417. *Ditertiary Arsine Complexes of Some* d^{10} *Metals* (Ag^{I}, Zn^{II}, Cd^{II}, *and* Hg^{II}).

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The ditertiary arsine complexes of several d^{10}-ions, *viz.*, those of Ag^{I}, Zn^{II}, Cd^{II}, and Hg^{II}, have been prepared and their properties investigated. Silver salts give rise to complexes of the type $[Ag(Diarsine)_2][AgX_2]$ where X = Cl, Br, I, or NO_2 and Diarsine = o-$C_6H_4(AsMe_2)_2$; the anion may be replaced by NO_3^- or ClO_4^-. Conductivities in various solvents suggest that in the case of the iodide an equilibrium with a dimeric non-electrolyte species occurs. The halides of zinc, cadmium, and mercury give rise to non-electrolytes of the type $[M^{II}(Diarsine)X_2]^0$ where X = Cl, Br, or I. In solution there is some formation of a salt of the type $[M^{II}(Diarsine)_2][M^{II}X_4]$; this is most evident for the complex $[Hg(Diarsine)I_2]^0$. Salts of the type $[M^{II}(Diarsine)_2][ClO_4]_2$ have also been isolated.

The relative stabilities of the diarsine complexes of the triads Cu^{I}, Ag^{I}, and Au^{I}, and Zn^{II}, Cd^{II}, and Hg^{II} are discussed with particular reference to the relative importance of polarising power of the metal and the possibility of its forming d_π–d_π-bonds to the ligand.

In all cases the zinc, cadmium, and mercury ions give rise to four-co-ordinate diarsine complexes, as is usual with these metals for readily polarisable ligands. Similarly, the silver ion is in all cases four-co-ordinate when attached to the diarsine.

The ditertiary arsine, o-phenylenebisdimethylarsine (Diarsine), is known to form very stable complexes with metals that have incomplete d-shells when these are in a variety of oxidation states. These complexes generally make use of inner d-orbitals for bonding, *e.g.*, $3d4s4p^2$-bonds in the complex $[Ni(Diarsine)_2][ClO_4]_2$. Relatively few Diarsine complexes of metal d^{10}-ions have been studied; those whose behaviour has been investigated previously are shown in the portion of Table 1 enclosed in lines.

TABLE 1.

Metal atoms with d^{10}-configurations.

(*a*) Ni^0	(*c*) Cu^I	Zn^{II}	Ga^{III}	Ge^{IV}
(*b*, *f*) Pd^0	Ag^I	Cd^{II}	In^{III}	(*d*) Sn^{IV}
(*f*) Pt^0	(*e*) Au^I	Hg^{II}	Tl^{III}	Pb^{IV}

(*a*) $[Ni(CO)_2Diarsine]^0$,[1] $[Ni(Diarsine)_2]^0$.[2] (*b*) The compound $PdDiarsinePPh_3$ has been reported.[3] (*c*) *E.g.*, $[Cu(Diarsine)_2]ClO_4$.[4] (*d*) *E.g.*, $[SnCl_4\ Diarsine]^0$.[5] (*e*) *E.g.*, $[Au(Diarsine)_2]ClO_4$.[6] (*f*) Complexes of the type $Pd^0(Diphosphine)_2$ and $Pt^0(Diphosphine)_2$ have recently been prepared.

In certain cases, *e.g.*, Pb^{IV} and Tl^{III}, the isolation of stable Diarsine derivatives is considered unlikely owing to the ease with which Diarsine is oxidised unless very strong bonds are formed between the chelate and the metal atom. Also it is usually necessary for the complex to be prepared by oxidation of the derivative of a lower halide {cf. the preparation of $[Pt(Diarsine)_2Cl_2]Cl_2$ from $[Pt(Diarsine)_2]Cl_2$ [2]}.

