

873. *Tertiary Arsine Complexes of Nickel, Palladium, and Platinum.*

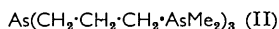
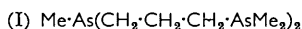
By G. A. BARCLAY, R. S. NYHOLM, and R. V. PARISH.

The preparation and properties of the tertiary arsine tridentate ligand, di-(3-dimethylarsinylpropyl)methylarsine (triarsine), are described. The complexes formed by this ligand with nickel, palladium, and platinum salts have been investigated. The bivalent metal halides form complexes having the general formula, $M^{II}X_2$ triarsine ($X = Cl, Br, \text{ or } I$). The nickel(II) compounds are non-electrolytes in nitrobenzene and hence involve a five-co-ordinated nickel atom, but the platinum(II) derivatives behave as 1 : 1 electrolytes in nitrobenzene. The latter are therefore formulated as $(Pt \text{ triarsine } X)^+X^-$; the ionised halide ion can be replaced by the perchlorate ion. The palladium(II) complexes are intermediate in their conductivity behaviour but resemble more closely the platinum than the nickel compounds; for example, they give perchlorates. The tendency to form five-co-ordinated complexes, *viz.*, $Pt^{II} < Pd^{II} \ll Ni^{II}$, is correlated with the $(n - 1)d^9 \rightarrow (n - 1)d^8 np$ energy separation in the free atom. The chemistry of five-co-ordinate d^8 -complexes as a class is discussed.

Each of these metals also gives salts of the type $[M^{II}(\text{triarsine})_2][ClO_4]_2$; these are bi-univalent electrolytes in nitrobenzene, and studies of the reactivity of the co-ordinated and unco-ordinated ligand towards methyl iodide support the conclusion that in all three cases the metal atom is six-co-ordinated.

The behaviour of the compounds towards halogens is discussed and some platinum(IV) derivatives of the type $[Pt \text{ triarsine } X_3]ClO_4$ are reported.

IN view of the variety of metals and the range of oxidation states which are stabilised by the tertiary arsine *o*-phenylenebisdimethylarsine,^{1,2} the behaviour of tri- and tetra-tertiary arsines is of considerable interest. Some years ago we synthesised the tertiary arsine³ (I), henceforth referred to as triarsine, and a tetra-tertiary arsine⁴ (II). The



co-ordinating ability of the triarsine towards certain metal salts was briefly reported;³ in the present paper we give details of the synthesis of the tridentate compound and discuss the nature and the structure of the complexes formed by nickel, palladium, and platinum.

The tertiary arsine is prepared by making use of simple Meyer⁵ and Grignard reactions as shown in the scheme. Starting from trimethylene chlorohydrin (III) the dichloro-3-chloropropylarsine (V) was prepared by the method of Gough and King.⁶ The later stages in the synthesis are straightforward. The triarsine was obtained as a colourless oil which was oxidised fairly rapidly in air, forming a colourless, hygroscopic solid.

¹ Chatt and Mann, *J.*, 1939, 610.

² See Nyholm and Sutton, *J.*, 1958, 560, and references quoted therein.

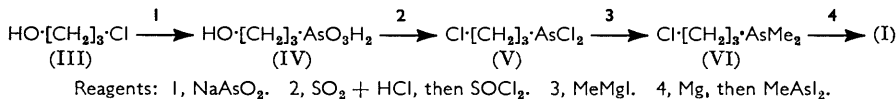
³ Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

⁴ Barclay, unpublished observations.

⁵ See Raiziss and Gavron, "Organic Arsenical Compounds," Chem. Catalogue Co., New York, 1923.

⁶ Gough and King, *J.*, 1928, 2432.

$M^{II}X_2$ triarsine Complexes.—When an alcoholic solution of nickel bromide or nickel iodide is treated with the triarsine, dark compounds NiX_2 triarsine are precipitated. The chloro-complex could not be obtained pure; this is not unusual; similar difficulty was experienced by Jensen ⁷ when preparing the $NiX_2 \cdot 2Et_3As$ compounds. These complexes



are virtually non-electrolytes in nitrobenzene; the molecular weight of the iodide in freezing nitrobenzene solution is that expected for a monomeric non-electrolyte (see Experimental section).

At first sight these data suggest that the nickel atom is five-co-ordinate but evidence as to the number of arsenic atoms which are co-ordinated is necessary to settle this point.

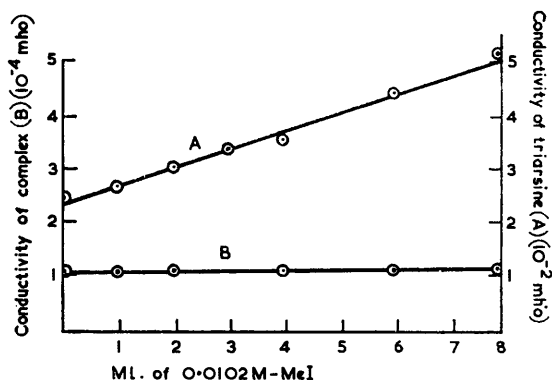


FIG. 1. Titration of the triarsine (A) and the complex $[Ni(triarsine)_2]^{2+}[ClO_4]^{-2}$ (B) with methyl iodide.

