \text{ClO}_4, \text{NO}_3$) are shown to be salts in which X is the univalent anion; the perchlorate is a good conductor in nitrobenzene solution. The ease of dissociation of these compounds emphasises the need for caution when interpreting the results of many physical measurements on inorganic complexes in solution.

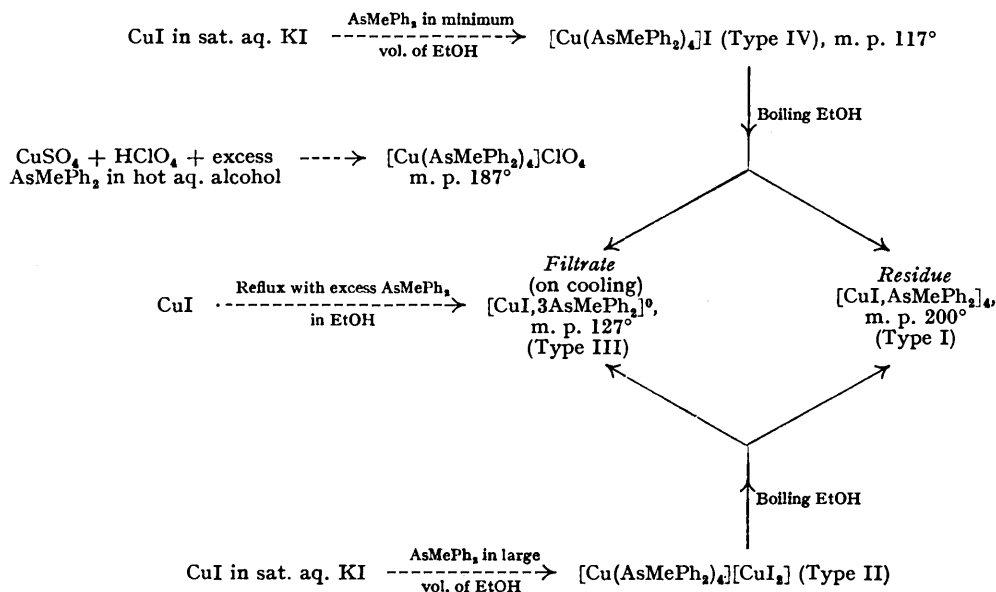
DURING a recent investigation of the structure of two apparently isomeric cuprous-cupric complexes of methyldiphenylarsine oxide (Part VIII, *J.*, 1951, 1767), it was found necessary to obtain more detailed information about the cuprous complexes of the tertiary arsine itself; the few data already available in the literature were insufficient for our purpose. The investigation of these cuprous complexes has led to the isolation of several compounds of a new and interesting type. This paper describes the preparation and properties of these compounds and discusses their dissociation phenomena.

Cuprous complexes of both methyldiphenylarsine (AsMePh_2) and dimethylphenylarsine (AsMe_2Ph) were first described by Burrows and Sandford (*J. Proc. Roy. Soc. N.S.W.*, 1935, 69, 182). From methyldiphenylarsine these workers prepared a chloride, bromide, and nitrate to all of which the general formula $\text{CuX}_2\text{AsMePh}_2$ was assigned; it was reported that all three were monomeric in freezing benzene. In addition, complexes of the empirical formula $\text{CuX}_2\text{As}_2\text{MePh}_2$ were isolated with the other tertiary arsine but their molecular complexity was not investigated. The claim that the former compounds were monomeric was in marked contrast with the work of Mann, Purdie, and Wells (*J.*, 1936, 1503), who prepared and studied very thoroughly a series of cuprous iodide and cuprous bromide complexes of trialkylarsines and trialkylphosphines. All of these had the empirical formula $\text{CuX}_2\text{R}_3\text{As(P)}$. From a study of their molecular weights in a variety of solvents, it was concluded that all the compounds were tetrameric; some dissociation occurred in solution

* Part X, *J.*, 1951, 3245.

but usually the association factor n in $[\text{CuX}_2\text{R}_3\text{As(P)}]_n$ lay between 3.5 and 4.0. Using X-rays, Wells (*Z. Krist.*, 1937, **94**, 447) studied the crystal structure of the cuprous iodide-triethylarsine compound and confirmed that polymerisation to form a tetramer took place. Each cuprous atom is tetrahedrally co-ordinated, for in addition to each covalently bound iodine atom, each copper atom is attached to two other iodine atoms by co-ordinate links and to one triethylarsine molecule (cf. Fig. 1, *J.*, 1936, 1504; *Ann. Reports*, 1938, **35**, 158). No chloride compounds were described; also, the only complexes isolated contained one molecule of the ligand to each molecule of cuprous halide.

