850. *The Ditertiary Arsine Complexes of Nickel, Palladium, and Platinum.*

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The ditertiary arsine complexes of bivalent platinum have been prepared and characterised. Their properties are compared with those of the corresponding compounds of bivalent nickel and palladium. Conductivity measurements and spectrophotometric studies in nitromethane show that all three metals give presumably five-co-ordinate cations of the type $[M^{II}(Diarsine)_2Hal]^+$. In water this complex cation is largely dissociated to yield the four-co-ordinate $[M^{II}(Diarsine)_2]^{2+}$ ion but the five-co-ordinate nickel ion is much more stable. Possible explanations for these differences are examined. Quadrivalent palladium and platinum complexes of the type $[M^{IV}(Diarsine)_2X_2][ClO_4]_2$ have been prepared for the first time. Their properties are discussed. The different kinds of ditertiary arsine complexes formed by nickel, palladium, and platinum in the various oxidation states are summarised.

The ditertiary arsine chelate *o*-phenylenebisdimethylarsine (Diarsine), was first prepared by Chatt and Mann,[1] who described the compounds $[Pd(Diarsine)Cl_2]^0$, $[Pd(Diarsine)_2][PdCl_4]$, and $[Pd(Diarsine)_2]Cl_2$. Later [2] we showed that in addition to quadricovalent palladium(II) complexes of the type $[Pd(Diarsine)_2][ClO_4]_2$, compounds of the general formula $[Pd(Diarsine)_2Hal]ClO_4$ could be prepared. The latter behave as uni-univalent electrolytes in nitrobenzene and it was concluded that the Pd^{II} atom was quinquecovalent, at least in this solvent. Continuous-variation spectrophotometric evidence in support of this 1 : 1 association of the $[Pd(Diarsine)_2]^{2+}$ ion with halide was also presented. Complexes of the type $Pd(Diarsine)_2Hal_2$ also behave as uni-univalent electrolytes in nitrobenzene. Single-crystal *X*-ray studies,[3] however, indicate that in the solid state the di-iodide contains a sexicovalent palladium(II) atom which is tetragonally co-ordinated. The apparently quinquecovalent complex ions of the type $[Pd(Diarsine)_2Hal]^+$ could also be sexicovalent in solution if the presence of a solvent molecule in the sixth position is postulated. This will be discussed below.

In the present investigation we studied the corresponding complexes of bivalent nickel and platinum in order to compare the tendencies of these three metal atoms to form quinque- and sexi-covalent complexes. We also wished to characterise and examine the Diarsine complexes of palladium and platinum when the oxidation state is greater than two.

Nickel Complexes.—The bivalent-nickel complexes $[Ni(Diarsine)_2][ClO_4]_2$ and $Ni(Diarsine)_2Hal_2$ (Hal = Cl, Br, I, and CNS) had been isolated previously [4] in connection with

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[1] Chatt and Mann, *J.*, 1939, 610.
[2] Harris and Nyholm, *J.*, 1956, 4375.
[3] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.
[4] Nyholm, *J.*, 1950, 2061.

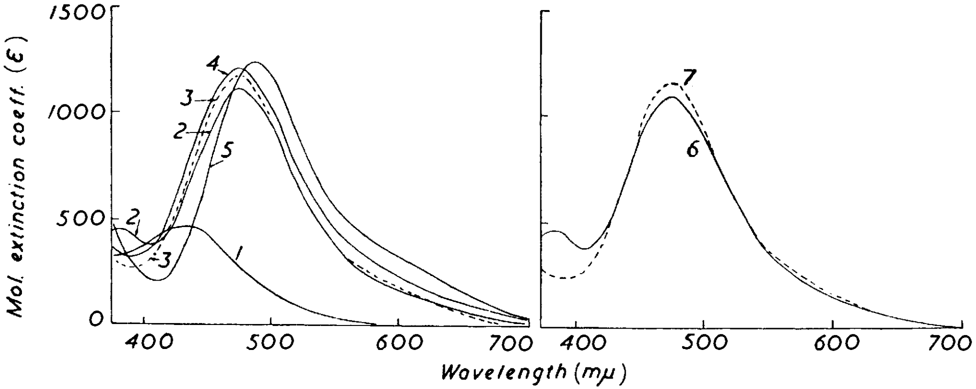
studies on the preparation of nickel(III) compounds but few of their physical properties had been studied in detail. Certain new halogeno-perchlorates have now been obtained. The spectra and conductivities in nitromethane of the various complexes investigated are listed in Table 1. The conductivity data indicate that the diperchlorate is markedly different from the other compounds listed. From studies on a large number of compounds it is known that the molecular conductivity of a 10^{-3}M-solution of a uni-univalent electrolyte in nitromethane is 70—80 r.o., whereas for a uni-bivalent electrolyte it is nearer 160 r.o.

TABLE 1.

Compound *	Colour	Mol. cond. (r.o.) at 25° in MeNO$_2$ (C = M/1000)	Spectrum $\lambda_{max.}$ (mμ)	ε
[Ni(Diarsine)$_2$][ClO$_4$]$_2$	Orange	157	433	470
[Ni(Diarsine)$_2$Cl]Cl	Red	73	383 475	460 1120
[Ni(Diarsine)$_2$Cl]ClO$_4$	Red	83	383 475	470 1110
[Ni(Diarsine)$_2$Br]Br	Brown	78	475	1190
[Ni(Diarsine)$_2$Br]ClO$_4$	Red-brown	82	475	1170
[Ni(Diarsine)$_2$SCN]SCN	Red-brown	83	475	1200
[Ni(Diarsine)$_2$I]I	Dark brown	80	485 620 w sh	1240 250
[Ni(Diarsine)$_2$NO$_3$]NO$_3$	Brown	93	—	—

* Compounds such as Ni(Diarsine)$_2$Cl$_2$ which behave as uni-univalent electrolytes in MeNO$_2$ are formulated as such, *i.e.*, [Ni(Diarsine)$_2$Cl]Cl. In the absence of crystal-structure data on these compounds it seems unwise to assume that they are all necessarily similar to Pd(Diarsine)$_2$I$_2$; see also reference below to Powell's work.[3]

FIG. 1. FIG. 2.