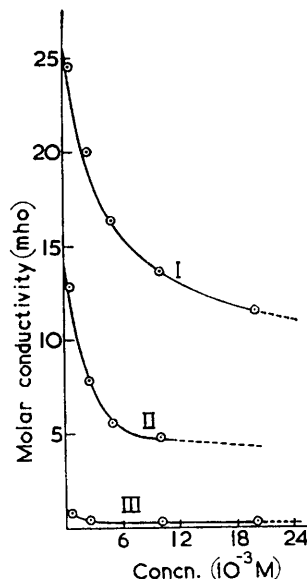


FIG. 2. Molar conductivity of (I) PtI_2 triarsine, (II) PdI_3 triarsine, and (III) NiI_2 triarsine.

This was established by titrating $[NiBr_2 \text{ triarsine}]^0$ and the triarsine with methyl iodide. Whilst the triarsine shows a steady increase in conductivity consequent upon the reaction $R \cdot AsMe_2 + MeI \rightarrow [R \cdot AsMe_3]^+ I^-$, the complex does not (cf. Fig. 1). We conclude that no free $AsMe_2$ group occurs in the complex. It is, nevertheless, important to emphasise that even if conductivity did rise this would not necessarily show that the $AsMe_2$ group is free, for the $Ni \leftarrow As$ bond could be quite reactive. In support of the view that all three arsenic atoms are co-ordinated, there is no evidence of oxidation of the nickel(II) complexes in air; a free $AsMe_2$ group might be expected to be oxidised readily in air. Also when the complex $NiBr_2$ triarsine is treated with bromine it is the nickel and not the $AsMe_2$ group that is oxidised. Finally, attempts to replace one of the halogen atoms by the perchlorate ion, as can be done with the palladium(II) and platinum(II) complexes, were unsuccessful; this suggests that neither halogen atom in the nickel complex is ionised.

The platinum complexes are much less intensely coloured than the nickel derivatives.

The former are soluble in certain polar solvents such as water and alcohol, but, unlike the nickel compounds, not in benzene or chloroform. This behaviour suggests that they are salts of the type $[\text{Pt triarsine X}]^+\text{X}^-$, which is confirmed by the molecular weight of the iodide in freezing nitrobenzene (see Experimental section) (it indicates virtually complete dissociation into two particles) and by the molar conductivity of the chloride, bromide, and iodide in nitrobenzene at 10^{-3}M -concentration (these are about 30 mho, the usual Λ_{M} value for a fully dissociated 1 : 1 electrolyte). Treatment of an alcoholic or aqueous solution of the PtX_2 triarsine complexes with perchloric acid yields compounds of the type $[\text{Pt triarsine X}]\text{ClO}_4$ which, as expected, are 1 : 1 electrolytes in nitrobenzene and nitromethane.

Palladium forms complexes of the type Pd^{II} triarsine X_2 and $[\text{Pd}^{\text{II}}$ triarsine $\text{X}]\text{ClO}_4$ although solubility relations sometimes preclude the isolation of pure specimens (*e.g.*, the preparation of $[\text{Pd triarsine Br}]\text{ClO}_4$ from $[\text{Pd triarsine Br}]\text{Br}$ is difficult. In good anion-solvating solvents such as water the Pd^{II} triarsine X_2 derivatives generally behave as 1 : 1 electrolytes but in nitromethane and nitrobenzene the molar conductivity of the iodide at 10^{-3}M -concentration suggests that about 50% of the molecules are dissociated into ions. This is supported by molecular-weight measurements for the iodide in freezing nitrobenzene: for a 0.325% solution (*i.e.*, $4.4 \times 10^{-3}\text{M}$) the apparent molecular weight is 570, compared with a calculated value of 745 for the undissociated molecule. An effective method for comparing the nickel(II), palladium(II) and platinum(II) compounds is by measuring the molar conductivity at progressive dilutions in nitrobenzene. As may be seen from Fig. 2 the conductivity of the compound $[\text{Pd triarsine I}]\text{I}$ is intermediate between those of the undissociated nickel complex and the largely ionised platinum compound.

The tendency for association of the type $[\text{M}^{\text{II}}$ triarsine $\text{X}]^+ + \text{X}^- \rightarrow [\text{M}^{\text{II}}$ triarsine $\text{X}_2]^0$ is thus in the order $\text{Ni}^{\text{II}} \gg \text{Pd}^{\text{II}} > \text{Pt}^{\text{II}}$. Similar behaviour with other ligands has been observed: the yellow $[\text{Ni}(\text{CN})_4]^{2-}$ ion readily associates⁸ with the CN^- ion to form the red 1 : 1 complex ion $[\text{Ni}(\text{CN})_5]^{3-}$; however, the reaction between the corresponding $[\text{Pd}(\text{CN})_4]^{2-}$ and $[\text{Pt}(\text{CN})_4]^{2-}$ ions and the CN^- ion is negligible.⁹ Similarly we have shown¹⁰ that, for their capacity to associate with halide ions, the order is $[\text{Ni}(\text{diarsine})_2]^{2+} > [\text{Pd}(\text{diarsine})_2]^{2+} > [\text{Pt}(\text{diarsine})_2]^{2+}$. The formation of a five-co-ordinate complex implies hybridisation of the $(n-1)d$, the ns , and the three np orbitals and this is most favoured if their energies are not too different. The energy separation between atomic orbitals increases with the formal charge on the metal atom and also with its effective nuclear charge.¹¹ Thus, the $ns \rightarrow np$ separations for Zn^+ and Ga^{2+} are respectively 6.00 and 8.08 eV,¹² whilst the values for Cu^0 , Ag^0 , and Au^0 are 3.79, 3.65, and 4.63 eV. The effect of reducing the formal positive charge for d^8 complexes is illustrated by the following compounds: $[\text{Cr}(\text{CO})_5]^{2-}$, $[\text{Mn}(\text{CO})_5]^-$, $[\text{Fe}(\text{CO})_5]$, and $[\text{Co}(\text{PhCN})_5]^+$ (see refs. 13–15), whereas Ni^{2+} is four- or five-co-ordinate depending upon the ligand. An estimate of the case with which the single p_z orbital can be hybridised with the four square $(n-1)d_{x^2-y^2}$, ns , np_x , np_y bonds is obtained from the energy required for the transition $(n-1)d^9 \rightarrow (n-1)d^{8*}np$, where d_s^* represents the spin-paired configuration, given in Table 1. The $(n-1)d \rightarrow np$ separation increases with positive charge, and also from the first to the second to the third transition series provided that the charge on the metal ion is 1+ or less. It seems reasonable to assume that charge on the nickel(II), palladium(II), and platinum(II) atoms in the triarsine compounds lies between 0 and 1+ and that it is probably nearer