In this investigation it has been found that by suitably varying the method of preparation, and by utilising favourable solubility relationships, complexes containing 1, 2, 3, or 4 molecules of the tertiary arsine to each cuprous atom can be isolated; these will be designated in order as Types I, II, III, and IV. Examples of Types III and IV have not been isolated previously, and the structure of those of Type II had not hitherto been investigated. The preparation and relationships between the four types are conveniently described in terms of the iodides, even though one of the iodo-complexes, $\text{CuI}_2\text{AsMePh}_2$, could not be obtained in a pure state. However, the corresponding bis-arsine bromide and chloride are easily obtained free from impurity. Two of the compounds, $\text{CuI}_4\text{AsMePh}_2$ and $\text{CuI}_2\text{AsMePh}_2$, were obtained by treating the arsine with cuprous iodide dissolved in cold aqueous potassium iodide solution, and the other two, $[\text{CuI}_2\text{AsMePh}_2]_4$ and $[\text{CuI}_2\text{AsMePh}_2]_3$, by the action of boiling alcohol upon the first two. As a modification, compounds of Type III can be prepared simply by heating under reflux an excess of the tertiary arsine in alcohol with the appropriate cuprous halide. The relations are summarised in the accompanying scheme.



In Part VII (*J.*, 1951, 38) it was observed that when the ditertiary arsine chelate group, *o*-phenylenebisdimethylarsine, dissolved in a *small* volume of alcohol, was treated with potassium iodocuprite(I) in cold water the compound $[\text{Cu}(\text{diarsine})_2]\text{I}$ was isolated. However, by using a *large* volume of alcohol, $[\text{Cu}(\text{diarsine})_2][\text{CuI}_2]$ was obtained instead. From the earlier experience with the ditertiary arsine it seemed likely that *salts* were produced when methylphenylarsine reacted with potassium iodocuprite(I) in the cold; these then decompose in hot solution to yield non-electrolytes. The properties of all the compounds prepared are given in the table. All the molecular weights were determined cryoscopically, and the conductivities were measured in nitrobenzene solution. Since dissociation occurred in *freezing* benzene and nitrobenzene, no attempt was made to

determine any molecular weights ebullioscopically. The various chloride and bromide complexes were prepared in a similar manner to that given above, but it was not possible to isolate the compounds $[\text{CuAs}(\text{MePh}_2)_4]\text{Cl}$ and $[\text{Cu}(\text{AsMePh}_2)_4]\text{Br}$, probably owing to their greater solubility. Two other compounds of Type IV, $[\text{Cu}(\text{AsMePh}_2)_4]\text{ClO}_4$ and $[\text{Cu}(\text{AsMePh}_2)_4]\text{NO}_3$ were also prepared by the reducing action of excess of the tertiary arsine on the corresponding cupric salt in aqueous-alcoholic solution.

Structure and Properties.—*Type I.* Complexes of this type are clearly the methyl-diphenylarsine analogues of the trialkylarsine complexes studied by Mann, Purdie, and Wells (*loc. cit.*). Molecular-weight measurements show that both the chloride and the bromide are polymerised in solution. Although the results are still less than those required for the tetramer in each case, this can be explained by partial decomposition in solution; with both the chloride and the bromide slow precipitation of the cuprous halide occurs during the measurement. Since each decomposing tetramer molecule produces *four* solute molecules in its place, a small amount of decomposition has a relatively large effect upon the observed molecular weight. The iodide was insufficiently soluble, both in benzene and in nitrobenzene, to permit a molecular-weight measurement in these solvents. In chloroform and bromoform decomposition appears to take place even more rapidly than in benzene and nitrobenzene. Our molecular-weight measurements do not agree with those of Burrows and Sandford (*loc. cit.*) but agree with the work of Mann, Purdie, and Wells (*loc. cit.*). However, it should be mentioned that the melting points which we observed are different from those reported by Burrows and Sandford (see p. 1258) and, therefore, it remains possible that these workers obtained isomeric two-covalent complexes. On the other hand, the extreme ease with which dissociation occurs in these compounds suggests that the compounds used may have been of mistaken identity. All three tetramers are poor conductors in nitrobenzene solution (see table, where Λ_m = molecular con-