FIGS. 1 and 2. *Absorption spectra of nitromethane solutions of*:

(1) [Ni(Diarsine)$_2$][ClO$_4$]$_2$; (2) [Ni(Diarsine)$_2$Cl]Cl; (3) [Ni(Diarsine)$_2$Br]Br; (4) [Ni(Diarsine)$_2$SCN]SCN; (5) [Ni(Diarsine)$_2$I]I; (6) [Ni(Diarsine)$_2$Cl]ClO$_4$; (7) [Ni(Diarsine)$_2$Br]ClO$_4$.

Thus, it is reasonable to postulate that, whereas the diperchlorate is a bi-univalent electrolyte in this solvent, one of the halogen atoms in all other compounds is covalently bound to the nickel atom. This can be correlated with the spectra of the compounds, all of which, except that of the diperchlorate, show a characteristic band near 480 mμ (see Figs. 1 and 2). The similarity between the dihalides and the halogeno-perchlorates is specially noteworthy. Continuous-variation spectroscopy has also been carried out on several compounds, and a 1 : 1 combination of [Ni(Diarsine)$_2$]$^{2+}$ ion with halide ion is confirmed.

A conductimetric titration of [Ni(Diarsine)$_2$][ClO$_4$]$_2$ in nitromethane with both triphenylmethylarsonium chloride and iodide has also been carried out. A sharp end-point is obtained when only one equivalent of the halide has been added. (See Figs. 3 and 4.)

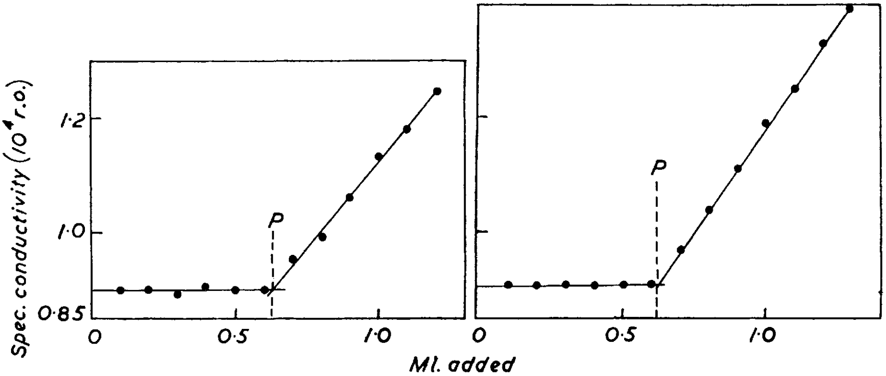
Platinum Complexes.—The properties of the bivalent platinum complexes which have been prepared are listed in Table 2. The conductivity values are similar to those of the

TABLE 2. *Molecular conductivities of platinum*(II)*-diarsine complexes in nitromethane.*

Compound	Colour	Mol. cond. (r.o.) at 25° in $MeNO_2$ (C = 0·9—1·2 × 10^{-3}M)	Compound	Colour	Mol. cond. (r.o.) at 25° in $MeNO_2$ (C = 0·9—1·2 × 10^{-3}M)
$[Pt(Diarsine)_2][PtCl_4]$	Pink	Insol.	$[Pt(Diarsine)_2Br]Br$	Yellow	75
$[Pt(Diarsine)_2][ClO_4]_2$	White	175	$[Pt(Diarsine)_2Br]ClO_4$	Yellow	93
$[Pt(Diarsine)_2NO_3]NO_3$	White	150	$[Pt(Diarsine)_2I]I$	Yellow	73
$[Pt(Diarsine)_2Cl]Cl$ ...	Pale yellow	76	$[Pt(Diarsine)_2I]ClO_4$	Yellow	78
$[Pt(Diarsine)_2Cl]ClO_4$	Pale yellow	108	$[Pt(Diarsine)_2SCN]SCN$	Pale yellow	100

nickel compounds except that there is evidence for a greater degree of dissociation to form the four covalent $[Pt(Diarsine)_2]^{2+}$ ion than occurs with nickel. The diperchlorate is clearly a bi-univalent electrolyte; the nitrate is similar but shows slight evidence of association.

FIG. 3. FIG. 4.



FIGS. 3 and 4. *Conductimetric titration of* 25·0 *ml. of* 5 × 10^{-4}M-$[Ni(Diarsine)_2][ClO_4]_2$ *with* (Fig. 3) 2 × 10^{-2}M-$[Ph_3MeAs]Cl$ *or* (Fig. 4) 2 × 10^{-2}M-$[Ph_3MeAs]I$ *in nitromethane at* 25°. P = *calc. end-point.*

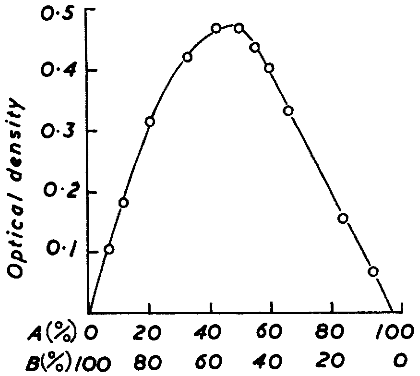


FIG. 5. *Continuous-variation study of* (*A*) M/500-NMe_4Br *and* (*B*) M/500-$[Pt(Diarsine)_2][ClO_4]_2$ *in nitromethane at* 377 mμ (*corr. for absorption by constituents*).

