858. *Metallic Complexes of Dimethyl-*o*-methylthiophenylarsine. Part I. Complexes of Nickel and Palladium.**

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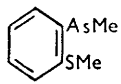
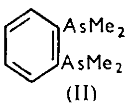
The preparation of dimethyl-*o*-methylthiophenylarsine (I), which can function as a chelating ligand, is described. Bivalent nickel forms complexes, $Ni(chel)_2X_2$ [chel = the arsine (I); X = Cl, Br, I], which are paramagnetic and poor conductors in nitrobenzene. Bivalent palladium forms complexes of three types: (*a*) $Pd\,chel\,X_2$, (X = Cl, Br, I, SCN); (*b*) $Pd(chel)_2X_2$, (X = Cl, Br, I); (*c*) $Pd(chel)_2(ClO_4)_2$. Complexes of type (*a*) are non-electrolytes in nitrobenzene. Molecular weights, conductivities, and absorption spectra indicate that in non-aqueous solutions of complexes of type (*b*) there is an equilibrium $[Pd(chel)_2X]X \rightleftharpoons [Pd\,chel\,X_2] + chel$. The compound $[Pd(chel)_2](ClO_4)_2$ has the conductivity expected for a bi-univalent electrolyte in nitrobenzene.

The chelating ligand *o*-phenylenebisdimethylarsine (II) was first prepared by Chatt and Mann,[1a] who described some of its complexes with palladium [1b]; Nyholm and his co-workers [2] have shown that it forms stable complexes with a large number of transition elements. The metal atom in some of these complexes displays an unusually high valency,[3] while in complexes of elements with a d^8-configuration (Pd^{II}, Pt^{II}, Au^{III}) the metal atom often exhibits an unusually high co-ordination number.[4, 5] Recently, a number of similar *o*-phenylene ligands containing nitrogen, phosphorus, sulphur, or arsenic have been prepared and their metal chelates examined.[6, 7]



(I)



(II)

Dimethyl-*o*-methylthiophenylarsine (I), a colourless liquid, was synthesized in order to study the types of transition-metal complex to which it would give rise. Chelate groups containing bicovalent sulphur are much less effective than tertiary arsines in forming stable complexes,[7] but this compound (I) contains a sulphur and an arsenic atom, each capable of forming a co-ordinate bond to form a five-membered ring, so it is of interest to compare its complexes with those of the diarsine (II).

The arsine (I) with nickel halides in alcoholic solution gives crystalline derivatives (Table 1) which are decomposed by water. The iodo-nickel complex is soluble in hot acetone to give a brown solution, changed to yellow by addition of a large excess (>100

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* This work was briefly reported in *Chem. and Ind.*, 1957, 143.

[1] Chatt and Mann, *J.*, 1939, (*a*) 610; (*b*) 1622.

[2] For a full list of references see Nyholm and Sutton, *J.*, 1958, 560.

[3] (*a*) Nyholm, *J.*, 1950, 2061; (*b*) *idem*, *J.*, 1951, 2602; (*c*) Nyholm and Parish, *Chem. and Ind.*, 1956, 470.

[4] Harris, Nyholm, and Stephenson, *Rec. Trav. chim.*, 1956, **75**, 687.

[5] Harris and Nyholm, *J.*, 1956, 4375; 1957, 63.

[6] Jones and Mann, *J.*, 1955, 4472; Mann and Stewart, *J.*, 1955, 1269; Hart and Mann, *Chem. and Ind.*, 1956, 574; *J.*, 1957, 3939; Mann and Watson, *J.*, 1957, 3945, 3950; Cochran, Hart, and Mann, *J.*, 1957, 2816.