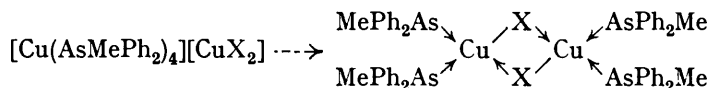
Type	Empirical formula	M. p.	Formula wt.	M in PhNO_2	Λ_m in PhNO_2 (M = formula wt.)	M in C_6H_6
I	CuCl,AsR_3	109°	343	>1205* (1.75%)	0.3 ($4.5 \times 10^{-3}M$)	>1020* (2.88%)
	CuBr,AsR_3	170	387.5	—	0.15 ($4.6 \times 10^{-3}M$)	>1260* (1.74%)
	CuI,AsR_3	200	434.5	—	0.7 ($4.98 \times 10^{-3}M$)	—
II	CuCl,2AsR_3	127	587	626 (1.79%) 758 (2.84%)	1.5 ($10.4 \times 10^{-3}M$)	730 (2.98%)
	CuBr,2AsR_3	138	631.5	955 (1.68%)	0.35 ($13.8 \times 10^{-3}M$)	858 (3.63%)
	CuI,2AsR_3	?	678.5	—	—	—
III	CuCl,3AsR_3	117	831	502 (2.03%)	2.3 ($4.9 \times 10^{-3}M$)	795 (5.40%)
	CuBr,3AsR_3	134	875.5	778 (2.26%)	0.6 ($5.7 \times 10^{-3}M$)	580 (2.72%)
	CuI,3AsR_3	128	922.5	715 (1.74%) 721 (2.45%)	0.1 ($3.9 \times 10^{-3}M$)	549 (1.99%)
IV	CuI,4AsR_3	117	1166.5	—	—	—
	$\text{CuClO}_4,4\text{AsR}_3$	187	1139	545 (1.17%) 548 (2.46%)	24.4 ($3.9 \times 10^{-3}M$)	—
	$\text{CuNO}_3,4\text{AsR}_3$	115	1101.5	908 (1.61%)	4.3 ($4.47 \times 10^{-3}M$)	509 (3.41%) 542 (4.14%)

* In each of these measurements a little cuprous halide was precipitated during the determination. Since each act of decomposition produces a *greater* number of solute particles than the original number of tetramer molecules, the observed molecular weight is *smaller* than it would be if no decomposition had occurred.

ductivity); this confirms that they exist in solution as non-electrolytes and, taken together with molecular-weight measurements, supports the structures assigned. It is noteworthy that the compound $[\text{CuCl,AsMePh}_2]_4$ is the first example of a polymerised chloride with tertiary arsines to be described. However, Wilkins and Burkin (*J.*, 1950, 127) have shown that similar polymerisation to give the tetramer occurs when cuprous chloride is co-ordinated with one molecule of a long-chain amine.

Type II. The molecular-weight and conductivity measurements upon complexes of this type do not permit one to decide with any certainty the structure of this class of compound. From the method of preparation it is probable that in the solid state they are salts with the structural formula $[\text{Cu}(\text{AsMePh}_2)_4][\text{CuX}_2]$, but in solution they undergo extensive dissociation, forming non-electrolytes. The low conductivities in nitrobenzene (see table) could be explained by the following possible types of dissociation: (a) a mixture

of the two non-electrolytes $[\text{CuX}, 3\text{AsMePh}_2]_0$ and $[\text{CuX}, \text{AsMePh}_2]_4$ is formed according to the reaction $4[\text{Cu}(\text{AsMePh}_2)_4][\text{CuX}_2] \dashrightarrow 4[\text{CuX}, 3\text{AsMePh}_2]_0 + [\text{CuX}, \text{AsMePh}_2]_4$, or (b) a mixture of the tertiary arsine and the tetramer is produced according to the reaction $2[\text{Cu}(\text{AsMePh}_2)_4][\text{CuX}_2] \dashrightarrow [\text{CuX}, \text{AsMePh}_2]_4 + 4\text{AsMePh}_2$, or (c) a change into the halogen-bridged dimer occurs as follows :