In this paper we describe the preparation and properties of the diarsine complexes formed by univalent silver and by bivalent zinc, cadmium, and mercury. Special interest attaches to the relative stabilities of these complexes as we pass across and down the Periodic Table. In view of the uncertainty as to the extent to which d_π-bonding arises with these d^{10}-elements [7] their behaviour towards the diarsine which can, but need not, form d_π-bonds with metals is of special interest.

Silver Complexes.—These are formed by heating a silver halide with the diarsine in alcohol or, in some cases, by mixing solutions of a silver salt (*e.g.*, the perchlorate and nitrate) with the diarsine. Complexes of two types have been isolated, having the general formula $[Ag(Diarsine)_2]X$ where $X = NO_3^-$ and ClO_4^-, and AgY,Diarsine where Y = Cl, Br, I, or NO_2. All these compounds are white and dissolve in nitromethane and nitrobenzene, some deposition of silver halide occurring on storage of solutions of the halogen complexes. The conductivites of these solutions have been investigated, with the results shown in Table 2.

TABLE 2.

Molecular conductivities of silver(I)–Diarsine complexes.

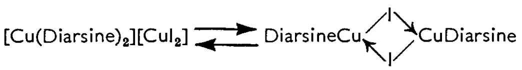
	$PhNO_2$ solution *		$MeNO_2$ solution *	
Compound †	Mol. cond. (ohm^{-1} cm.^{2} at 25°)	Concn. (10^{-3}M)	Mol. cond. (ohm^{-1} cm.^{2} at 25°)	Concn. (10^{-3}M)
$[AgD_2][AgCl_2]$	25·7	0·95		
$[AgD_2][AgBr_2]$	Only sparingly soluble in the usual solvents			
$[AgD_2][AgI_2]$	9·6	0·83		
$[AgD_2][Ag(NO_2)_2]$	17·6	1·00		
$[AgD_2]NO_3$			90·8	1·12
$[AgD_2]ClO_4$			84·0	1·27

* 1 : 1 Electrolytes (10^{-3}M-solutions) usually have molecular conductivities in nitrobenzene of 20—30 ohm^{-1} cm.^{2} and in nitromethane of 70—80 ohm^{-1} cm.^{2} † D = Diarsine.

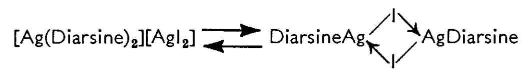
With the exception of AgI,Diarsine and $AgNO_2$,Diarsine all the compounds tend to form strong electrolytes of the $[Ag(Diarsine)_2]^+$ cation. The low conductivity of the iodide

[1] Nyholm, *J.*, 1952, 2906.
[2] See Harris, Nyholm, and Phillips, *J.*, 1960, 4379.
[3] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208.
[4] Kabesh and Nyholm, *J.*, 1951, 38.
[5] Allison and Mann, *J.*, 1950, 2915.
[6] Harris and Nyholm, *J.*, 1957, 63.
[7] Nyholm, *Proc. Chem. Soc.*, 1961, 273.

in nitrobenzene parallels the behaviour shown by the corresponding cuprous complex.[4] It was suggested earlier [4] that an equilibrium of the type



occurs and this seems likely here also. This behaviour was not observed for aurous iodide complexes. An excess of Diarsine was added to a solution of the iodo-salt in an attempt to convert all the silver in the $[AgI_2]^-$ ion and in the dimer in the equilibrium mixture



into the $[Ag(Diarsine)_2]^+$ ion; the conductivities of the silver complexes have been determined and are shown in Table 3. It is clear that the reaction with Diarsine is still not complete even though the equilibrium point in the reaction

$$[Ag(Diarsine)_2][AgI_2] + 2Diarsine \rightleftharpoons 2[Ag(Diarsine)_2]^+ + 2I^-$$

is displaced towards the right. The greater affinity of the silver ion for the iodide ion is scarcely due to bond strengths since these usually decrease in the order M–Cl > M–Br > M–I; we conclude that the phenomenon is more likely to be explained by the smaller solvation energy of the iodide ion in the solvents used.

TABLE 3.