⁷ Jensen, *Z. anorg. Chem.*, 1935, **229**, 265.

⁸ McCullough, Jones, and Penneman, *J. Inorg. Nuclear Chem.*, 1960, **13**, 286.

⁹ Reddy, Thesis, London, 1961.

¹⁰ Harris, Nyholm, and Phillips, *J.*, 1960, **4379**.

¹¹ Slater, "Quantum Theory of Atomic Structure," McGraw Hill, New York, 1960.

¹² Moore, "Atomic Energy Levels," U.S. Nat. Bur. Standards, Circular 467, 1952, Vol. II.

¹³ Behrens and Kohler, *Z. Naturforsch.*, 1959, **14b**, 463; Behrens and Haag, *ibid.*, p. 600.

¹⁴ Hieber and Wagner, *Z. Naturforsch.*, 1957, **12b**, 478.

¹⁵ Malatesta, in "Progress in Inorganic Chemistry," Vol. I, ed. F. A. Cotton, Interscience Publ., Inc., New York, 1959; Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **273**, 241.

		Promotion energies (ev) for d^9 atoms and ions. ¹²								
	Atom or ion	Co ⁰	Ni ⁺	Cu ²⁺	Rh ⁰	Pd ⁺	Ag ²⁺	Ir ⁰	Pt ⁺	Au ²⁺
$(n-1)d^9 \longrightarrow$	$(n-1)d^8np$									
separation ^a	0.85	2.90	6.01	1.60	3.39	5.76	2.4	3.05	5.2
		^a <i>I.e.</i> , $d^9(2D) \longrightarrow d^8(1D)p(2F)$.								

the former; ¹⁶ if so, then the order of the $(n-1)d \longrightarrow np$ separation (1st row < 2nd row < 3rd row) agrees with the relative ease with which one can form the five-co-ordinate [M^{II} triarsine X₂]⁰ complexes. It is unlikely that the extra bond using the p_z orbital would be energetically equivalent to the other four bonds, and this should be reflected in the stereochemistry and bond lengths. We are indebted to Mr. H. M. Powell¹⁷ and his colleagues for an X-ray crystal-structure study of [Ni^{II} triarsine Br₂]⁰, and this supports the above hypothesis. The structure (Fig. 3) shows that the Ni-Br bond normal to the square is notably longer (2.69 Å) than the other (2.37 Å). Some distortion of the bromine atom in the square occurs, probably owing to steric effects due to CH₂ groups, but the basic shape is that of a square pyramid with one long bond normal to the square. Crystal-structure data on the palladium(II) and platinum(II) compounds are incomplete but their structures are quite different, the complexes being essentially salts with the second bromine atom present as an ion.¹⁸

Whilst the chloro- and bromo-complexes of palladium(II) appear to exist only as salts of the type [Pd triarsine X]⁺X⁻, the iodide (at least in nitrobenzene) exists in equilibrium with the non-ionic [Pd triarsine I₂]⁰ form, the tendency to form the non-ionic form

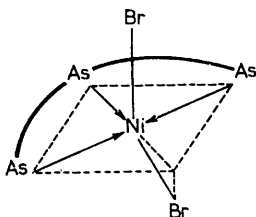


FIG. 3. Structure of NiBr₂ triarsine (AsAsAs = Me₂As·[CH₂]₃·AsMe·[CH₂]₃·AsMe₂).

increasing as the polarisability of the anion rises. An increase in polarisability is expected to decrease the charge on the metal atom to decrease the $(n-1)d \longrightarrow np$ separation, and hence to facilitate formation of the fifth bond. To sum up, the tendency to form five-co-ordinate d^8 complexes increases as: (i) the formal charge on the metal atom (oxidation state decreases), *i.e.*, Ni^{II} < Co^I < Fe⁰; (ii) the effective nuclear charge on the metal atom decreases, *i.e.*, Pt^{II} < Pd^{II} < Ni^{II}; (iii) the polarisability of the anion increases, *i.e.*, Cl⁻ < Br⁻ < I⁻. Earlier¹⁰ we had noted that the relative ease with which nickel(II), palladium(II), and platinum(II) formed five-co-ordinate [M^{II}diarsine₂ X]⁺ ions was in the *reverse* order to their Haissinsky electronegativities, *i.e.*, Ni (1.7) > Pd (2.0) > Pt (2.1). Electronegativities are related to ionisation potentials and these, in turn, are roughly proportional to promotion energies. Thus the approaches *via* electronegativity and promotion energies are not as different as they might appear. We now prefer the argument given in this paper to the simple charge picture because we consider it is probably more closely related to the actual situation obtaining around the metal atom. It is of interest to compare the structure of the five-co-ordinate NiX₂ triarsine complexes with that of other d^8 compounds. Infrared and dipole moment data¹⁹ on [Fe(CO)₃(RNC)₂] and the infrared spectrum²⁰ of the cation [Co(CO)₃(Ph₃P)₂]⁺ indicate that these have a trigonal bipyramidal arrangement. This suggests that, as we pass from nickel(II) to

¹⁶ Pauling, "The Nature of the Chemical Bond," Oxford Univ. Press, 1960, p. 399.