Neither molecular-weight measurements nor preparative experience gives much support for (c), although this may occur to a limited extent in solution. For (b) one requires a molecular weight much smaller than that actually observed. Hypothesis (a) seems the most likely. However, it should be borne in mind that without definite evidence as to the nature of the actual species present in solution, all three (and possibly other) types of dissociation may occur to some extent. This dissolution of a salt in solvents such as benzene and nitrobenzene with the formation of non-electrolytes has been reported previously with this tertiary arsine. In Part II (*J.*, 1950, 848) it was shown that the compounds $[\text{PtBr}(\text{AsMePh}_2)_3]\text{Br}$ and $[\text{PdBr}(\text{AsMePh}_2)_3]\text{Br}$ dissolve readily in organic solvents, forming an equimolecular mixture of the tertiary arsine and the non-electrolytes $[\text{PtBr}_2, 2\text{AsMePh}_2]_0$ and $[\text{PdBr}_2, 2\text{AsMePh}_2]_0$. The ease with which such dissociations may be reversed was demonstrated by the fact that in acetone solution at low temperatures partial re-formation of the salt takes place, at least with the palladium complex. The essential point is that any conclusions which one may draw concerning the state of a complex in solution need not necessarily provide information concerning the structure of the substance in the solid state, particularly when one is dealing with a labile ligand such as methyl-diphenylarsine.

Type III. These compounds appear to be the easiest to formulate, but again their behaviour in solution indicates considerable dissociation. The conductivities in nitrobenzene solution are all fairly small, showing that the products of dissociation are chiefly non-electrolytes, including possibly the tertiary arsine. The molecular weights in solution in all cases, both in benzene and in nitrobenzene, are less than those required for the simple tris-arsine non-electrolyte. It seems likely that the main dissociation is as follows : $4[\text{CuX}, 3\text{AsMePh}_2]_0 \dashrightarrow [\text{CuX}, \text{AsMePh}_2]_4 + 8\text{AsMePh}_2$. Some support for this view is afforded by the fact that a suspension of the tetramer in benzene solution dissolves to a clear solution very easily on the addition of excess of tertiary arsine. Nevertheless, one might expect that the above dissociation would occur to only a limited extent since the tetramer itself is only slightly soluble in benzene. Only in the case of the chloride is the conductivity in nitrobenzene appreciable; this suggests that here, at least, noticeable amounts of the compound $[\text{Cu}(\text{AsMePh}_2)_4][\text{CuCl}_2]$ are formed in solution in this solvent. Compounds of this type have not been described previously. Mann, Purdie, and Wells mentioned the probability of their existence but the ligands used by these workers yielded only the tetramers. A major factor deciding whether they can be isolated with a particular tertiary arsine is undoubtedly the relative solubility of the different forms; although the tetramer is less soluble than the tris-arsine complex, in this instance the equilibrium can be forced to favour the formation of the latter by using a sufficient excess of the tertiary arsine.

Type IV. The physical properties of the iodide, $[\text{Cu}(\text{AsMePh}_2)_4]\text{I}$, could not be studied in much detail because the compound decomposed readily when treated with solvents. However, the corresponding perchlorate and nitrate were isolated and these have the properties typical of salts. A sulphate was also obtained but it is difficult to isolate in a pure state owing to its high solubility in aqueous alcohol. The perchlorate is readily soluble in nitrobenzene and the conductivity therein indicates a strong electrolyte. In Part VII (*loc. cit.*) it was shown that uni-univalent electrolytes of this kind usually have a molecular conductivity of the order of 20—30 mho in $m/1000$ -solution; the conductivity of this perchlorate (see table) is in this range. The practically complete dissociation in nitrobenzene is confirmed by the molecular weight, which is about half of the formula weight, as expected. The compound is not sufficiently soluble in cold benzene to enable