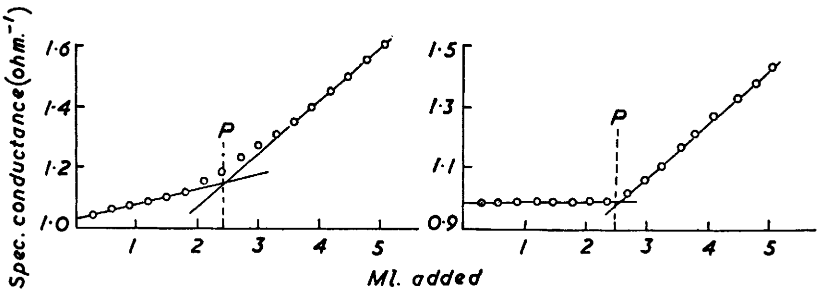
The other compounds have conductivities which indicate uni-univalent electrolytes except that in certain cases, *e.g.*, the thiocyanate, there is definite evidence for dissociation of the $[Pt(Diarsine)_2CNS]^+$ ion.

As with the nickel complexes a continuous-variation spectrophotometric study was carried out to study the reaction between the $[Pt(Diarsine)_2]^{2+}$ ion and halide ions. The result for the bromide ion is shown in Fig. 5, a 1 : 1 combination occurring. Finally, the 1 : 1 combination may also be demonstrated by conductimetric titration. Figs. 6 and 7 are graphs for the conductimetric titration of $[Pt(Diarsine)_2][ClO_4]_2$ in nitromethane with tetraethylammonium chloride and iodide: a sharp break in the curve occurs after one equivalent of the halide ion has been added.

Thus, it has been demonstrated that, as with the $[Pd(Diarsine)_2]^{2+}$ ion, the co-ordination numbers of both the nickel(II) and platinum(II) complex ions increase from four to five in nitromethane solution on the addition of a halide ion; the complex cation can be isolated in all cases as the perchlorate.

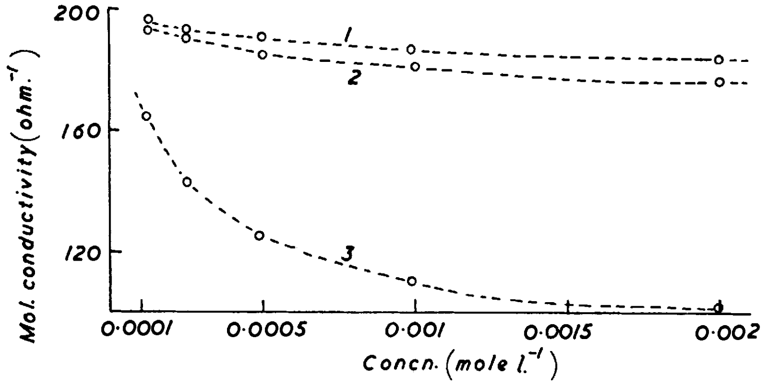
It is of interest to compare the relative ease with which the ions $[Ni(Diarsine)_2]^{2+}$, $[Pd(Diarsine)_2]^{2+}$, and $[Pt(Diarsine)_2]^{2+}$ attach a halide ion. One method for doing this is to study the equilibrium, $[M(Diarsine)_2]^{2+} + Hal^-_{(solv.)} \rightleftharpoons [M(Diarsine)_2Hal] + Solvent$, in a solvent such that the solvation energy of the halide ion is competing with the metal–halogen bond energy: it is assumed, of course, that the solvation of the complex cation is small enough for any differences between the three metals to be ignored. Clearly a more strongly solvating medium for the halide ion than nitromethane is needed if appreciable dissociation is to occur, and water is convenient for this purpose. The molecular conductivity of a 10^{-3}M-aqueous solution of complexes of the type $M(Diarsine)_2Cl_2$ at 20° increases in the order $Ni(Diarsine)_2Cl_2$ (109 r.o.) $<$ $Pd(Diarsine)_2Cl_2$ (180 r.o.) $\simeq$ $Pt(Diarsine)_2Cl_2$ (186 r.o.). A plot of Λ_M against concentration is given in Fig. 8. There is not much difference between the behaviour of $Pd(Diarsine)_2Cl_2$ and $Pt(Diarsine)_2Cl_2$, but the nickel compound shows very much greater association. No attempt is made here to obtain from these Figures degrees of dissociation of the $[M(Diarsine)_2X]^+$ ions, owing to uncertainty as to the values of the ionic mobilities. Indeed attempts to do this are largely vitiated owing to the insolubility of the $[M^{II}(Diarsine)_2][ClO_4]_2$ complexes in water at the concentrations employed, from which values the ionic mobility of the $[M(Diarsine)_2]^{2+}$ ions

FIG. 6. FIG. 7.



FIGS. 6 and 7. *Conductimetric titration of* 25·0 ml. *of* 5×10^{-4}M-$[Pt(Diarsine)_2][ClO_4]_2$ *by* (Fig. 6) 0·01M-NMe_4Cl *and* (Fig. 7) 0·01M-NEt_4I. *P = calc. end-point. Specific conductance is corrected for dilution.*

FIG. 8. *Molecular conductivity, in water, of* $M^{II}(Diarsine)_2Cl_2$ *at* 20°. M = (1) Pt, (2) Pd, (3) Ni.



could be obtained. Nevertheless, it is clear that, in water, the relative tendencies for halogen ions to associate with the $[M^{II}(Diarsine)_2]^{2+}$ ions are in the order Ni $>$ Pd $\gtrsim$ Pt. It has been found that the molecular conductivities of the dibromides in water and the dinitrates in nitromethane indicate the same sequence.