Limiting molecular conductivities of $[Ag(Diarsine)_2][AgX_2]$ compounds in nitrobenzene in the presence of excess of the Diarsine (at 25°).

Compound	Concn. (10^{-3}M)	Initial specific cond. (10^5 ohm^{-1} cm.$^{-1}$)	Limiting specific cond. in presence of Diarsine (10^5 ohm^{-1} cm.$^{-1}$)	Diarsine added * (g.)	Final mol. cond. (calc. for monomeric mol. wt.) (ohm^{-1} cm.$^{-2}$)
$[AgD_2][AgCl_2]$	0·95	2·48	4·56	0·212	23·9
$[AgD_2][AgBr_2]$ † ...	0·66	—	2·89	0·424	21·8
$[AgD_2][AgI_2]$	0·82	0·80	2·14	0·424	13·0
$[AgD_2][Ag(NO_2)_2]$...	1·00	1·76	5·92	0·424	29·6

* Diarsine was added to 10-ml. portions of the conductivity solutions. The addition of 0·424 g. of Diarsine to 10 ml. of a 1·00 × 10^{-3}M-solution corresponds to a 148-fold molar excess of the ligand.

† This compound, although very sparingly soluble in nitrobenzene, dissolves readily in the presence of excess of the diarsine.

Thus the complexes formed by univalent silver are very similar to those of univalent copper and gold, the chelate group giving rise to a four-co-ordinate, undoubtedly tetrahedral, Ag^{I} atom. There is, however, one important difference, namely, that the silver halide complexes are less stable in nitrobenzene solution than are the cuprous or aurous complexes. This behaviour has been observed with other monodentate arsine and phosphine complexes of silver.[8] The effect could arise from the lower effective electronegativity (χ) of silver, this being an indication of the strength of the covalent bonds which it forms. (As a measure of χ the first ionisation potentials of copper, silver, and gold are, respectively, 7·72, 7·57, and 9·22 v.) Alternatively, the high lattice energy and insolubility of the silver halides may be an important, if not the most important, factor involved.

Zinc, Cadmium, and Mercury.—In all these cases the halide complexes were prepared by allowing the diarsine and the metal halide to react in alcoholic solution. The products have the general formula MX_2,Diarsine. The mercury and cadmium complexes were deposited immediately but to afford the more soluble zinc derivatives the solution required concentration. Each of the complexes is a poor conductor of electricity in nitrobenzene

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[8] Mann, Wells, and Purdie, *J.*, 1937, 1828; Cass, Coates, and Hayter, *J.*, 1955, 4007; Cotton and Goodgame, *J.*, 1961, 5267; Cochran, Hart, and Mann, *J.*, 1957, 2816.

solution, the values for the various complexes at different concentrations being given in Table 4.

TABLE 4.

Molecular conductivities of zinc^{II}–, cadmium^{II}–, and mercury^{II}–Diarsine complexes (at 25°).

Compound *	Concn. (10^{-3}M)	Mol. cond. (ohm^{-1} cm.^{2})	Mol. cond. in presence of excess of Diarsine † (ohm^{-1} cm.^{2})	Solvent
[ZnDBr$_2$]	1·25	3·3	23·3	MeNO$_2$
[ZnDI$_2$]	1·55	1·3	21·7	MeNO$_2$
[ZnDI$_2$]	1·03	2·0	—	Me$_2$CO
[ZnDI$_2$]	1·00	1·2	—	PhNO$_2$
[ZnD$_2$][ClO$_4$]$_2$	0·40	194	—	MeNO$_2$
[CdDCl$_2$]	2·13	2·5	3·3	EtOH
[CdDBr$_2$]	1·51	2·4	3·4	EtOH
[CdDI$_2$]	1·10	6·8	13·8	MeNO$_2$
[CdDI$_2$]	1·25	1·9		Me$_2$CO
[CdDI$_2$]	1·37	0·9	—	PhNO$_2$
[CdD$_2$][ClO$_4$]$_2$	0·48	179	—	MeNO$_2$
[HgDCl$_2$]	1·08	5·7	39·8	MeNO$_2$
[HgDBr$_2$]	0·96	4·7	38·5	MeNO$_2$
[HgDI$_2$]	1·72	5·0	14·7	MeNO$_2$
[HgDI$_2$]	1·01	6·3	—	Me$_2$CO
[HgDI$_2$]	1·13	1·8	—	PhNO$_2$
[HgD$_2$][ClO$_4$]$_2$	0·35	192	—	MeNO$_2$