a cryoscopic molecular-weight measurement to be done in this solvent. By a similar method of preparation to that used for the perchlorate, the nitrate $[\text{Cu}(\text{AsMePh}_2)_4]\text{NO}_3$ was prepared. This is readily soluble in alcohol and in organic solvents such as nitrobenzene, and benzene; however, it is one of the very few nitrates which are highly insoluble in water. The molecular weight in nitrobenzene is surprisingly high, suggesting that the compound is only dissociated to the extent of about 20% in this solvent. Since it is inconceivable that the cuprous atom is five-covalent, it is probable that ion-pair formation occurs to a large extent at the concentration used. This hypothesis is supported by the molecular conductivity in nitrobenzene solution; this is only about one-fifth of that usually observed for a fully ionised and dissociated electrolyte in this solvent. Taken together, these data indicate that very little, if any, dissociation to form $[\text{CuNO}_3, 3\text{AsMePh}_2]^0$ and AsMePh_2 occurs in nitrobenzene solution. The molecular weight in benzene is surprisingly low, a value less than half of the formula weight being observed in two separate determinations. Since benzene is not as good an ionising solvent as nitrobenzene, it is apparent that considerable dissociation of a different kind is taking place. This must involve loss of tertiary arsine but the other products of dissociation are uncertain; they could be the non-electrolytes $[\text{CuNO}_3, 3\text{AsMePh}_2]^0$ or $[\text{CuNO}_3, \text{AsMePh}_2]^0$. Burrows and Sandford claimed to have prepared the latter substance and stated that it was monomeric in benzene solution. Several attempts in these laboratories to repeat this preparation have been unsuccessful, the only compound which crystallises from solution being the tetraarsine complex nitrate. All previous work on the chemistry of cuprous complexes shows that the metal atom is very reluctant to form covalent bonds with oxygen; whenever an oxy-anion is used the cuprous atom prefers to complete its four-fold co-ordination with less electronegative ligands while the anion is left with its negative charge, *e.g.*, in the compound $[\text{Cu}(\text{ethylenethiourea})_4]\text{NO}_3$. However, the fact that complexes such as $[\text{CuNO}_3, 3\text{AsMePh}_2]^0$ have not been isolated does not mean that they do not exist in solution, and the molecular-weight determination upon $[\text{Cu}(\text{AsMePh}_2)_4]\text{NO}_3$ is best understood if dissociation to form an equimolecular solution of $[\text{CuNO}_3, 3\text{AsMePh}_2]^0$ and AsMePh_2 takes place. This hypothesis requires that benzene favours dissociation into non-electrolytes more than does nitrobenzene; in view of the difference in dielectric constants, this is not unreasonable. With neighbouring metals there is evidence that $-\text{NO}_3$ can be attached by covalent bonds. Thus the compound $[\text{Ni}(\text{NO}_3)_2, 2\text{PEt}_3]^0$ was isolated by Jensen (*Z. anorg. Chem.*, 1936, 229, 265) and shown to be monomeric in benzene solution. The large dipole moment (8.85 D) indicates either a *cis*-planar or a tetrahedral configuration; the magnetic moment (3.05 B.M.) points to the use of the higher $4s4p^3$ tetrahedral covalent bond orbitals rather than the lower $3d4s4p^2$ orbitals, which would result in a planar diamagnetic molecule. Cuprous copper is not isoelectronic with bivalent nickel but its tetrahedral complexes make use of the same bonding orbitals and there appears to be no fundamental theoretical objection to a complex of the type $[\text{CuNO}_3, 3\text{AsMePh}_2]^0$ even though it has not been isolated.

All the compounds prepared are quite stable in air and except in the presence of moisture show no tendency towards oxidation. However, they are powerful reducing agents in solution and, with the exception of the nitrate and perchlorate, react instantly with silver nitrate in aqueous-alcoholic suspension to yield a mixture of metallic silver and the silver halide. The nitrate and perchlorate of course yield no silver halide.

