639. *Metallic Complexes of Dimethyl-*o*-methylthiophenylarsine. Part V.*[1] *Complexes of Rhodium and Iridium.*

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Complexes of the chelate group, dimethyl-*o*-methylthiophenylarsine (As–S), with tervalent rhodium and iridium have been investigated. Rhodium forms compounds $2RhX_3,3(As-S),nH_2O$ (where X = Cl, *n* = 3; X = Br, *n* = 2; X = I, *n* = 0). Evidence is given supporting the formulation of the compounds as salts $[Rh(As-S)_2X_2][Rh(As-S)X_4],nH_2O$. Iridium forms complexes of a different type, *viz.*, $IrX_3,2(As-S)$. These compounds are poor conductors in nitrobenzene and probably contain septacovalent iridium.

PREVIOUS parts[1-3] of this series have reported the complexes formed by dimethyl-*o*-methylthiophenylarsine, *o*-$C_6H_4(AsMe_2)\cdot SMe$ (As–S), with certain transition elements. Except with silver and gold, where some doubt exists concerning the structure of the complexes, the ligand *o*-$C_6H_4(AsMe_2)\cdot SMe$ behaves as a bidentate chelate group. This communication reports the compounds formed by this ligand with tervalent rhodium and tervalent iridium. The principal valency state of both these elements is three, although stable compounds of quadrivalent iridium are well known and a number of arsine[4] and pyridine[5] complexes of bivalent rhodium and arsine complexes of bivalent iridium[6] have been reported. In complexes in which they are tervalent, both elements exhibit a co-ordination number of six.

By reaction of the arsine with rhodium(III) halides in aqueous-alcoholic solution compounds were isolated having the general formula $2RhX_3,3(As-S)$ (X = Cl, Br, or I). The chloro- and bromo-complexes are hydrated with three and two molecules of water, respectively. These compounds can be formulated in three ways: (*a*) $[Rh(As-S)_3][RhX_6]$, (*b*) $[Rh(As-S)_2X_2]_3[RhX_6]$, (*c*) $[Rh(As-S)_2X_2][Rh(As-S)X_4]$. On the basis of the molecular formula, $2RhX_3,3(As-S)$, these compounds would be expected to have molecular conductivities in nitrobenzene as follows: (*a*) 75—90, (*b*) 38—45, (*c*) 25—30 mho. The chloro-compound has a value for the molecular conductivity in nitrobenzene of 30 mho and is pale yellow, while the compounds K_3RhCl_6 and Na_3RhCl_6 are red. A molecular-weight determination on the chloro-complex in freezing nitrobenzene—*M* (obs.), 670; *M* (calc.), 1156—gave the value of the van t'Hoff factor as 1·73, which is consistent with the dissociation of the compound into two ions in nitrobenzene solution. These facts suggest that the formula is neither (*a*) nor (*b*), but is most likely (*c*). A pentaiodide of

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[1] Part IV, Chiswell and Livingstone, *J.*, 1960, 1071.
[2] Livingstone, *J.*, 1958, 4222.
[3] Chiswell and Livingstone, *J.*, 1959, 2931; 1960, 97.
[4] Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1941, **75**, 127; 1942, **76**, 133.
[5] Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1942, **76**, 275.
[6] Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1943, **77**, 116.

the cation $[Rh(As{-}S)_2I_2]^+$ was also isolated; however, it is insoluble in all solvents. The compounds, all of which are diamagnetic, are listed in Table 1.

TABLE 1. *Complexes of rhodium with dimethyl-o-methylthiophenylarsine.*

Compound	Colour	Λ in $PhNO_2$ (10^{-3}M) at 25° (mho)
$[Rh(As{-}S)_2Cl_2][Rh(As{-}S)Cl_4],3H_2O$	Pale yellow	30·0
$[Rh(As{-}S)_2Br_2][Rh(As{-}S)Br_4],2H_2O$	Yellowish-orange	28·1
$[Rh(As{-}S)_2I_2][Rh(As{-}S)I_4]$	Reddish-brown	15·4
$[Rh(As{-}S)_2I_2]I_5$	Brown	Insol.

As can be seen in Table 1, the chloro- and bromo-complexes have molecular conductivities in the range expected for uni-univalent electrolytes but the iodo-complex has a conductivity which is little more than half this value. The values for the molecular conductivity (Λ_{1000}) of the iodo-complex in nitromethane (42·8 mho) and in acetone (82·4 mho) are also a little over half that of a uni-univalent electrolyte in these solvents. At a concentration of 10^{-4}M the molecular conductivity (18·8 mho) in nitrobenzene is unaltered in the presence of a 100-fold molar excess of the ligand. It is clear that no dissociation, involving the splitting off of a molecule of ligand, occurs in nitrobenzene solution. No explanation is offered for the low conductivity of this compound.