In 10^{-3}M-solution in acetone 1 : 1 electrolytes usually have molecular conductivities of 130—150 ohm^{-1} cm.^{2} and in ethanol of 35—45 ohm^{-1} cm.^{2}. For 2 : 1 electrolytes in nitromethane values of 160—180 ohm^{-1} cm.^{2} are usual.

* D = Diarsine. † 0·7 g. of Diarsine was added to 10-ml. samples of the conductivity solutions. With 10^{-3}M-solutions this corresponds to a 246-fold molar excess.

It is obvious that all complexes of the type ZnDiarsine,X$_2$ exist almost entirely as the non-electrolyte; the small conductivity suggests, however, some small amount (<5%) of change-over to form either [ZnDiarsine,X,PhNO$_2$]$^+$X$^-$ or, more probably, [Zn(Diarsine)$_2$]-[ZnX$_4$]. Much the same holds for the complexes of cadmium, but for the mercury complexes the conductivity is definitely higher, suggesting that the amount of [HgX$_4$]$^{2-}$ ion formed is appreciable. Displacement of the equilibrium 2[MDiarsine,X$_2$] $\rightleftharpoons$ [M(Diarsine)$_2$]$^{2+}$[MX$_4$]$^{2-}$ to the right is expected to be favoured by solvents which stabilise ions (*i.e.*, those solvents with a high dielectric constant and good solvating power for ions—the latter implying that they have polar centres available to facilitate attachment of solvent to the ions).

Molecular-weight data for the iodides of each of these three metals in acetone are shown in Table 5. It is clear that in this solvent decomposition of ZnI$_2$,Diarsine is much more marked than for Cd or the cadmium or mercury analogue. (This cannot be the equilibrium 2M^{II}-Diarsine,I$_2$ $\rightleftharpoons$ [M(Diarsine)$_2$][MI$_4$] since the number of particles is the same on each side.) We presume that, in the case of the zinc complex, acetone enters the co-ordination sphere, liberating iodide ions. An equilibrium of the type [ZnDiarsine,I$_2$] + Acetone $\rightleftharpoons$ [ZnDiarsineAcetone,I]$^+$ + I$^-$, is envisaged. Similar equilibria have been postulated for various cobaltous complexes dissolved in acetone.[9]

TABLE 5.

Molecular weights, determined in acetone by isothermal distillation at 25°. All the complexes described are colourless.

Compound	Molecular weight found	Molecular weight calc.	Concn. (% w/w)
[ZnDiarsineI$_2$]	391	605	0·61
[CdDiarsineI$_2$]	516	652	1·06
[HgDiarsineI$_2$]	655	740	1·84

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[9] Buffagni and Dunn, *Nature*, 1960, **188**, 4754.

Addition of an excess of Diarsine causes a marked increase in conductivity; the equilibrium MDiarsine,X_2 + Diarsine $\rightleftharpoons$ [M(Diarsine)$_2$]$^{2+}$ + 2X^- being displaced to the right. However, it is noteworthy that the maximum conversion (with HgDiarsineCl_2), as indicated by the increase in conductivity, is only 10—20%.