As found in previous work, the results of this investigation are consistent with the view that a co-ordination number of four is displayed by cuprous copper whenever it is attached to tertiary arsines in cationic or non-ionic complexes. As is well known, the co-ordination number 2 occurs in anionic complexes such as the $[\text{CuCl}_2]^-$ ion. This is in keeping with the fairly general rule that metals which have more than one co-ordination number tend to show the maximum co-ordination number in cationic complexes, decreasing through non-ionic compounds to anionic complexes. The extent to which dissociation occurs in solution with these compounds makes other physical measurements difficult to interpret, and for this reason dipole-moment determinations, which were originally envisaged, were not carried out on these compounds. As this investigation was undertaken primarily in order to determine the stereochemistry of these substances no attempt has been made to study

the dissociation equilibria in solution in any detail. This might possibly be done by studying the ultra-violet absorption spectra of the various complexes, and of the free arsine itself, in solution. This problem will be examined, particularly in reference to the dissociation of the complex nitrate in benzene solution.

EXPERIMENTAL

Tetrakis[methyldiphenylarsinemonochlorocopper(I)].—Cuprous chloride (2.0 g., excess) was first freed from cupric salts by heating it with dilute alcoholic hydrochloric acid, followed by several washings, with alcohol. The cuprous salt was then heated under reflux for 30 minutes with methyldiphenylarsine (2.0 g.) in alcohol (75 ml.), and the solution filtered quickly at the pump. On rapid cooling, white crystals were obtained which were recrystallised from hot alcohol containing excess of cuprous chloride in suspension, the filtration and cooling being again rapid to prevent dissociation. The *compound* (1.4 g.) was obtained as a microcrystalline powder, m. p. 109° (Found: C, 45.9; H, 4.15; Cl, 10.3. $C_{52}H_{52}As_4Cl_4Cu_4$ requires C, 45.5; H, 3.79; Cl, 10.35%). When recrystallising the compound it is essential to redissolve it in alcohol in the presence of cuprous chloride and to filter and cool the solution rapidly, otherwise decomposition occurs yielding some of the trisarsine complex. The substance is soluble in benzene, chloroform, and nitrobenzene and slightly soluble in acetone, but in these solvents slow decomposition takes place with the precipitation of cuprous chloride. The compound is insoluble in water, ether, and light petroleum. Burrows and Sandford reported m. p. 104° for this compound.

Tetrakis(methyldiphenylarsine)copper(I) Dichlorocuprite(I).—Cuprous chloride (0.5 g.) was dissolved in a cold aqueous saturated solution of potassium chloride (20 ml.) containing 10N-hydrochloric acid (1 drop), and the solution warmed to 40°, and filtered into a stoppered flask. Methyldiphenylarsine (2.5 g.), dissolved in alcohol (20 ml.), was added, and the mixture well shaken for 10 minutes in an atmosphere of carbon dioxide. A white precipitate containing some potassium chloride appeared at once. Water (10 ml.) was added after 10 minutes to redissolve the potassium chloride, and the solution left for 24 hours with occasional shaking. The impure *dichlorocuprite* (2.8 g.) was then filtered off, well washed with alcohol and water, and recrystallised from cold benzene–light petroleum; it had m. p. 127° (Found: C, 53.0; H, 4.35; Cl, 5.9. $C_{52}H_{52}As_4Cl_2Cu_2$ requires C, 53.2; H, 4.45; Cl, 6.03%). The compound is readily soluble in chloroform, benzene, and nitrobenzene, and moderately soluble in acetone; it is insoluble in water, light petroleum, and cold alcohol but is decomposed by boiling alcohol.

Tris(methyldiphenylarsine)monochlorocopper(I).—Cuprous chloride (0.1 g.) was heated under reflux for 15 minutes with methyldiphenylarsine (0.8 g.) in alcohol (40 ml.), and the solution filtered hot and concentrated to 10 ml. On cooling, rhombic crystals (0.7 g.) separated. These were filtered off and recrystallised from a little alcohol containing a trace of arsine; m. p. 117° (Found: C, 56.35; H, 5.1; Cl, 4.2. $C_{39}H_{39}As_3ClCu$ requires C, 56.1; H, 4.7; Cl, 4.3%). The *compound* is readily soluble in benzene, acetone, and nitrobenzene, and very soluble in chloroform; it is insoluble in water and light petroleum.