[7] Backhouse, Foss, and Nyholm, *J.*, 1957, 1714; Backhouse and Nyholm, personal communication.

fold) of the arsine (I). The only compound isolated from this solution was the original nickel complex, $Ni(chel)_2I_2$. This colour change and the conductivities of the nickel complexes in nitrobenzene solution containing a large excess of arsine suggest the formation in solution of the unstable ion $[Ni(chel)_3]^{2+}$:

TABLE 1. *Nickel complexes of dimethyl-*o*-methylthiophenylarsine.*

Compound	Colour	Magnetic moment (B.M.)	Molecular cond. in $PhNO_2$ (10^{-3}M) at 25° (mho)	Molecular cond. in $PhNO_2$ (2×10^{-4}M) containing 800-fold excess of (I) at 25° (mho)
$Ni(chel)_2Cl_2$ ...	Blue	3·08	0	0·9
$Ni(chel)_2Br_2$ ...	Green	3·20	1·0	8·6
$Ni(chel)_2I_2$ ...	Brown	3·05	5·8	30·5

$$Ni(chel)_2X_2 + chel \rightleftharpoons [Ni(chel)_3]^{2+} + 2X^-$$

The equilibrium lies farther to the right when X = I, as might be expected in a non-aqueous solvent, if we regard the order of relative strengths of the nickel–halogen bonds to be Cl > Br > I.

The substitution of one $-AsMe_2$ group by —SMe in the ligand (II) markedly alters the properties of the bivalent nickel complexes. Those of *o*-phenylenebisdimethylarsine (II) are diamagnetic and uni-univalent electrolytes in nitrobenzene[3a, 8] while those of dimethyl-*o*-methylthiophenylarsine (I) are paramagnetic and poor conductors in this solvent.

Bivalent palladium forms with the arsine (I) complexes which are non-electrolytes in nitrobenzene. In these complexes, $Pd\ chel\ X_2$ (Table 2), the palladium atom has its usual covalency of four. Treatment of the complex $Pd\ chel\ X_2$ (X = Cl, Br, I) with one molar equivalent of the arsine (I) in aqueous acetone, followed by concentration and cooling of the solution, causes deposition of crystals of the corresponding complex, $Pd(chel)_2X_2$. The chloro-compound with perchloric acid in aqueous solution gives the perchlorate, $Pd(chel)_2(ClO_4)_2$, which can be recrystallized from water (Table 2).

TABLE 2. *Molecular conductivities of palladium complexes of dimethyl-*o*-methylthiophenylarsine in nitrobenzene at* 25°.

Compound	Colour	Molar concn.	Molecular cond. (mho)
$Pd\ chel\ Cl_2$	Pale yellow	10^{-3}	0·1
$Pd\ chel\ Br_2$	Yellowish-orange	10^{-3}	0·1
$Pd\ chel\ I_2$	Deep red	10^{-3}	0·1
$Pd\ chel\ (SCN)_2$	Yellowish-orange	10^{-3}	0·1
$Pd(chel)_2Cl_2$	Deep orange	10^{-3}	4·6
$Pd(chel)_2Br_2$	Orange-brown	10^{-4}	4·5
$Pd(chel)_2I_2$	Reddish-brown	10^{-4}	4·6
$Pd(chel)_2(ClO_4)_2$	Yellowish-orange	10^{-4}	57·4

The conductances of nitrobenzene solutions of the compounds $Pd(chel)_2X_2$ are increased on the addition of the arsine (I). The molecular conductivity ($\Lambda_{10,000}$) of the compound $Pd(chel)_2Cl_2$ was measured at 25° in nitrobenzene containing varying amounts of the arsine (I). The molecular conductivity reaches a limiting value (25—26 mho) when the arsine (I) is present in concentrations above 300-fold molar excess. The molecular conductivities ($\Lambda_{10,000}$) of the corresponding bromo- and iodo-complexes $Pd(chel)_2Br_2$ and $Pd(chel)_2I_2$ at 25° in nitrobenzene containing the arsine (I) in 800-fold excess were 27·2 and 25·5 mho, respectively.

Molecular weights of the chloro- and iodo-complexes are listed in Table 3.

The absorption spectra of the iodo-complexes, shown in Fig. 1, indicate that $Pd(chel)_2I_2$ dissociates to a considerable extent in acetone to $Pd\ chel\ I_2$. In the presence of a large excess of the chelate (I) the compound $Pd(chel)_2I_2$ does not yield any appreciable concentration of $Pd\ chel\ I_2$ in solution.