As a separate investigation we are studying these equilibria by spectrophotometric measurements, paying particular attention to the rôle of the solvent and possible metal–solvent interaction.

At present it is not possible to be certain of the reason for the above order. It is perhaps significant, however, that the Haissinsky electronegativities increase in the order Ni (1·7) $<$ Pd (2·0) $\leqslant$ Pt (2·1); also the sums of the first and the second ionisation potentials for Ni, Pd, and Pt are respectively 25·8, 28·2, and 27·5 v. If the electronegativity be taken as a measure of the charge transfer in the σ-bond from the donor (As) atom to the metal atom, then a larger electron-transfer from the ligand to the metal occurs with palladium and platinum than with nickel.

As a result the positive charge on the metal atom decreases in the order Ni $>$ Pd $\geqslant$ Pt. This could be visualised as providing a means of attaching the negative halogen ion and hence might explain the observed order. So far we have ignored the possible effect of d_π–d_π bonding which would also increase the positive charge on the metal atom and hence facilitate the attachment of the halogen atom in the fifth position. There is no simple way of comparing the relative capacity of these three metals for d_π–d_π bond formation. If we assume that carbonyl complexes are the ideal examples of double-bond formation between metal and ligand it may be significant that, whereas nickel carbonyl is easily prepared, palladium and platinum carbonyls are unknown, at least as yet. If this is attributed to a decreasing capacity of the metal to form d_π-bonds as we pass from nickel to palladium and platinum, an alternative reason for a steady decrease in the positive charge on the metal in the sequence Ni $>$ Pd $\gtrapprox$ Pt is provided. Thirdly, it is known that the energy separation $ns \longrightarrow np$ for platinum(II) is much greater than for the other two metals. This is undoubtedly a contributing factor. The subject will be discussed shortly.

The number of known compounds in which the co-ordination number of bivalent diamagnetic nickel, palladium, and platinum exceeds four is relatively small. Although it is possible to obtain quinque- and sexi-co-ordinate complexes of palladium in solution, given a sufficiently high concentration of halide ions [5] (*e.g.* $[PdCl_6]^{4-}$ and $[PdBr_6]^{4-}$), it is usually necessary to use easily polarisable ligands such as tertiary arsines. The tritertiary arsine $MeAs([CH_2]_3{\cdot}AsMe_2)_2$ gives rise to sexicovalent complexes of the type $[M^{II}(Triarsine)_2]^{2+}$ with all three metals,[6,7] and methyl cyanide gives [8] the sexico-ordinate platinum compound $[Pt(MeCN)_2(NH_3)_4]Cl_2$. There is little doubt that many more quinque- and sexi-co-ordinate complexes could be obtained by suitable choice of ligands. Owing to the d^8 spin-paired configuration one expects all these sexico-ordinate complexes to be tetragonal.

Complexes of Oxidation State Higher than Two.—Earlier [4,9] we described tervalent and quadrivalent nickel complexes of the types $[Ni^{III}(Diarsine)_2X_2]X$ and $[Ni^{IV}(Diarsine)_2X_2]^{2+}[ClO_4]_2$ ($X = Cl$ and Br), and we have now examined the behaviour of both palladium(II)- and platinum(II)-diarsine complexes towards oxidising agents. No definite evidence for the existence of complexes of palladium(III) or platinum(III) has been obtained although some impure weakly paramagnetic derivatives were obtained on oxidation with dilute nitric acid; these are being further investigated. However, derivatives of palladium(IV) and platinum(IV) in complexes of the general type $[M^{IV}(Diarsine_2X_2]^{2+}[Y^-]_2$ ($X = Cl$, Br, I; $Y = ClO_4^-$ or NO_3^-) have been obtained readily. The platinum derivatives are the more stable, as is usual. The simplest preparation is by treating the complex $M^{II}(Diarsine)_2X_2$, *e.g.*, $Pt(Diarsine)_2Cl_2$, with concentrated nitric acid (containing

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[5] Sundaram and Sandell, *J. Amer. Chem. Soc.*, 1955, **77**, 855.

[6] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

[7] Parish, Thesis, London, 1958.

[8] Tschugaev and Lebedinsky, *Compt. rend.*, 1915, **161**, 563.

[9] Nyholm, *J.*, 1951, 2602.

a little hydrochloric acid in the case of the chloride). Oxidation occurs and addition of perchloric acid to the resulting solution yields the quadrivalent-metal complex. The properties of these complexes are given in Table 3.

TABLE 3. *Properties of diarsine complexes of platinum*(IV) *and palladium*(IV).

Compound	Colour	Mol. cond. (r.o.) in $MeNO_2$ at 25° ($C = 10^{-3}$M)
$[Pt(Diarsine)_2Cl_2][ClO_4]_2$	Pale yellow	172
$[Pt(Diarsine)_2Br_2][ClO_4]_2$	Yellow	168
$[Pt(Diarsine)_2I_2][ClO_4]_2$	Orange-red	161 *
$[Pt(Diarsine)_2I_2][NO_3]_2$	Orange-red	—
$[Pt(Diarsine)_2Cl_2][ClO_4]_2$	Orange	176
$[Pt(Diarsine)_2Br_2][ClO_4]_2$	Red	169

* $C = 0{\cdot}6 \times 10^{-3}$M.