Tetrakis[methyldiphenylarsinemonobromocopper(I)].—This compound can be prepared by treating $[Cu(AsMePh_2)_4][CuBr_2]$ with boiling alcohol; decomposition occurs and the tetramer remains insoluble while the tris-arsine bromo-complex passes into solution. It is more conveniently obtained as follows. Cupric bromide (1.1 g.) in alcohol (40 ml.) was heated to boiling and treated with methyldiphenylarsine (1.2 g.), the solution turning colourless immediately. Heating on the water-bath yielded white crystals; the solution was cooled, and the compound filtered off and well washed with alcohol. This was then treated with boiling alcohol twice in order to remove traces of the tris-arsine complex, leaving the substantially pure tetramer. To remove any cuprous bromide formed by decomposition, this was then dissolved in cold benzene, and the solution filtered and precipitated with light petroleum, giving a microcrystalline powder (1.0 g.) (Found: C, 40.6; H, 3.5. $C_{52}H_{52}As_4I_4Cu_4$ requires C, 40.3; H, 3.35%), m. p. 170° (Burrows and Sandford reported m. p. 133° for the substance which they described). The *compound* is soluble in benzene, chloroform, and nitrobenzene, and slightly soluble in acetone, some cuprous bromide being slowly deposited.

Tetrakis(methyldiphenylarsine)copper(I) Dibromocuprite(I).—Cuprous bromide (0.6 g.) was dissolved in a saturated aqueous solution of potassium bromide (15 ml.), and the solution filtered and treated in the cold with methyldiphenylarsine (1.25 g.) in alcohol (10 ml.). The mixture was well shaken for an hour in a stoppered flask in an atmosphere of carbon dioxide, a white precipitate of the required *dibromocuprite* being formed. This (1.6 g.) was filtered off,

well washed with saturated potassium bromide solution, then alcohol, and finally with water (Found : 49.95; H, 4.15; Br, 12.9. $C_{52}H_{52}As_4Br_2Cu_2$ requires C, 49.4; H, 4.1; Br, 12.7%). The compound is easily soluble in chloroform, benzene, acetone, and nitrobenzene.

Tris(methyldiphenylarsine)monobromocopper(I).—Cuprous bromide (0.3 g.) was heated under reflux with methyldiphenylarsine (1.8 g.) in alcohol (70 ml.) for several hours, most of the cuprous halide dissolving. At first a yellow insoluble compound was formed, probably $[CuBr, AsMePh_2]_4$, but if broken up this slowly dissolved on further refluxing. The solution was then filtered from traces of residue, and on cooling, sparkling white plates (1.4 g.) were obtained. The compound was filtered off, well washed with cold alcohol, and recrystallised from alcohol containing a little tertiary arsine; it had m. p. 134° (Found : C, 53.5; H, 4.55; Br, 9.4. $C_{39}H_{39}As_3BrCu$ requires C, 53.5; H, 4.45; Br, 9.2%), readily soluble in chloroform, nitrobenzene, acetone, and benzene. It may also be obtained from the filtrate when $[Cu(AsMePh_2)_4][CuBr_2]$ is boiled with alcohol.

Tetrakis(methyldiphenylarsine)monoiodocopper(I).—The compound $[Cu(MePh_2As)_4]I$ (2.0 g.), prepared as below, was boiled with alcohol several times then filtered off at the pump; the tetra-arsine complex decomposed, yielding the required tetramer as a heavy, white, insoluble powder. This (1.1 g.) was washed many times with hot alcohol to remove any tris-arsine complex but it could not be recrystallised without some decomposition; it had m. p. 200° (Found : C, 35.7; H, 3.0; I, 29.7. $C_{52}H_{52}As_4I_4Cu_4$ requires C, 35.8; H, 3.0; I, 29.3%). The compound is soluble in chloroform and slightly soluble in nitrobenzene, cuprous iodide being slowly deposited; it is practically insoluble in benzene and other solvents.