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[8] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

TABLE 3. *Molecular weights, M, and van t'Hoff factors, i, determined cryoscopically in nitrobenzene.*

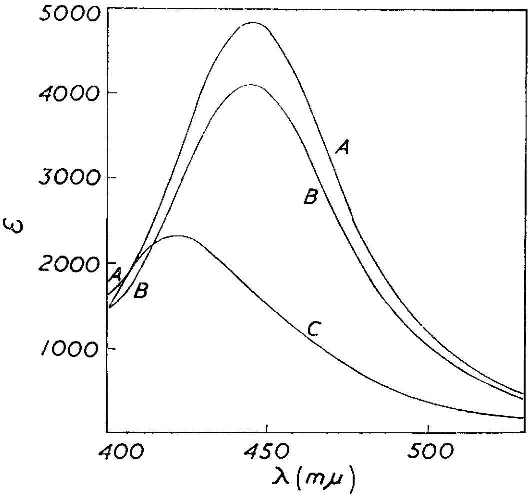
Compound	Concn. (% w/w)	*M* (obs.)	*M* (calc.)	*i*
$Pd(chel)_2Cl_2$	0·73	385	634	1·65
$Pd(chel)_2I_2$	1·23	499	817	1·64

The evidence from conductivity measurements, molecular weight determinations, and absorption spectra indicates that in acetone and nitrobenzene there exists an equilibrium:

$$[Pd(chel)_2X]^+X^- \rightleftharpoons [Pd\ chel\ X_2] + chel$$

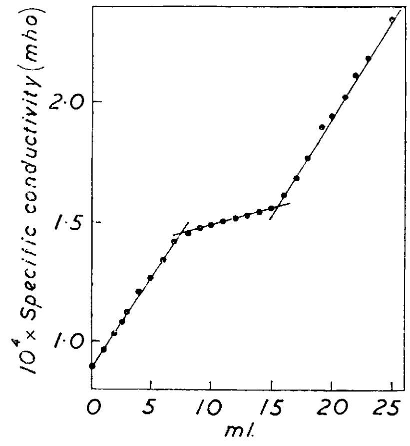
This does not necessarily mean that in these solvents the palladium atom is quinquecovalent, since the sixth position is probably occupied by a molecule of the solvent. The conductivity of the compound $Pd(chel)_2(ClO_4)_2$ indicates that the palladium atom is quadricovalent, as might be expected since the perchlorate ion shows no tendency to co-ordinate to palladium.[9]

FIG. 1. *Absorption spectra of iodo-complexes* (2×10^{-4}M-*solutions in acetone*).



A, Pd chel I_2. *B*, $Pd(chel)_2I_2$. *C*, $Pd(chel)_2I_2$ with 800-fold excess of chel.

FIG. 2. *Conductimetric titration of* $Pd(chel)_2(ClO_4)_2$ (150 *ml. of* 5×10^{-4}M-*solution*) *with* 10^{-2}M-*sodium iodide in acetone at* 25° (*corrected for dilution*). *Theoretical end points* 7·5 *ml. and* 15·0 *ml.*



Conductimetric titration of $[Pd(chel)_2](ClO_4)_2$ with iodide ions in acetone solution (Fig. 2) shows that two iodide ions react with the complex. The absorption spectrum of the solution at the completion of the titration displays a maximum at 443·7 mμ with the same value for the extinction coefficient ($\log \varepsilon = 3{\cdot}61$) as was obtained for $Pd(chel)_2I_2$ in acetone.