The bis-Diarsine metal diperchlorates of each of the three elements have been prepared, and their molecular conductivities in nitromethane indicate that they are all strong electrolytes. As in earlier work on monodentate arsines, all zinc(II), cobalt(II), and mercury(II) complexes are four-co-ordinate.[10]

The variation in stability of the copper(I), silver(I), and gold(I), and the zinc(II), cadmium(II), mercury(II) triads calls for comment. The two most obvious factors likely to influence this stability, so far as the metal is concerned, are: (i) the capacity of the metal atom to form (dative) d_π–d_π-bonds to the arsenic atom by using electrons of the d^{10}-shell of the metal atom; (ii) the polarising power of the metal atom and hence its tendency to form covalent rather than ionic bonds and to favour co-ordination with the arsenic atom rather than with the solvent in aqueous-alcoholic solution.

For reasons developed elsewhere,[7] we do not consider that double bonding is important in these Diarsine complexes. It is considered that the relative order of double bonding is related to the ionisation potential of the non-bonding d^{10}-shell of the metal atom.[7] The value for Ni^0 is 5·83 v; for Pd^0 and Pt^0, which do not appear even to form carbonyls, the values are 8·3 and 8·2 v, respectively. The ionisation potentials of Cu^{1+}, Ag^{1+}, and Au^{1+} are 20·3, 21·5, and 20·5 v, respectively; for Zn^{2+}, Cd^{2+}, and Hg^{2+} they are 39·7, 44·5, and 34·2 v, respectively. It seems difficult to believe that, in these circumstances, double bonding to the arsenic atom plays an important role for the Group I or Group II atoms considered above.

When we consider, however, the polarising power of the metal atoms we find that there is a much greater tendency for covalent-bond formation by Au^+ and Hg^{2+} than by the lighter elements in their respective groups. Elsewhere[11] we have used the ratio R = I.P.(r/e) (where I.P. = total ionisation potential, e = formal charge corresponding to the oxidation state, and r = ionic radius for the ion) as a rough guide as to the relative ease with which covalent, compared with ionic, bonding will occur. We also take this value as a guide to the stability of Diarsine complexes with respect to the more polar water molecule. Values of R for Cu^+, Ag^+, and Au^+ are, respectively, 7·4, 9·5, and 12·7. For Zn^{2+}, Cd^{2+}, and Hg^{2+} the values are 10·1, 12·6, and 16·1. It is not easy to compare the former owing to the ease with which the silver complexes decompose, depositing silver halide. However, zinc, cadmium, and mercury complexes are all soluble, so their comparison is easier. It is apparent that the much greater resistance of HgDiarsine,X_2 than of Zn^{2+} and Cd^{2+} complexes to aquation can be explained readily in terms of the trend of R values, namely, that $R_{Hg^{2+}} > R_{Cd^{2+}} > R_{Zn^{2+}}$. It is known[12] that the hydration energy of Zn^{2+} (491·5 kcal. mole^{-1}) is considerably larger than that of Cd^{2+} (436·5 kcal. mole^{-1}) or Hg^{2+} (440·9 kcal. mole^{-1}), in agreement with the view developed above that, relatively, Zn^{2+} evolves more energy in forming an essentially ionic bond than does Cd^{2+} or Hg^{2+}.

EXPERIMENTAL

All the complexes described are colourless.

*Di-(*o*-phenylenebisdimethylarsine)silver*(I) *Dichloroargentate*(I).—Silver chloride (0·2 g.) was refluxed with Diarsine (0·8 g.) in alcohol (50 ml.); after 4 hr. most of the solid had dissolved and the filtered solution was evaporated under reduced pressure to 20 ml. After addition of ether (250 ml.) the solution was left overnight. The crystals which were formed were filtered

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[10] Anderson and Burrows, *J. Proc. Roy. Soc., N.S.W.*, 1936, **70**, 63; Burrows and Lench, *ibid.*, pp. 218, 222; Evans, Mann, Pieser, and Purdie, *J.*, 1940, 1209.

[11] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

[12] "Chemistry and Metallurgy of Miscellaneous Materials," ed. L. L. Quill, McGraw Hill, New York, 1960, p. 167.

off (0·35 g.), washed with alchol and ether, and dried *in vacuo* (Found: C, 27·8; H, 3·8; Ag, 24·8. $C_{20}H_{32}Ag_2As_4Cl_2$ requires C, 28·0; H, 3·8; Ag, 25·1%). The *complex* is insoluble in water and alcohol and sparingly soluble in nitrobenzene. When heated, the complex decomposed without melting, as did practically all others.