The iodo-compound $[Pt^{IV}(Diarsine)_2I_2](NO_3)_2$ was also isolated. When this dinitrate is treated with potassium iodide in aqueous solution, an insoluble greenish-black compound $Pt(Diarsine)_2I_4$ is precipitated. If this had the structure $[Pt^{IV}(Diarsine)_2I_2][I]_2$ an orange-reddish colour would be expected (in accord with known colour of the cation). The actual colour and an absorption band similar to that of the I_3^- ion suggest the presence of *bivalent* platinum; however, owing to its low solubility this complex was not further investigated. Use of halogens as oxidising agents leads to products which are of indefinite composition but appear to be impure platinum(IV) derivatives. As confirmation it is possible, after addition of perchloric acid, to isolate fairly pure complexes of the type $[Pt(Diarsine)_2X_2][ClO_4]_2$. The quadrivalent derivatives are all reduced by sulphur dioxide in aqueous suspension to the white complex $[Pt^{II}(Diarsine)_2][ClO_4]_2$.

In the case of palladium the complexes $[Pd(Diarsine)_2Cl_2][ClO_4]_2$ and $[Pd(Diarsine)_2Br_2][ClO_4]_2$, but not the corresponding iodo-compound, have been prepared. Oxidation was again more conveniently effected with nitric acid rather than with halogens. These compounds are appreciably more stable than the corresponding derivatives of monodentate arsines,[10] *e.g.*, as prepared by the action of halogens on $[Pd(Ph_2MeAs)_2Br_2]^0$.

In Table 4 the known compounds of these three metals with the Diarsine are shown and their inter-relations are indicated. In the Table there are certain compounds for which new physical data are available, which have not been published previously and it is convenient to record this information here.

TABLE 4. *Summary of known ditertiary arsine complexes of nickel, palladium, and platinum.*

(Unless otherwise specified, X may be Cl, Br, I, CNS, NO_2, or NO_3.)

Oxid. state	Co-ordin. no.	Ni	Pd	Pt
0	4	$[Ni(CO)_2Diarsine]^0$	—	—
		$[Ni(Diarsine)_2]^0$ [a]	—	—
	6	$[Ni(Diarsine)_3][ClO_4]_2$	—	—
		$[Ni(Diarsine)_2I_2]^0$ in crystal.[b]	$[Pd(Diarsine)_2I_2]^0$ in crystal.	$[Pt(Diarsine)_2I_2]^0$ in crystal.
II	5	$[M(Diarsine)_2X]ClO_4$ (M = Ni, Pd, and Pt) in solvents such as $MeNO_2$ and $PhNO_2$. Probably sexicovalent in the crystal [c]		
	4	$[Ni(Diarsine)X_2]^0$ (X = Br, I)	$[Pd(Diarsine)X_2]^0$ (X = Br, I)	—
		$M(Diarsine)_2][ClO_4]_2$ (M = Ni, Pd, and Pt)		
III	5	$[Ni(Diarsine)Br_3]^0$	—	—
	6	$[Ni(Diarsine)_2Cl_2]Cl$	—	—
IV	6	$[M(Diarsine)_2Cl_2][ClO_4]_2$ (M = Ni, Pd, and Pt)		

[a, b, c] See text.

(*a*) $[Ni(Diarsine)_2]^0$. This compound was prepared by D.V. Ramana Rao by heating $Ni(CO)_2$Diarsine with Diarsine *in vacuo*; it is similar to the corresponding diphosphine

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[10] Nyholm, unpublished observations.

described by Chatt and Hart.[11] The two carbon monoxide groups are much more difficult to remove from Ni(Diarsine)$(CO)_2$ than are the first two from nickel carbonyl.

(*b*) Ni$(\text{Diarsine})_2I_2$. It was noted some years ago that two forms of this compound can be prepared, a brown stable modification and a green unstable one. When solutions of nickel iodide and the ditertiary arsine in acetone or alcohol solution are mixed, the brown compound is precipitated. If, however, an aqueous solution of $[\text{Ni(Diarsine)}_2]\text{Cl}_2$ is treated with iodine ions a green precipitate is formed. This changes to the brown form instantly when moistened with acetone and it was suspected that this green form was simply a hydrate. However, both forms dissolve in nitrobenzene to green solutions from which the green form is precipitated by light petroleum. It is possible that the isomers are *cis*- and *trans*-forms of a sexicovalent complex, but it seems more likely that one is a sexicovalent non-electrolyte (the green form) and the other a salt. Without an *X*-ray examination speculation on these hypotheses is unprofitable.

(*c*) It is assumed that, in the solid state, the nickel and platinum compounds involve a sexicovalent metal atom with a tetragonal arrangement of the ligands as occurs with the palladium compound.[3] Nothing is known of the stereochemistry of the quinquecovalent ions such as occurs in $[\text{Ni(Diarsine)}_2\text{Br}]\text{ClO}_4$. In solution it seems likely that the five ligands are arranged about the metal atom in a square-pyramidal arrangement probably with a solvent molecule in the sixth position. *X*-Ray studies on these compounds are in progress in Mr. H. M. Powell's laboratory at Oxford. He has, however, already examined compounds of the type $\text{M}^{\text{II}}\text{X}_2$·Triarsine, where $\text{M}^{\text{II}} =$ Pt, Pd, and Ni, and reports[12] that "The nickel atom in NiBr_2·Triarsine in the crystal is five-covalent; the five attached atoms have an arrangement which may be regarded as a considerably distorted square pyramid." With regard to the palladium compound,[13] "The corresponding palladium complex is not five-covalent in the crystal, one bromine atom being at too great a distance from the palladium atom."

EXPERIMENTAL

The compounds described below are new or previous procedures are modified. Those nickel complexes not described here were prepared according to Nyholm,[4] and the palladium complexes by the procedure of Harris and Nyholm.[1] (For naming of compounds see footnote to Table 1.)