¹⁷ Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1961, 415.

¹⁸ Powell, personal communication, 1961; see also *Proc. Chem. Soc.*, 1961, 170.

¹⁹ Parish and Cotton, *J.*, 1960, 1440.

²⁰ Vohler, *Chem. Ber.*, 1958, 91, 1235.

copper(I) to iron(0), not only does the tendency to form five-co-ordinate complexes increase, but also that the trigonal bipyramid tends to become the preferred structure. Thus it seems that as the formal positive charge on a metal ion decreases towards zero—or becomes negative—the stereochemistry is best discussed from a valence-bond or bond-pair repulsion picture; when the positive charge is appreciable, the converse is true.²¹ More simply, the d^8 core in iron(0) is more easily polarised than in Ni^{2+} ; if the five ligands around the Fe^0 atom then take up positions of maximum symmetry, a trigonal bipyramid will arise. However, in the Ni^{2+} ion the d^8 core is expected to be less easily polarised and hence to influence the position of ligands. To oversimplify, for a positively charged metal ion, on crystal-field theory, the more "rigid" non-bonding shell tends to decide where the ligands will go, whereas for a readily polarised ion the ligands tend to decide where the non-bonding electrons will be located. All of these arguments assume, of course, that steric effects are negligible. This is not always true, as has been demonstrated¹⁷ in the case of the "planar" bromine atom in the $NiBr_2$ triarsine complex; further, the difference in energy between the square pyramid and the trigonal bipyramid arrangement is relatively small and steric effects alone might well, on occasions, cause a change from one shape to another. Thus, the square pyramidal shape of the five-co-ordinate cation $[PtI, QAS]^+$, where QAS is tris(*o*-diphenylarsinophenyl)arsine, is attributed¹⁸ to the steric requirements of the quadridentate group.

Bistriarsine Complexes.—Compounds having the general formula $[M^{II}(\text{triarsine})_2][ClO_4]_2$ are conveniently prepared by treating the perchlorate of the metal with the triarsine in aqueous alcohol. However, one may also start from the monotriarsine derivative; addition of an excess of triarsine and perchloric acid effects conversion into the bistriarsine cation. In the case of nickel the bis-triarsine cation is produced when water is added to an acetone solution of $NiBr_2$ triarsine or the iodide. The almost black solution of the former becomes purple, owing to the reaction $2[Ni \text{ triarsine } Br_2]^0 + \text{water} \longrightarrow [Ni(\text{triarsine})_2]^{2+} + [Ni(H_2O)_6]^{2+} + 4Br^-(aq.)$. A study of the optical density of the solution confirms that half of the nickel is present as the bistriarsine cation. This behaviour is similar to that of $[Ni en_2 Br_2]^0$ which is reported²² to react with water to yield the trisethylenediamine cation and bromide ions. The corresponding palladium compound is red and the platinum complex is yellow. In all cases the molecular conductivity in nitrobenzene (~ 60 mho) and in nitromethane (~ 230 mho) at $10^{-3}M$ -concentration indicates that the complexes are bi-univalent electrolytes. The diamagnetism of the palladium and the platinum complex is not unexpected, but in the case of nickel the diamagnetism raises the question of the co-ordination number and in particular whether all three arsenic atoms are co-ordinated to the metal. As discussed above, titrations (Fig. 1) suggest very strongly that there is no free $AsMe_2$ group. Co-ordination of one or two $AsMe_2$ groups might reduce the reactivity of the third so much that it no longer reacts readily with methyl iodide, but this is most unlikely since the arsenic atoms are separated by three methylene groups and there is no reason to suppose that significant inductive effects would be felt through this chain. The supporting evidence—absence of oxidation of $AsMe_2$ groups (see above)—is confirmed by absorption spectra (Fig. 4). The cation $[Ni(\text{triarsine})_2]^{2+}$ produces peaks at about the same wavelengths as does the complex ion $[Ni(\text{diarsine})_3]^{2+}$ (*viz.*, 430 and 540 $m\mu$),²³ but the intensities are different. The spectra of the five-co-ordinate iodo- and bromo-triarsinenickel(II) complexes are characterised by a very strong band ($\epsilon \sim 1500$ — 2000) at about 400 $m\mu$; this parallels the corresponding band near 490 $m\mu$ shown by the $[Ni(\text{diarsine})_2 Br]^+$ and $[Ni(\text{diarsine})_2 I]^+$ ions. In addition, however, the $Ni^{II}X_2$ triarsine complexes show further bands at longer wavelengths (~ 500 — 600 $m\mu$), perhaps arising from the greater asymmetry of the triarsine complexes.

Believing that in $[M^{II} \text{ triarsine}_2]^{2+}$ ions the metal is six-co-ordinate, we presume, for

²¹ Nyholm, Tilden Lecture, *Proc. Chem. Soc.*, 1961, 273.