Di-(o-*phenylenebisdimethylarsine*)*silver*(I) *Dibromoargentate*(I).—Silver bromide (0·2 g.) was treated with Diarsine (0·61 g.) in alcohol (50 ml.), as described above for the chloro-complex. Crystals (0·25 g.) of the required *compound* were obtained (Found: C, 25·8; H, 3·8; Ag, 22·5. $C_{20}H_{32}Ag_2As_4Br_2$ requires C, 25·3; H, 3·4; Ag, 22·8%). The compound has solubilities similar to those of the chloro-complex.

Di-(o-*phenylenebisdimethylarsine*)*silver*(I) *Di-iodoargentate*(I).—Silver nitrate (0·17 g.) in aqueous alcohol (10 ml.) was treated with Diarsine (0·57 g.) in alcohol. The solution was warmed, filtered, and treated with a solution of potassium iodide (1·0 g.) in water (10 ml.). The precipitated crystals were filtered off (0·35 g.), washed with alcohol and ether, and dried *in vacuo* (Found: C, 22·95; H, 3·2; Ag, 20·45. $C_{20}H_{32}Ag_2As_4I_2$ requires C, 23·1; H, 3·1; Ag, 20·7%). The *compound* has solubilities similar to those of the chloro-complex. Nitrobenzene solutions slowly deposited a white decomposition product.

Di-(o-*phenylenebisdimethylarsine*)*silver*(I) *Dinitroargentate*(I).—Silver nitrite (0·15 g.) was refluxed with Diarsine (0·57 g.) in alcohol (30 ml.) for 3 hr., by which time the solid had nearly dissolved; the filtered solution was then treated with ether (300 ml.) and left overnight in the refrigerator. The resulting crystals (0·25 g.) of the *complex* were washed with alcohol and ether and dried *in vacuo* (Found: C, 27·3; H, 3·8; N, 2·9. $C_{20}H_{32}Ag_2As_4N_2O_4$ requires C, 27·3; H, 3·7; N, 3·2%). The complex is sparingly soluble in nitrobenzene, water, and alcohol.

Di-(o-*phenylenebisdimethylarsine*)*silver*(I) *Nitrate*.—Silver nitrate (0·17 g.) was dissolved in alcohol (25 ml.) containing Diarsine (0·57 g.). The solution was warmed, filtered, and evaporated under reduced pressure. The resulting crystals (0·65 g.) were washed with alcohol and ether (Found: C, 32·6; H, 4·5; N, 1·9; At, 14·75. $C_{20}H_{32}AgAs_4NO_3$ requires C, 32·4; H, 4·3; N, 1·9; Ag, 14·5%). The *complex* is soluble in water, alcohol, and nitromethane and insoluble in benzene.

Di-(o-*phenylenebisdimethylarsine*)*silver*(I) *Perchlorate*.—Silver nitrate (0·17 g.) was dissolved in aqueous alcohol (20 ml.) and treated with Diarsine (0·57 g.) in alcohol (20 ml.). The solution was warmed, filtered, and treated with 72% perchloric acid (5 ml.). The resulting precipitate (0·6 g.) was washed with alcohol and ether and dried *in vacuo* (Found: C, 31·1; H, 4·3; Ag, 13·7. $C_{20}H_{32}AgAs_4ClO_4$ requires C, 30·8; H, 4·1; Ag, 13·8%). The *complex* is soluble in alcohol, acetone, and nitromethane and insoluble in water.