*Di-(*o*-phenylenebisdimethylarsine)nickel*(II) *Perchlorate Monohydrate*.—To $[\text{Ni(H}_2\text{O)}_6](\text{ClO}_4)_2$ (3·7 g.) in boiling acetone (100 ml.) was added Diarsine (*o*-phenylenebisdimethylarsine) (5·7 g.) in acetone (20 ml.). After cooling of the red solution, the orange crystalline monohydrate (7·7 g.) which was precipitated was filtered off and washed with acetone, and the excess of acetone was removed under a vacuum, leaving the anhydrous *complex* (Found: C, 28·3; H, 3·9. $\text{C}_{20}\text{H}_{34}\text{As}_4\text{Cl}_2\text{NiO}_9$ requires C, 28·3; H, 4·0%). The compound did not lose weight at 140°.

*Monoiododi-(*o*-phenylenebisdimethylarsine)nickel*(II) *Iodide*.—To $[\text{Ni(Diarsine)}_2][\text{ClO}_4]_2,\text{H}_2\text{O}$ (0·5 g.) in boiling acetone (100 ml.) containing water (10 ml.) was added, in one lot, an excess of sodium iodide (1·0 g.) in 80% acetone (10 ml.). The deep purple solution deposited the dark-brown compound (0·45 g.) which was washed with cold acetone (Found: C, 27·2; H, 3·7. Calc. for $\text{C}_{20}\text{H}_{32}\text{As}_4\text{I}_2\text{Ni}$: C, 27·1; H, 3·7%).

*Monobromodi-(*o*-phenylenebisdimethylarsine)nickel*(II) *Bromide*.—$[\text{Ni(Diarsine)}_2](\text{ClO}_4)_2,\text{H}_2\text{O}$ (0·60 g.) in boiling acetone (130 ml.) containing water (13 ml.) was treated all at once with an excess of lithium bromide (1·0 g.) in acetone (10 ml.) and water (5 ml.). The brown crystals (0·49 g.) of the compound were isolated as for the iodide (Found: C, 30·5; H, 3·9. Calc. for $\text{C}_{20}\text{H}_{32}\text{As}_4\text{Br}_2\text{Ni}$: C, 30·3; H, 4·1%).

*Monochlorodi-(*o*-phenylenebisdimethylarsine)nickel*(II) *Perchlorate*.—The deep red solution formed on addition of triphenylmethylarsonium chloride (0·17 g.) in acetone (25 ml.) to $[\text{Ni(Diarsine)}_2][\text{ClO}_4]_2,\text{H}_2\text{O}$ (0·42 g.) in boiling acetone (800 ml.) was evaporated to 100 ml. and left for 1 hr. The precipitated red *salt* (0·20 g.) was washed quickly with cold acetone and dried *in vacuo* (Found: C, 31·1; H, 4·1; Cl, 4·8. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{Cl}_2\text{NiO}_4$ requires C, 31·35; H, 4·2; Cl, 4·6%).

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[11] Chatt and Hart, *Chem. and Ind.*, 1959, 1474.

[12] Maier and Powell, personal communication.

[13] Henn and Powell, personal communication.

Monobromodi-(o-*phenylenebisdimethylarsine*)*nickel*(II) *Perchlorate.*—The procedure used for the chloro-perchlorate, but with lithium bromide (0·043 g.) in acetone (20 ml.) and [Ni-(Diarsine)$_2$][ClO]$_2$,H_2O (0·42 g.) in acetone (800 ml.), gave dark brown crystals (0·25 g.) (on evaporation to 100 ml.). The *salt* was washed with acetone and vacuum-dried (Found: C, 29·4; H, 3·95; Br, 9·8; Ni, 7·3. $C_{20}H_{32}As_4BrClNiO_4$ requires C, 29·65; H, 4·0; Br, 9·9; Ni, 7·25%).

The Mixed Compound [Ni(Diarsine)$_2$][ClO_4]$_2$,2[Ni(Diarsine)$_2$I]ClO_4.—The salt [Ni(Diarsine)$_2$][ClO_4]$_2$,H_2O (0·42 g.) in boiling acetone (800 ml.) was treated with sodium iodide (0·07 g.) in acetone (5 ml.); the deep purple solution was concentrated to 50 ml. and set aside for 12 hr. The resulting black crystals of *complex* were washed with acetone and dried in a vacuum (Found: C, 28·3; H, 3·8; I, 9·9. $C_{60}H_{96}As_{12}Cl_4I_2Ni_3O_{16}$ requires C, 28·3; H, 3·8; I, 10·0%). The absorption spectrum of the compound in nitromethane was almost identical with that calculated from its constituent compounds.

Mononitrodi-(o-*phenylenebisdimethylarsine*)*nickel*(II) *Nitrite.*—Nickel acetate tetrahydrate (0·2 g.) in aqueous alcohol (1 : 1) was treated with the Diarsine (0·46 g.) in alcohol (20 ml.). The green solution became deep reddish-brown. To this solution was added sodium nitrite (5·0 g.) in water (10 ml.). After a few minutes brown crystals (0·3 g.) of the required *compound* were precipitated. These were filtered off, washed with water, and ether, and dried *in vacuo* (Found: C, 33·6; H, 4·85; N, 3·6. $C_{20}H_{32}As_4N_2NiO_4$ requires C, 33·2; H, 4·4; N, 3·9%).

Mononitratodi-(o-*phenylenebisdimethylarine*)*nickel*(II) *Nitrate.*—Nickel nitrate hexahydrate (0·2 g.) in alcohol (10 ml.) was treated with the Diarsine (0·4 g.) in alcohol (10 ml.). A red colour developed at once and, after a few minutes' heating on the water-bath, brown crystals (0·3 g.) appeared. This *salt* was washed with acetone and ether and dried in *vacuo* (Found: C, 31·65; H, 4·3; N, 3·8. $C_{20}H_{32}As_4N_2NiO_6$ requires C, 31·8; H, 4·2; N, 3·7%).