²² Hieber and Levy, *Z. Electrochem.*, 1933, **39**, 26.

²³ Nyholm, *J.*, 1950, 2061.

reasons developed elsewhere,²⁴ that the metal atom is tetragonally co-ordinated as shown in Fig. 5, but until X-ray data are forthcoming this remains unproved.

Action of Oxidising Agents.—It was expected that halogens might react with the $[M^{II} \text{ triarsine } X_2]$ derivatives, producing complexes of the metal in higher oxidation states. As summarised recently,¹⁰ the Ni^{II} diarsine complexes can be oxidised to both nickel(III) and nickel(IV) compounds, whereas palladium(II) and platinum(II) compounds give complexes of the quadrivalent metal. It was found that bromine and $NiBr_2$ triarsine in chloroform gave a black paramagnetic complex which was easily reduced back to the bivalent state. Attempts to prepare an analytically pure specimen of the compound $NiBr_3$ triarsine were not successful. The compound $PdBr_2$ triarsine with bromine in

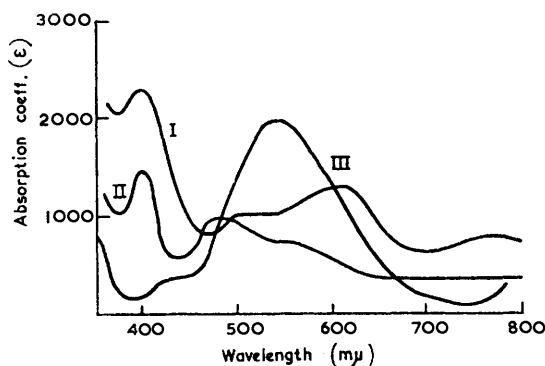


FIG. 4. Visible and ultraviolet absorption spectra of (I) NiI_2 triarsine, (II) $NiBr_2$ triarsine, and (III) $[Ni(\text{triarsine})_2]^{2+}[\text{ClO}_4]^{-2}$.

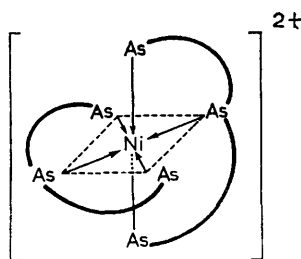


FIG. 5.

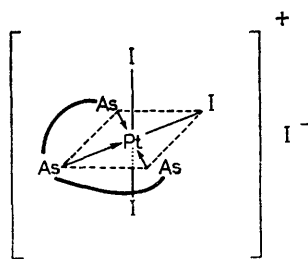


FIG. 6.

chloroform also gives a dark brown solution but it was not possible to isolate a pure palladium(IV) compound; the brown solution rapidly became clear, yielding the original yellow colour of the palladium(II) complex in solution. Presumably part of the arsine is oxidised by the palladium(IV) complex. With the platinum(II) compounds, however, oxidation takes place readily. Titration of $[Pt \text{ triarsine } Br]ClO_4$ in chloroform (followed spectrophotometrically) uses up two equivalents of bromine, and the orange platonic complex, $[Pt \text{ triarsine } Br_3]ClO_4$, crystallises from the solution. This complex is a uni-univalent electrolyte in nitromethane, which confirms its formulation. The iodo-compound $[Pt \text{ triarsine } I]I$ with iodine in chloroform gives similarly a red, stable platonic complex $Pt \text{ triarsine } I_4$. The molecular conductivity of this compound in nitromethane indicates that it is a uni-univalent electrolyte and hence is a typical octahedral platinum(IV) complex of the type $[Pt \text{ triarsine } I_3]I$.* Since it is likely that the added iodine atoms take up *trans*-positions the structure is presumably that shown in Fig. 6.

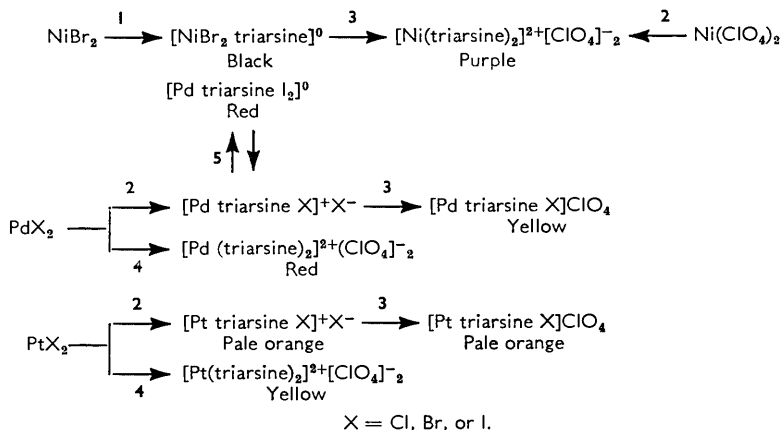
Isoelectronic octahedral complexes RhX_3 triarsine are also formed by trivalent rhodium; they will be described later.

* The possibility that this compound is the tri-iodide $[Pt \text{ triarsine } I]I_3$ seems ruled out by the spectrum.

²⁴ Harris and Nyholm, *J.*, 1956, 4375; Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

It is clear that although the triarsine stabilises certain higher oxidation states of the transition metals it is not as effective as the diarsine for this purpose.

The relations between the various compounds described above are shown in the annexed chart.



Reagents: 1, Triarsine in EtOH. 2, Triarsine in aq. EtOH. 3, HClO₄ in aq. EtOH. 4, Excess of triarsine + HClO₄ in aq. EtOH. 5, I⁻ where X = I.