Dibromomono-(o-*phenylenebisdimethylarsine*)*zinc*(II).—Anhydrous zinc bromide (0·34 g.), dissolved in alcohol (5 ml.), was treated with Diarsine (0·43 g.). The resulting colourless solution was evaporated nearly to dryness in a vacuum-desiccator, yielding crystals. These (0·4 g.) were washed with small portions of acetone and ether (Found: C, 23·35; H, 3·5; Br, 31·15. $C_{10}H_{16}As_2Br_2Zn$ requires C, 23·5; H, 3·15; Br, 31·3%). The *complex* is soluble in acetone and alcohol and sparingly soluble in benzene. It decomposed immediately on treatment with water, yielding free Diarsine.

Di-iodomono-(o-*phenylenebisdimethylarsine*)*zinc*(II).—Anhydrous zinc iodide (0·32 g.), dissolved in alcohol (10 ml.), was treated with Diarsine (0·28 g.), as described above for the bromo-complex, yielding crystals (0·5 g.) (Found: C, 19·5; H, 3·0. $C_{10}H_{16}As_2I_2Zn$ requires C, 19·8; H, 2·7%). Rapid dissociation occurs on freezing of a 0·49% solution; the value of M from the first freezing of a 0·49% solution was 579, but values in the range 440—450 were obtained in successive freezings. The *complex* is soluble in acetone and alcohol and very soluble in ether and benzene. It decomposed immediately on treatment with water, yielding free Diarsine.

Di-(o-*phenylenebisdimethylarsine*)*zinc*(II) *Perchlorate*.—Zinc nitrate hexahydrate (0·049 g.), in alcohol (14 ml.), was treated with Diarsine (0·24 g.) in alcohol (6 ml.), and the resulting solution refluxed for a few minutes. 72% Perchloric acid (20 ml.) was added, giving a precipitate (0·12 g.) that after several hours was filtered off, washed with alcohol and ether, and vacuum-dried (Found: C, 28·7; H, 3·8. $C_{20}H_{32}As_4Cl_2O_8Zn$ requires C, 28·7; H, 3·9%). The *complex* is very sparingly soluble in acetone and nitromethane and is decomposed by water.

Dichloromono-(o-*phenylenebisdimethylarsine*)*cadmium*(II).—A solution of cadmium chloride dihydrate (0·31 g.) in alcohol (10 ml.) was treated with Diarsine (0·38 g.). The white precipitate was redissolved in alcohol (30 ml.) by boiling. On cooling, the solution deposited needles (0·3 g.). These were filtered off, washed with ether, and vacuum-dried (Found: C, 25·8; H, 3·7; Cl, 15·0. $C_{10}H_{16}As_2CdCl_2$ requires C, 25·6; H, 3·4; Cl, 15·1%). The *complex* is soluble in alcohol and insoluble in nitromethane. It was decomposed immediately by water.

Dibromomono-(o-*phenylenebisdimethylarsine*)*cadmium*(II).—Cadmium bromide (0·11 g.) in alcohol (4 ml.) was treated with Diarsine (0·11 g.). The white precipitate was dissolved in alcohol (2 ml.) by boiling. On cooling, crystals (0·15 g.) were deposited. These were washed with ether and vacuum-dried (Found: C, 21·7; H, 2·8. $C_{10}H_{16}Ag_2Br_2Cd$ requires C, 21·5; H, 2·9%). The *complex* has similar solubilities to those of the cadmium chloro-complex.

Di-iodomono-(o-*phenylenebisdimethylarsine*)*cadmium*(II).—Cadmium iodide (0·15 g.) in alcohol (5 ml.) was added to Diarsine (0·12 g.) in warm alcohol (5 ml.). On cooling, the solution deposited needles (0·25 g.). These were washed with ether and vacuum-dried (Found: C, 18·5; H, 2·8; I, 39·2. $C_{10}H_{16}As_2I_2Cd$ requires C, 18·4; H, 2·5; I, 38·9%. Fairly rapid dissociation appeared to occur in freezing nitrobenzene solution. The values of *M* obtained on successive freezings of a 0·53% solution were 582, 500, 465. The *complex* is soluble in alcohol, acetone, and nitromethane but is decomposed by water.