Monochlorodi-(o-*phenylenebisdimethylarsine*)*platinum*(II) *Chloride.*—Sodium chloroplatinite (1·35 g.) in water (50 ml.) was added to a hot solution of the Diarsine (1·72 g.) in alcohol (70 ml.) containing 10N-hydrochloric acid (7·5 ml.). The resulting pink suspension of [Pt(Diarsine)$_2$][$PtCl_4$], when refluxed, gave way to a clear solution, and concentration gave colourless crystals (2·2 g.) of the *chloride* which was extracted with alcohol, reprecipitated with ether, and *dried in vacuo* (Found: C, 28·9; H, 4·3; Pt, 23·5. $C_{20}H_{32}As_4Cl_2Pt$ requires C, 28·6; H, 3·8; Pt, 23·3%). The compound may be prepared also from [Pt(Diarsine)$_2$][ClO_4) and lithium chloride in hot acetone, but contamination with lithium chloride may occur.

Monobromodi-(o-*phenylenebisdimethylarsine*)*platinum*(II) *Bromide.*—To Pt(Diarsine)$_2$$Cl_2$ (0·75 g.), prepared as above, in water (20 ml.) was added a concentrated aqueous solution of potassium bromide, and the white precipitate (0·4 g.) was washed with 5N-hydrobromic acid, followed by acetone. The compound became yellow when washed with acetone, owing to dehydration. It was extracted with alcohol, the solution evaporated under reduced pressure, and the precipitated *compound* dried *in vacuo* (Found: C, 26·2; H, 3·2; Br, 16·9; Pt, 21·05. $C_{20}H_{32}As_4Br_2Pt$ requires C, 25·95; H, 3·45; Br, 17·8; Pt, 21·1%). Preparation of the compound by treating a hot acetone solution of [Pt(Diarsine)$_2$][ClO_4]$_2$ with lithium bromide in acetone is not recommended as an impure product is obtained.

Monoiododi-(o-*phenylenebisdimethylarsine*)*platinum*(II) *Iodide.*—Prepared as for the bromide, the *iodide* formed yellow crystals (Found: C, 24·0; H, 3·35; I, 24·5; Pt, 19·05. $C_{20}H_{32}As_4I_2Pt$ requires C, 23·55; H, 3·1; I, 24·9; Pt, 19·1%).

Di-(o-*phenylenebisdimethylarsine*)*platinum*(II) *Tetrachloroplatinate*(II).—Sodium chloroplatinite (0·5 g.) in alcohol (20 ml.) was treated with Diarsine (0·32 g.) in alcohol (8 ml.) with vigorous stirring. The pink precipitate (0·52 g.) was filtered off and washed with water and alcohol (Found: C, 21·7; H, 3·25; Pt, 35·4. $C_{20}H_{32}As_4Cl_4Pt_2$ requires C, 21·7; H, 2·9; Pt, 35·4%). The compound is moderately soluble in warm dilute hydrochloric acid but insoluble in water and the usual organic solvents.

Di-(o-*phenylenebisdimethylarsine*)*platinum*(II) *Diperchlorate.*—The compound [Pt(Diarsine)$_2$][$PtCl_4$] (0·24 g.) was dissolved in 6N-hydrochloric acid (30 ml.), and the filtered solution treated with 73% perchloric acid (5 ml.). The white precipitated *diperchlorate* (0·12 g.) was filtered off and washed with water (Found: C, 24·85; H, 3·55; Pt, 20·25. $C_{20}H_{32}As_4Cl_2O_8Pt$ requires C, 25·0; H, 3·3; Pt, 20·2%).

Monochlorodi-(o-*phenylenebisdimethylarsine*)*platinum*(II) *Perchlorate.*—To [Pt(Diarsine)$_2$][ClO_4]$_2$ (0·5 g.) in warm acetone (400 ml.) was added lithium chloride (0·022 g.) in acetone (10 ml.). The resulting yellow solution was concentrated to 100 ml. and set aside. The pale yellow crystals of *product* (0·18 g.) which were formed were collected and washed with acetone (Found: C, 26·8; H, 4·0; Pt, 21·4. $C_{20}H_{32}O_4As_4Pt$ requires C, 26·6; H, 3·55; Pt, 21·6%).

*Monobromodi-(*o*-phenylenebisdimethylarsine)platinum*(II) *Perchlorate.*—To [Pt(Diarsine)$_2$][ClO_4]$_2$ (0·5 g.) in warm acetone (600 ml.) was added lithium bromide (0·044 g.) in acetone (9 ml.). The yellow solution, concentrated to 100 ml. and set aside, yielded golden-yellow crystals of *monoperchlorate* (0·23 g.), which were filtered off and washed with acetone (Found: C, 25·5; H, 3·75; Br, 8·65. $C_{20}H_{32}As_4BrClO_4Pt$ requires C, 25·4; H, 3·4; Br, 8·4%).

*Monoiododi-(*o *-phenylenebisdimethylarsine)platinum*(II) *Perchlorate.*—To [Pt(Diarsine)$_2$][ClO_4]$_2$ (0·5 g.) in warm acetone (500 ml.) was added lithium iodide (0·078 g.) in acetone (10 ml.). The yellow solution was concentrated to 80 ml. and set aside. The yellow crystalline *complex* (0·1 g.) was washed with acetone (Found: C, 24·3; H, 3·55; I, 12·5. $C_{20}H_{32}As_4ClIO_4Pt$ requires C, 24·2; H, 3·2; I, 12·8%).