Bivalent metal complexes.

EXPERIMENTAL

Dichloro-3-chloropropylarsine.—Trimethylene chlorohydrin (190 g.), by the method of Gough and King,⁶ gave 100 g. of the dichloroarsine, b. p. 115—117°/12 mm.

3-Chloropropyl-dimethylarsine.—A Grignard reagent, from methyl iodide (142 g.), magnesium (24 g.), and sodium-dried ether (300 ml.), was filtered through glass wool and added slowly to a solution of dichloro-3-chloropropylarsine (100 g.) in dry ether (250 ml.), with stirring by a stream of dry nitrogen during the addition and in all subsequent operations. In a vigorous reaction a yellow solid separated, but this eventually disappeared, two layers being formed. After the addition the mixture was refluxed for 10 min. and decomposed with ammonium chloride solution. The ethereal layer was separated, and washed with water, saturated sodium hydrogen carbonate solution, and water. After drying (MgSO₄), the ether was removed in an atmosphere of nitrogen and the residue distilled, giving the *arsine* (65 g.), b. p. 60—62°/10 mm. (Found: C, 32.85; H, 6.4. C₅H₁₂AsCl requires C, 32.9; H, 6.6%), as a colourless oil with a garlic odour.

Bis-(3-dimethylarsinylpropyl)methylarsine.—Reaction of magnesium (8 g.), 3-chloropropyl-dimethylarsine (64 g.), and dried ether (200 ml.) when initiated with methyl iodide, became vigorous. When reaction had subsided the mixture was refluxed for 15 min. and decanted from the excess of magnesium. Di-iodomethylarsine (56 g.), in the minimum quantity of benzene, was added slowly to the Grignard reagent. A vigorous reaction took place; the mixture was then refluxed for 20 min. and worked up as usual, giving the *triarsine* (32 g.), b. p. 180—182°/8 mm. (Found: C, 34.7; H, 6.9. C₁₁H₂₇As₃ requires C, 34.4; H, 7.1%), with a garlic-like unpleasant odour. As the triarsine darkened in air, forming a colourless solid, it was sealed in an inert atmosphere.

General.—All of the compounds described below are diamagnetic (all the results reported refer to 10⁻³M-solutions at 25°). In nearly all cases they decompose near 250° without melting.

Dibromotriarsinenickel(II).—A warm solution of nickel bromide trihydrate (0.40 g.) in alcohol (5 ml.) was treated with the triarsine (0.57 g.) in alcohol (10 ml.). The resulting blue-black solution was heated under reflux for 10 min., then concentrated to about 5 ml. On cooling, the dark *complex* separated which recrystallised from alcohol as black plates (0.32 g.) (Found: C, 22.1; H, 4.5; Br, 26.6. C₁₁H₂₇As₃Br₂Ni requires C, 21.9; H, 4.5; Br, 26.5%), soluble in common organic solvents such as chloroform and benzene, but insoluble in ether, virtually a non-electrolyte in nitrobenzene (Λ_M 1.3 mho).

Di-iodotriarsinenickel(II).—Nickel chloride hexahydrate (0.24 g.) and sodium iodide (0.40 g.) in water (3 ml.) were added to a solution of the triarsine (0.38 g.) in alcohol (10 ml.) and kept at 0° for several hours. The black product which separated recrystallised from acetone (0.45 g.) (Found: C, 18.9; H, 4.0%; *M*, cryoscopic in 0.42% nitrobenzene solution, 710. $C_{11}H_{27}As_3I_2Ni$ requires C, 18.9; H, 3.9%; *M*, 697). The compound, m. p. 275°, is soluble in acetone, chloroform, benzene, and nitrobenzene and is virtually a non-electrolyte in the latter (Λ_M 0.8 mho).

Bistriarsinenickel(II) Diperchlorate.—Nickel perchlorate heptahydrate (0.38 g.) in water (10 ml.) was treated with the triarsine (0.77 g.) in alcohol (20 ml.), and the resulting dark purple solution heated under reflux for 10 min. On cooling, the purple salt was deposited which recrystallised from acetone (yield 0.57 g.). (Found: C, 25.3; H, 5.3. $C_{22}H_{54}As_6Cl_2NiO_8$ requires C, 25.7; H, 5.3%). The compound is sparingly soluble in water and alcohol but soluble in acetone, nitrobenzene, and nitromethane. It behaves as a bi-univalent electrolyte in the last two solvents (Λ_M 52 mho in $PhNO_2$, 172 mho in $MeNO_2$).

Chlorotriarsinepalladium(II) Chloride.—Dichloroamminepalladium(II) (0.57 g.) in alcohol (30 ml.) was heated under reflux with the triarsine (0.40 g.) until evolution of ammonia ceased and all solid material dissolved (several hours). The solution was filtered and evaporated and the sticky residue washed several times with ice-cold acetone; on drying, a pale yellow powder (1.2 g.) remained (Found: C, 23.8; H, 5.0; Cl, 12.3. $C_{11}H_{27}As_3Cl_2Pd$ requires C, 23.5; H, 4.9; Cl, 12.6%). The complex is soluble in water, alcohol, nitrobenzene, and nitromethane but is insoluble in acetone, chloroform, and benzene. It behaves as a uni-univalent electrolyte in nitromethane and nitrobenzene (Λ_M 75.8 mho in $MeNO_2$ and 20.4 in $PhNO_2$). A potentiometric titration with silver nitrate in aqueous alcohol and a silver-silver chloride electrode showed that only one chlorine atom was ionised.