Bivalent palladium can possess a co-ordination number greater than four; the compound $Pd(diarsine)_2I_2$ [diarsine = (II)] possesses a distorted octahedral configuration in the solid state [8] and exists in nitrobenzene as a uni-univalent electrolyte.[5] The chloropalladate(II) ion, having more than four chlorine atoms per palladium atom, exists in aqueous solution,[10] and the ion $[PdBr_6]^{4-}$ exists in nitrobenzene solutions containing the tetrabromopalladate(II) ion, $[PdBr_4]^{2-}$, and bromide ion.[11] The crystalline compounds $Pd(chel)_2X_2$ show marked differences in colour from the compounds Pd chel X_2. In the solid state the former undoubtedly possess a distorted octahedral configuration, similar to that found for $Pd(diarsine)_2I_2$.

[9] Livingstone, *J.*, 1957, 5091.

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

[11] Harris, Livingstone, and Reece, *Austral. J. Chem.*, 1957, **10**, 282.

The ligand (I) appears to be less effective than *o*-phenylenebisdimethylarsine (II) in stabilizing sexicovalent palladium. A detailed discussion of the type of bonding present in sexicovalent palladium complexes has been published.[5] On ligand-field theory the filled d_{z^2} orbital of the palladium atom projects along the line of approach to the two vacant octahedral sites. Harris and Nyholm [5] postulate double bonding between palladium and two of the four arsenic atoms in the compounds $Pd(diarsine)_2X_2$, thereby causing the palladium atom to possess a residual positive charge. If we consider similar π-bonding to occur in the complexes $Pd(chel)_2X_2$, the greater electronegativity of sulphur (2·5) than of arsenic (2·0) [12] will produce a lower residual positive charge on the palladium atom. Accordingly, a greater repulsion will be exerted along the *z*-axis on any incoming negatively charged ligands in the fifth and sixth octahedral positions, leading to lower stability of the palladium complexes of ligand (I) than of ligand (II).

EXPERIMENTAL

*Dimethyl-*o*-methylthiophenylarsine.*—*o*-Methylthioaniline (100 g.), prepared from *o*-mercaptoaniline,[13] was treated with 5M-sulphuric acid (400 ml.). This solution was diazotized at 10° by the addition of a solution of sodium nitrite (58 g.), then 5M-sodium hydroxide (215 ml.) was added. The diazotized solution was treated quickly below 10° with a solution containing arsenious oxide (14 g.), sodium hydroxide (120 g.), and copper sulphate pentahydrate (25 g.) in water (1 l.). The mixture was acidified with acetic acid and filtered. The filtrate was concentrated to 800 ml. and made acid to Congo Red paper with hydrochloric acid. The crude product was filtered off and recrystallised from 50% alcohol, yielding pure *o-methylthiophenylarsonic acid* (63 g.), m. p. 154—154·5 (Found: C, 34·0; H, 3·8; $C_7H_9O_3SAs$ requires C, 33·9; H, 3·7%). Sulphur dioxide was passed for several hours into a solution of the arsonic acid (63 g.) in 7M-hydrochloric acid. The resulting crystalline precipitate contained water, which was removed by dissolution of the crude product in benzene and separation of the aqueous layer. The benzene solution was dried (Na_2SO_4) and, on being concentrated and cooled, yielded colourless crystals of *dichloro-*o*-methylthiophenylarsine* (52 g.), m. p. 66—67° (Found: C, 31·3; H, 2·6. $C_7H_7Cl_2SAs$ requires C, 31·3; H, 2·6%). The dichloroarsine (62 g.) was dissolved in ether (500 ml.) and treated with an ethereal solution of the Grignard reagent from methyl iodide (78·5 g.) and magnesium (13 g.). The yellow addition product was decomposed with ammonium chloride solution. The ether layer was separated, dried, and evaporated to give a crude oil (54 g.) which was distilled under reduced pressure (coal gas), yielding *dimethyl-*o*-methylthiophenylarsine* (42·7 g.), b. p. 122—124°/3·5 mm., n_D^{25} 1·6278 (Found: C, 47·2; H, 5·8. $C_9H_{13}SAs$ requires C, 47·4; H, 5·7%).