*Monoisothiocyanatodi-(*o*-phenylenebisdimethylarsine)platinum*(II) *Isothiocyanate.*—To [Pt(Diarsine)$_2$]Cl_2 (0·7 g.) in water (25 ml.) was added excess of potassium thiocyanate in water. The white precipitate was filtered off and recrystallised from aqueous alcohol containing a little potassium thiocyanate. The *product* (0·57 g.) became yellow when washed with acetone, presumably owing to dehydration (Found: C, 29·7; H, 3·65; N, 3·1; Pt, 22·1. $C_{22}H_{32}As_4N_2PtS_2$ requires C, 29·9; H, 3·6; N, 3·2; Pt, 22·1%).

*Di-(*o*-phenylenebisdimethylarsine)platinum*(II) *Dinitrate.*—To [Pt(Diarsine)$_2$]Cl_2 (0·28 g.) in water (10 ml.) was added sodium nitrate (0·8 g.) in water (4 ml.). The white crystalline *dinitrate* (0·2 g.) was washed with small amounts of water and alcohol (Found: C, 26·7; H, 4·2; Pt, 21·7. $C_{20}H_{32}As_4N_2O_6Pt$ requires C, 26·95; H, 3·6; Pt, 21·9%).

*Dichlorodi-(*o*-phenylenebisdimethylarsine)platinum*(IV) *Diperchlorate.*—This compound was prepared by two different methods of oxidation of Pt(Diarsine)$_2Cl_2$—by chlorine and by concentrated nitric acid. Details of both are given since the latter has been used to obtain the corresponding quadrivalent iron and nickel complexes.

(i) To Pt(Diarsine)$_2Cl_2$ (0·4 g.) was added a mixture of 15N-nitric acid (20 ml.) and 10N-hydrochloric acid (1·5 ml.). The yellow solution was filtered and treated with 72% perchloric acid (8 ml.) followed by water (130 ml.). The pale yellow *product* (0·4 g.) was filtered off and washed many times with water (Found: C, 23·0; H, 3·15; Pt, 18·75; N, 0·0. $C_{20}H_{32}As_4Cl_4O_8Pt$ requires C, 23·2; H, 3·1; Pt, 18·8%).

(ii) The compound Pt(Diarsine)$_2Cl_2$ (0·3 g.) was dissolved in water and treated with gaseous chlorine, the colour gradually becoming yellow. The solution was filtered and treated with 72% perchloric acid (5 ml.), and the pale yellow precipitate (0·2 g.) filtered off (Found: C, 23·5; H, 3·05%).

*Dibromodi-(*o*-phenylenebisdimethylarsine)platinum*(IV) *Diperchlorate.*—This salt was prepared as in (i) for the corresponding chloride and obtained as yellow crystals (Found: C, 21·35; H, 3·05; Pt, 17·5; N, 0·0. $C_{20}H_{32}As_4Br_2Cl_2O_8Pt$ requires C, 21·34; H, 2·84; Pt, 17·34; N, 0·0%).

*Di-iododi-(*o*-phenylenebisdimethylarsine)platinum*(IV) *diperchlorate* was also prepared as for the corresponding bromide; it was deep red (Found: C, 20·1; H, 2·9; Pt, 16·15 $C_{20}H_{32}As_4Cl_2I_2O_8Pt$ requires C, 20·0; H, 2·6; Pt, 16·0%).

*Di-iododi-(*o*-phenylenebisdimethylarsine)platinum*(IV) *Dinitrate.*—To Pt(Diarsine)$_2I_2$ (0·66 g.) was added 10N-nitric acid (30 ml.), and the resulting red solution was filtered. On addition of water (100 ml.) and shaking, deep red crystals (0·6 g.) were formed slowly. These were filtered off and washed with small quantities of water. When dried *in vacuo* this *dinitrate* became orange-red owing to loss of water of crystallisation (Found: C, 20·8; H, 3·0; Pt, 17·05. $C_{20}H_{32}As_4I_2N_2O_6Pt$ requires C, 21·0; H, 2·8; Pt, 17·05%). On exposure to the atmosphere the dried complex quickly absorbed water, becoming deep red and forming the trihydrate as shown by the increase in weight (4·9%).

*Dichlorodi-(*o*-phenylenebisdimethylarsine)palladium*(IV) *Diperchlorate.*—This *salt* was prepared by the above two methods but oxidation by nitric acid gives the purer product (Found: C, 25·3; H, 3·95; Pd, 11·5. $C_{20}H_{32}As_4Cl_4O_8Pd$ requires C, 25·35; H, 3·4; Pd, 11·3%). The orange compound decomposes fairly rapidly in aqueous solution.

*Dibromodi-(*o*-phenylenebisdimethylarsine)palladium*(IV) *diperchlorate,* prepared as for the corresponding platinum(IV) compound by use of nitric acid, was obtained as red crystals (Found: C, 23·05; H, 3·6; Pd, 10·4. $C_{20}H_{32}Br_2Cl_2O_8Pd$ requires C, 23·2; Pt, 3·1; Pd, 10·3%).

*Di-(*o*-phenylenebisdimethylarsine)platinum*(IV) *Tetraiodide.*—A solution of the nitrate [Pt(Diarsine)$_2I_2$][NO_3]$_2$ (0·4 g.) in warm water (250 ml.) was filtered and treated with saturated sodium iodide solution (3 ml.), to yield a greenish-black precipitate of *iodide* (0·4 g.) which was washed with water (Found: C, 18·7; H, 2·6; Pt, 15·0. $C_{20}H_{32}As_4I_4Pt$ requires C, 18·8; H, 2·5; Pt, 15·3%).

Magnetic Susceptibility Measurements.—These were carried out by the Gouy method at 20°; figures are not quoted since all compounds described are diamagnetic.

Analyses.—All elements were determined as previously described.[1,4] Platinum was determined by ignition. Conductivity and spectrophotometric measurements were carried out as in the earlier work on bivalent palladium.[1]

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