Chlorotriarsinepalladium(II) Perchlorate.—An aqueous-alcoholic solution of the compound [Pd triarsine Cl]Cl, prepared as above, was treated dropwise with 72% perchloric acid until no more precipitate was formed. The pale yellow perchlorate, obtained almost quantitatively, was washed with a little water and dried (Found: C, 21.3; H, 4.5. $C_{11}H_{27}As_3Cl_2O_4Pd$ requires C, 21.1; H, 4.4%). It is sparingly soluble in acetone, chloroform, and nitromethane and insoluble in water, alcohol, and nitrobenzene. It behaves as a uni-univalent electrolyte in nitromethane (Λ_M 77 mho).

Bromotriarsinepalladium(II) Bromide.—Dibromodiamminepalladium(II) (0.31 g.) was heated under reflux for several hours with the triarsine (0.38 g.) in alcohol (30 ml.). The resulting yellow solution was filtered, cooled, treated with ether, and left at 0° for several hours. The compound separated as yellow crystals (0.4 g.) (Found: C, 20.8; H, 4.6. $C_{11}H_{27}As_3Br_2Pd$ requires C, 20.3; H, 4.2%). It is readily soluble in acetone, nitrobenzene, and nitromethane but insoluble in benzene and chloroform. It behaves as a uni-univalent electrolyte in both nitromethane (Λ_M 79 mho) and nitrobenzene (Λ_M 18.0 mho).

Bromotriarsinepalladium(II) Perchlorate.—Prepared as was the corresponding chloro-perchlorate, the compound was obtained as a yellow crystalline powder (Found: C, 19.6; H, 4.1. $C_{11}H_{27}O_4As_3BrClPd$ requires C, 19.7; H, 4.1%). Solubilities are similar to those of the compound [Pd triarsine Cl]ClO₄. It behaves as a uni-univalent electrolyte in nitromethane (Λ_M 80 mho).

Iodotriarsinepalladium(II) Iodide.—Palladous hydroxide (0.14 g.), dissolved in a slight excess of dilute hydriodic acid, was treated with a solution of the triarsine (0.38 g.) in alcohol (10 ml.). The dark red solution was heated under reflux for a few minutes, filtered, and cooled; the compound (0.26 g.) separated as dark red needles which were washed with alcohol and dried (Found: C, 17.9; H, 3.8; I, 34.6%; *M*, cryoscopic in 0.325% solution in nitrobenzene, 570. $C_{11}H_{27}As_3I_2Pd$ requires C, 17.7; H, 3.7; I, 34.1%; *M*, 745). Solubilities are similar to, but less than, those of the compound [Pd triarsine Br]Br. The compound is partly ionised in both nitrobenzene and nitromethane (Λ_M 10.5 mho in $PhNO_2$ and 48 mho in $MeNO_2$).

Iodotriarsinepalladium(II) Perchlorate.—Considerable difficulty was encountered in preparing this derivative because it is more soluble than the iodo-iodide; it could not be obtained pure. The compound [Pd triarsine I]I (0.13 g.) in boiling alcohol (15 ml.) was treated with an excess of 72% perchloric acid (0.25 ml.). On cooling, orange-brown crystals (0.1 g.) separated and these were washed with alcohol and dried (Found: C, 19.6; H, 3.8. $C_{11}H_{27}As_3ClIO_4Pd$ requires C, 18.4; H, 3.8%). Solubilities are similar to those of the bromo-perchlorate. It is a uni-univalent electrolyte in nitromethane (Λ_M 83 mho).

Bistriarsinepalladium(II) Diperchlorate.—Palladium hydroxide (0.30 g.), suspended in 25%

perchloric acid (3 ml.), was treated with the triarsine (1.5 g.) in alcohol (10 ml.). The mixture was heated under reflux for 15 min., filtered, and cooled; the red *perchlorate* obtained recrystallised from aqueous acetone (Found: C, 24.7; H, 5.6. $C_{22}H_{54}As_6Cl_2O_8Pd$ requires C, 24.6; H, 5.1%). The complex is soluble in water, alcohol, acetone, nitrobenzene, and nitromethane and behaves as a bi-univalent electrolyte in the last of these (Λ_M 37.9 mho).

Chlorotriarsineplatinum(II) Chloride.—Sodium tetrachloroplatinate(II) tetrahydrate (0.45 g.) was shaken with the triarsine (0.38 g.) in absolute alcohol (20 ml.) until the liquid phase was colourless. The mixture was filtered, concentrated, diluted with ether, and cooled at 0°. White crystals of the *complex* (0.40 g.) separated (Found: C, 20.9; H, 4.7. $C_{11}H_{27}As_3Cl_2Pt$ requires C, 20.3; H, 4.2%). They were soluble in water, alcohol, and nitromethane, and sparingly soluble in nitrobenzene, but insoluble in acetone, chloroform and benzene. The product behaved as a uni-univalent electrolyte in nitromethane (Λ_M 68.2 mho).