*Dichlorobisdimethyl-*o*-methylthiophenylarsinenickel*(II).—Dimethyl-*o*-methylthiophenylarsine (1 g.) in alcohol (5 ml.) was added to a warm solution of anhydrous nickel chloride (0·59 g.) in alcohol (10 ml.). On cooling, the solution deposited blue crystals of the *nickel complex*; these were filtered off and washed with alcohol (Found: C, 37·1; H, 4·8; Cl, 12·0. $C_{18}H_{26}Cl_2S_2As_2Ni$ requires C, 36·9; H, 4·5; Cl, 12·1%).

*Dibromobisdimethyl-*o*-methylthiophenylarsinenickel*(II).—Prepared from anhydrous nickel bromide as for the chloro-complex, the bright green crystals of the *compound* were filtered off and washed with alcohol and a little acetone (Found: C, 31·8; H, 4·0; Br, 23·6; N, 8·9. $C_{18}H_{26}Br_2S_2As_2Ni$ requires C, 32·0; H, 3·9; Br, 23·7; Ni, 8·7%).

*Di-iodobisdimethyl-*o*-methylthiophenylarsinenickel*(II).—Dimethyl-*o*-methylthiophenylarsine (0·8 g.) in alcohol (5 ml.) was added to a hot solution of nickel perchlorate hexahydrate (1·3 g.) and lithium iodide (0·5 g.) in alcohol. The dark brown crystals of the *iodo-complex* were filtered off and washed with a little alcohol (Found: C, 28·4; H, 3·4; I, 32·9; Ni, 8·0. $C_{18}H_{26}I_2S_2As_2Ni$ requires C, 28·1; H, 3·4, I, 33·0; Ni, 7·6%).

*Dichloro(dimethyl-*o*-methylthiophenylarsine)palladium*(II).—Dimethyl-*o*-methylthiophenylarsine (2·7 g.) in alcohol was added to potassium chloropalladate(II) (3·9 g.) in water (75 ml.). The yellow precipitate was filtered off, washed with water, and recrystallized from acetone (450 ml.) containing 10% of water, to yield pale yellow crystals of the *complex* (4·1 g.) (Found: C, 26·5; H, 3·2; Cl, 17·5; Pd, 26·5. $C_9H_{13}Cl_2SAsPd$ requires C, 26·6; H, 3·2; Cl, 17·5; Pd, 26·3%).

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[12] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 2nd edn., 1940, p. 60.

[13] Livingstone, *J.*, 1956, 437.

*Dibromo(dimethyl-*o*-methylthiophenylarsine)palladium*(II).—An aqueous solution of potassium bromopalladate(II) (1·1 g.) was treated with dimethyl-*o*-methylthiophenylarsine (0·5 g.) in alcohol. The orange precipitate was filtered off, washed with water, and recrystallized from 90% acetone to give orange crystals of the *bromo-complex* (0·44 g.) (Found: C, 22·4; H, 2·6; Br, 32·1; Pd, 22·0. $C_9H_{13}Br_2SAsPd$ requires C, 21·9; H, 2·6; Br, 32·3; Pd, 21·6%).

*Di-iodo(dimethyl-*o*-methylthiophenylarsine)palladium*(II).—The chloro-complex (0·9 g.) was dissolved in hot 90% acetone (200 ml.) and added to lithium iodide (5 g.) in hot 90% acetone (50 ml.). The deep red solution was concentrated to 100 ml. and cooled to give red crystals of the *compound*, which was recrystallized from 90% acetone (yield, 1·0 g.) (Found: C, 18·3; H, 2·1; I, 43·0; Pd, 18·2. $C_9H_{13}I_2SAsPd$ requires C, 18·4; H, 2·2; I, 43·1; Pd, 18·1%).

*Dithiocyanato(dimethyl-*o*-methylthiophenylarsine)palladium*(II).—The chloro-complex (0·4 g.) was dissolved in hot 90% acetone (85 ml.) and added to a solution of lithium thiocyanate (2 g.) in aqueous acetone. The reddish-orange solution, after being concentrated to 40 ml. and cooled, deposited yellowish-orange crystals of the *compound*, which was recrystallized from aqueous acetone (yield, 0·25 g.) (Found: C, 29·6; H, 3·1; N, 6·4; Pd, 23·7. $C_{11}H_{13}N_2S_3AsPd$ requires C, 29·3; H, 2·9; N, 6·2; Pd, 23·6%).