Di-(o-*phenylenebisdimethylarsine*)*cadmium*(II) *Perchlorate*.—A solution of cadmium chloride dihydrate (0·11 g.) in water (5 ml.) and alcohol (10 ml.) was treated with Diarsine (0·29 g.) in alcohol (10 ml.). The resulting solution was boiled and treated with 72% perchloric acid (10 ml.). The *complex* was filtered off after 0·5 hr., washed with alcohol and ether, and vacuum-dried (Found: C, 27·5; H, 3·8. $C_{20}H_{32}As_4Cl_2O_8Cd$ requires C, 27·2; H, 3·65%). It is sparingly soluble in acetone and nitromethane but is decomposed by water.

Dichloromono-(o-*phenylenebisdimethylarsine*)*mercury*(II).—A solution of mercuric chloride (0·16 g.) in alcohol (20 ml.) was added in small portions to Diarsine (0·34 g.) in alcohol (20 ml.). The resulting solution was warmed; on cooling, it deposited needles (0·4 g.). These were washed with alcohol and ether and vacuum-dried (Found: C, 21·7; H, 3·0. $C_{10}H_{16}As_2Cl_2Hg$ requires C, 21·5; H, 2·9%). The *complex* is soluble in alcohol, acetone, and nitromethane, but insoluble in cold water, no decomposition occurring, but in boiling water.there was slight decomposition.

Dibromomono-(o-*phenylenebisdimethylarsine*)*mercury*(II).—Mercuric bromide (0·18 g.) in alcohol (10 ml.) was added in small portions, with shaking, to Diarsine (0·29 g.) in alcohol (10 ml.). The precipitate dissolved when the solution was boiled; crystals that were deposited from the cold solution were washed with alcohol and ether and vacuum-dried (0·4 g.) (Found: C, 18·8; H, 2·8. $C_{10}H_{16}As_2Br_2Hg$ requires C, 18·6; H, 2·5%). The *complex* is soluble in alcohol and acetone and insoluble in cold water in which it is not decomposed.

Di-iodomono-(o-*phenylenebisdimethylarsine*)*mercury*(II).—A solution of mercuric iodide (0·23 g.) in hot alcohol (10 ml.) was added to Diarsine (0·28 g.) in alcohol (10 ml.). The crystals (0·3 g.) deposited on cooling were washed with alcohol and ether and vacuum-dried (Found: C, 16·5; H, 2·5. $C_{10}H_{16}As_2I_2Hg$ requires C, 16·2; H, 2·2%. The *complex* is soluble in alcohol, acetone, and benzene.

Di-(o-*phenylenebisdimethylarsine*)*mercury*(II) *Perchlorate*.—Mercuric chloride (0·14 g.) in alcohol (20 ml.) containing 10N-hydrochloric acid (5 ml.) was warmed and then treated with Diarsine (0·49 g.) in alcohol (20 ml.). 72% Perchloric acid (10 ml.) was added, giving a precipitate. After 2 hr. the suspension was warmed and the precipitate filtered off (0·2 g.), washed with water and alcohol, and vacuum-dried (Found: C, 25·0; H, 3·5. $C_{20}H_{32}As_4Cl_2HgO_8$ requires C, 24·7; H, 3·3%). A few hours after precipitation the *complex* had become pale pink. It is sparingly soluble in acetone and nitromethane and insoluble in water in which it is not decomposed.

Magnetic-susceptibility Measurements.—These were carried out by the Gouy method. In all cases the compounds are diamagnetic.

Isopiestic Molecular-weight Determinations.—The Signer isothermal distillation method, as described by Clark,[13] was used. Recrystallised azobenzene was used as the standard.

Analyses.—Some of the carbon, hydrogen, and nitrogen micro-analyses were carried out by the Micro-analytical Department of the Imperial College of Science and Technology. Silver was determined electrolytically in aqueous potassium cyanide. Halogen was determined gravimetrically.

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[13] Clark, *Ind. Eng. Chem., Analyt.*, 1941, **13**, 820.