Chlorotriarsineplatinum(II) Perchlorate.—Sodium tetrachloroplatinate(II) tetrahydrate (0.9 g.) in hot water (10 ml.) was added to the triarsine (0.70 g.) in hot alcohol (10 ml.), and the mixture was evaporated to dryness. The residue was extracted with hot alcohol (10 ml.) and the cooled, filtered solution treated dropwise with perchloric acid until precipitation was just complete. (An excess of perchloric acid causes the precipitate to redissolve.) The white *perchlorate* recrystallised from aqueous acetone (yield, 0.5 g.) (Found: C, 18.8; H, 4.2; Pt, 27.0. $C_{11}H_{27}As_3Cl_2O_4Pt$ requires C, 18.5; H, 3.8; Pt, 27.3%). It is soluble in acetone, nitrobenzene, and nitromethane, and sparingly soluble in hot alcohol, but insoluble in benzene and chloroform. It is a uni-univalent electrolyte in nitrobenzene (Λ_M 28.8 mho) and in nitromethane (Λ_M 87.7 mho).

Bromotriarsineplatinum(II) Bromide.—Tetrammineplatinum(II) dibromide (0.30 g.) in hot water (10 ml.) was refluxed with the triarsine (0.27 g.) in alcohol (10 ml.) for several hours (until evolution of ammonia ceased). The solution was evaporated to dryness at reduced pressure and the residue washed several times with ice-cold acetone, leaving pale yellow crystals (0.4 g.) of the *complex*; these recrystallised from chloroform–light petroleum (Found: C, 17.9; H, 3.9. $C_{11}H_{27}As_3Br_2Pt$ requires C, 17.6; H, 3.6%). The compound is soluble in water, alcohol, and nitromethane, and sparingly soluble in acetone and chloroform, but insoluble in benzene and nitrobenzene. It behaves as a uni-univalent electrolyte in nitromethane (Λ_M 68.2 mho).

Bromotriarsineplatinum(II) Perchlorate.—An aqueous solution of the compound [Pt triarsine Br]Br, prepared as above, was treated dropwise with perchloric acid and cooled to 0°. The white crystals of the *perchlorate* were filtered off and washed with ice-cold water (Found: C, 17.3; H, 3.6; Pt, 25.8. $C_{11}H_{27}As_3BrClO_4Pt$ requires C, 17.1; H, 3.6; Pt, 25.9%). The compound is soluble in acetone, chloroform, nitromethane, and nitrobenzene, but insoluble in water and alcohol. In nitrobenzene it behaves as a uni-univalent electrolyte (Λ_M 83.3 mho).

Iodotriarsineplatinum(II) Iodide.—This was prepared by treating an aqueous solution of the chloro-complex [PtCl triarsine]Cl with an excess of sodium iodide; the solution was evaporated until crystallisation began. The *compound* was obtained as large orange crystals, m. p. 252° (Found: C, 15.9; H, 3.3; Pt, 23.2%; *M*, cryoscopic in 0.57% nitrobenzene solution, 398. $C_{11}H_{27}As_3I_2Pt$ requires C, 15.8; H, 3.2; Pt, 23.4%; *M*, 833), soluble in acetone, chloroform, nitromethane and nitrobenzene, and sparingly soluble in warm alcohol, but insoluble in water. In both nitrobenzene (Λ_M 24 mho) and nitromethane (Λ_M 79 mho) it behaves as a uni-univalent electrolyte.

Bistriarsineplatinum(II) Diperchlorate.—Sodium tetrachloroplatinate(II) tetrahydrate (0.45 g.) in hot water (10 ml.) was added to the triarsine (0.77 g.) in alcohol (20 ml.). The yellow solution was warmed (5 min.), filtered hot, and treated with an excess of perchloric acid. On cooling, the required *perchlorate* (1.0 g.) was obtained as bright yellow crystals which recrystallised from aqueous alcohol (Found: C, 21.7; H, 5.0; Pt, 16.3. $C_{22}H_{54}As_3Cl_2O_8Pt$ requires C, 22.7; H, 4.7; Pt, 16.8%). The complex is soluble in acetone, nitrobenzene, and nitromethane but only sparingly soluble in water and alcohol. In both nitrobenzene (Λ_M 48 mho) and nitromethane (Λ_M 175 mho) it is a bi-univalent electrolyte.

Tribromotriarsineplatinum(IV) Perchlorate.—The compound [Pt triarsine Br]ClO₄ (0.5 g.) in chloroform (90 ml.) was treated with bromine (0.11 g.) in carbon tetrachloride (13 ml.). The platinum *complex* (0.6 g.) separated after a few minutes as orange leaflets; after some hours it was filtered off and washed with chloroform (Found: C, 14.9; H, 3.0; Pt, 21.2. $C_{11}H_{27}As_3Br_3ClO_4Pt$ requires C, 14.4; H, 2.9; Pt, 21.2%); it is less soluble than the platinum

derivatives but is slightly soluble in nitromethane and nitrobenzene in which it is a uni-univalent electrolyte.

Tri-iodotriarsineplatinum(IV) Iodide.—The complex [Pt triarsine I]I (0.5 g.) in chloroform (30 ml.) was treated with iodine (0.16 g.) in carbon tetrachloride (40 ml.). The solution was left for several hours at 0° and deposited a dark red powder. This *complex* recrystallised from acetone as red plates (0.6 g.) (Found: C, 12.2; H, 2.6; I, 47.5. $C_{11}H_{27}As_3I_4Pt$ requires C, 12.2; H, 2.5; I, 46.8%). As with the above Pt(IV) perchlorate, the compound is slightly soluble in nitromethane and in nitrobenzene in both of which it behaves as a uni-univalent electrolyte.

Analyses.—Platinum and palladium were determined by ignition of the compound after it had been moistened with concentrated sulphuric acid. Nickel was precipitated as the dimethylglyoxime complex after Kjeldahl decomposition of the compound.

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