Tris(methyldiphenylarsine)monoiodocopper(I).—This compound crystallised on cooling from the first filtrates of the above preparation of $[CuI, AsMePh_2]_4$. Recrystallised from an alcoholic solution containing a little tertiary arsine, it had m. p. 128° (Found : C, 50.9; H, 4.15; I, 13.6. $C_{39}H_{39}As_3ICu$ requires C, 50.8; H, 4.2; I, 13.8%). It may be prepared more conveniently in larger quantities by heating an alcoholic solution of excess of the tertiary arsine with cuprous iodide. The solution was filtered hot, and the required compound crystallised on cooling. Solubilities are similar to those of other tris-arsine complexes.

Tetrakis(methyldiphenylarsine)copper(I) Monoiodide.—Cuprous iodide (0.4 g.) was dissolved in a saturated aqueous potassium iodide solution (80 ml.) containing 10N-hydrochloric acid (1 drop), and the solution filtered. Methyldiphenylarsine (2.0 g.) was added but no visible reaction occurred before the addition of alcohol (5 ml.), after which a white precipitate appeared. The mixture was well shaken for 15 minutes, and the yellowish-white precipitate (2.3 g.) filtered off and well washed with potassium iodide solution, water, and dilute aqueous alcohol (Found : C, 52.8; H, 4.4. $C_{52}H_{52}As_4ICu$ requires C, 53.4; H, 4.5%). Further purification was difficult because the compound tends to lose some of the arsine very easily; the analysis indicates that some slight loss occurred during filtration. The complex dissolved in chloroform, nitrobenzene, and benzene but with decomposition; it had m. p. 117°.

Tetrakis(methyldiphenylarsine)copper(I) Perchlorate.—Copper sulphate pentahydrate (0.25 g.) in water (25 ml.) containing excess of perchloric acid was added to a solution of methyldiphenylarsine (1.5 g.) in alcohol (100 ml.) and water (50 ml.). The mixture was heated on the water-bath for about an hour. Some white precipitate appeared at once and the blue colour gradually faded. The white, flaky, crystalline perchlorate was filtered off, washed many times with alcohol, and dried in a desiccator; its m. p. was 187° (1.05 g.) [Found : C, 55.0; H, 4.57; Cl(Carius), 2.8; Cu, 5.66. $C_{52}H_{52}As_4O_4ClCu$ requires C, 55.1; H, 4.55; Cl, 3.1; Cu, 5.58%]. The substance was insoluble in water and in organic solvents except nitrobenzene and hot benzene. Prolonged heating with concentrated nitric acid and aqueous silver nitrate did not yield any silver chloride, showing that all the halogen was present as the perchlorate ion. The compound was diamagnetic and, for the powder form at 21°, $\chi_g = -0.45 \times 10^{-6}$.

Tetrakis(methyldiphenylarsine)copper(I) Nitrate.—Cupric nitrate hexahydrate (1.2 g.) in water (10 ml.) was treated with the tertiary arsine in excess (4.0 g.) in alcohol (70 ml.), and the solution heated on the water-bath for several hours. Aqueous alcohol was added gradually as the evaporation took place; the blue colour gradually decreased in intensity and white crystals were deposited. When the solution had become almost colourless, the nitrate was filtered off (3.0 g.) on cooling and well washed with aqueous alcohol; recrystallised from a small volume of alcohol, it had m. p. 115° (Found : C, 56.7; H, 4.8; N, 1.4. $C_{52}H_{52}As_4O_2NCu$ requires C, 56.7; H, 4.7; N, 1.3%). Unless water is added during the preparation of this compound, reduction to the cuprous state is very slow. The compound dissolves readily in benzene, chloroform, acetone, nitrobenzene, and even in alcohol. However, it is quite insoluble in water.

Conductivities were determined as in Part VIII (*loc. cit.*); magnetic susceptibility measurements were carried out as described in Part III (*J.*, 1950, 851). Molecular-weight measurements in nitrobenzene were determined by Roberts and Bury's method (*J.*, 1923, 123, 2037); steady freezing points are obtained by adding excess of anhydrous sodium sulphate together with a drop of water, giving the constant aqueous vapour tension of the decahydrate.

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