*Dichlorobisdimethyl-*o*-methylthiophenylarsinepalladium*(II).—Dimethyl-*o*-methylthiophenylarsine (0·55 g.) was added to a suspension of dichloro(dimethyl-*o*-methylthiophenylarsine)-palladium(II) (1 g.) in 90% acetone (100 ml.) to give a deep orange solution. The solution was evaporated on a steam-bath to a viscous gum, which, when scratched, crystallised. The deep orange crystals of the *compound* were triturated with ether and dried *in vacuo* (P_2O_5) (yield 1·20 g., m. p. 88°) (Found: C, 32·6; H, 4·1; Cl, 11·0; Pd, 16·6. $C_{18}H_{26}Cl_2As_2Pd$ requires C, 34·1; H, 4·2; Cl, 11·2; Pd, 16·8%). The compound is hygroscopic.

*Dibromobisdimethyl-*o*-methylthiophenylarsinepalladium*(II).—Dimethyl-*o*-methylthiophenylarsine (0·4 g.) was added to dibromo(dimethyl-*o*-methylthiophenylarsine)palladium(II) (0·67 g.) in 90% acetone. The solution was concentrated to small bulk (8 ml.) and kept overnight; orange crystals of the *complex* separated. The crystals were filtered off, washed with ether, and dried *in vacuo* (P_2O_5) (Found: Br, 21·8; Pd, 14·7. $C_{18}H_{26}Br_2S_2As_2Pd$ requires Br, 22·1; Pd, 14·7%).

*Di-iodobisdimethyl-*o*-methylthiophenylarsinepalladium*(II).—Dimethyl-*o*-methylthiophenylarsine (1·25 g.) was added to a suspension of di-iodo(dimethyl-*o*-methylthiophenylarsine)-palladium(II) (1 g.) in 80% acetone (150 ml.), producing a red solution, which was concentrated to 50 ml. and cooled. The solution deposited brownish-orange crystals of the pure *compound* which were filtered off, washed with ether, and dried (yield, 0·90 g.) (Found: C, 26·7; H, 3·2; I, 31·0; Pd, 13·0. $C_{18}H_{26}I_2S_2As_2Pd$ requires C, 26·5; H, 3·2; I, 31·0; Pd, 13·0%).

*Bisdimethyl-*o*-methylthiophenylarsinepalladium*(II) *Perchlorate*.—Dichlorobisdimethyl-*o*-methylthiophenylarsinepalladium(II) in hot water (15 ml.) was treated with 72% perchloric acid (2 ml.). The resulting yellow precipitate was filtered off, washed with a little water, and recrystallised from water, washed with acetone, and dried (yield of the pure *compound*, 0·2 g.) (Found: C, 28·1; H, 3·4; Pd, 13·9. $C_{18}H_{26}O_8Cl_2S_2As_2Pd$ requires C, 28·4; H, 3·4; Pd, 14·0%).

Magnetic-susceptibility Measurements.—The magnetic susceptibilities of the nickel complexes were measured on the solid compounds at room temperature. The values for the diamagnetic corrections are taken from Selwood.[14] The magnetic data are as follows:

Compound	T(°K)	$10^6\chi_g$	$10^6\chi_M$	$10^6\chi_M$ (corr. for diamagnetism)	$\mu_{eff.}$ (B.M.)
$Ni(chel)_2Cl_2$	288	6·35	3722	4064	3·08
$Ni(chel)_2Br_2$	295	5·91	3997	4360	3·20
$Ni(chel)_2I_2$	298	4·49	3455	3846	3·05

Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the microanalytical laboratory of this University.

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[14] Selwood, " Magnetochemistry," Interscience Publ. Inc., New York, 1943, p. 52.