It is noteworthy that the ligand, *o*-phenylenebisdimethylarsine (As–As), gives with tervalent rhodium complexes which have two halogen atoms and two molecules of the chelate in the cation; these were isolated as the halides, $[Rh(As{-}As)_2X_2]X$ (As–As = *o*-phenylenebisdimethylarsine and X = Cl, Br, or I).[7]

By reaction of ammonium chloroiridate(III) with the arsine in aqueous alcohol in the presence of the appropriate halide ion the compounds, $IrX_3,2(As{-}S)$ (X = Cl, Br, or I), can be obtained. These compounds, which are listed in Table 2, are diamagnetic and are insoluble in water, but moderately soluble in acetone, nitrobenzene, and nitromethane. The chloro- and iodo-complexes are monomeric in freezing nitrobenzene. The conductivities of these compounds in the three solvents, nitrobenzene, nitromethane, and acetone, are interesting. The usual values for the conductivity of uni-univalent electrolytes in these solvents are 25—30, 75—90, and 130—150 mho, respectively. The three complexes are only slightly dissociated in nitrobenzene solution, but the iodo-complex is appreciably more so than the other two. In the more polar solvents, nitromethane and acetone, the degree of ionic dissociation is greater than in nitrobenzene; it is slightly greater for the bromo- than for the chloro-complex. However, in both solvents the iodo-complex behaves as a uni-univalent electrolyte.

TABLE 2. *Complexes of iridium with dimethyl-o-methylthiophenylarsine.*

		Λ (10^{-3}M) at 25° (mho)		
Compound	Colour	$PhNO_2$	$MeNO_2$	Me_2CO
$Ir(As{-}S)_2Cl_3$	Yellow	1·2	27·3	24·4
$Ir(As{-}S)_2Br_3$	Orange	1·7	29·3	39·4
$Ir(As{-}S)_2I_3$	Yellowish-brown	4·3	85·3	134

It was thought that these compounds in solution may lose a molecule of ligand; this occurs with the complexes of palladium [2] and platinum [1] with this ligand. Consequently, the molecular conductivity ($\Lambda_{10,000}$) of the iodo-complex was measured first in nitrobenzene and secondly in nitrobenzene containing a 100-fold molar excess (above that contained in the complex) of the ligand: the value of 4·8 mho was obtained in each case. The absorption spectra of solutions of the iodo-complex in (*a*) nitrobenzene and (*b*) nitrobenzene containing a 100-fold molar excess of the ligand were identical over the range 430—850 mμ ($\lambda_{max.}$ 795 mμ; ε 400). The absorption spectra of solutions of the iodo-complex in (*c*) acetone and (*d*) acetone containing a 100-fold molar excess of the ligand were also measured. These spectra are identical ($\lambda_{max.}$ 390 mμ; ε 3700; $\lambda_{max.}$ 800 mμ;

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[7] Nyholm, *J.*, 1950, 857.

ε 370) and very similar to the spectra of the nitrobenzene solutions. These results show that in solution in these solvents there is no dissociation which involves a splitting off of a molecule of ligand from the complex. Attempts to isolate a perchlorate and a picrate of the complex ion, $[Ir(As{-}S)_2I_2]^+$, were unsuccessful.

It is known that both arsines [8] and alkyl sulphides [9] form stable complexes with tervalent iridium; hence it seems most likely that the ligand is behaving as a chelate group in these complexes and that both arsine and sulphur atoms are covalently bound to the iridium atom. Such a structure requires septacovalent iridium. Although no compounds of iridium with a co-ordination number of seven have been reported hitherto, septacovalency has been established for iodine,[10] zirconium,[11] niobium,[12] tantalum,[12] and probably for rhodium.[13] It has been shown that with bivalent palladium [2] and bivalent platinum [1] the ligand forms complexes in which the metal atom has a co-ordination number greater than the usual value of four. Nothing can be said with certainty concerning the orbitals used for bonding by septacovalent iridium(III), but it seems reasonable to assume that the bonding pairs are $5(d\gamma)^4 6(s)^2 6(p)^6 6(d\varepsilon)^2$.

EXPERIMENTAL

*Dichlorobis(dimethyl-*o*-methylthiophenylarsine)rhodium*(III) *Tetrachloro(dimethyl-*o*-methylthiophenylarsine)rhodate*(III) *Trihydrate*.—The arsine (0·5 g.) in alcohol (20 ml.) was added to a solution of rhodium(III) hydroxide (0·3 g.) in 10N-hydrochloric acid (10 ml.). The mixture was shaken for 5 min. then the precipitate was filtered off and recrystallized from 50% aqueous alcohol to give the crystalline *compound*, which was dried (P_2O_5) (yield, 0·6 g.) (Found: C, 28·1; H, 4·1; Cl, 18·1; Rh, 17·6%; *M*, cryoscopically in 0·35% nitrobenzene, 670. $C_{27}H_{45}O_3Cl_6S_3As_3Rh_2$ requires C, 28·1; H, 3·9; Cl, 18·4; Rh, 17·7%; *M*, 1156).

*Dibromobis(dimethyl-*o*-methylthiophenylarsine)rhodium*(III) *Tetrabromo(dimethyl-*o*-methylthiophenylarsine)rhodate*(III) *Dihydrate*.—This *compound* (0·3 g.) was prepared similarly by using hydrobromic acid (Found: C, 23·3; H, 3·3; Br, 34·2; Rh, 14·7. $C_{27}H_{43}O_2Br_6S_3As_3Rh_2$ requires C, 23·1; H, 3·1; Br, 34·2; Rh, 14·6%).

*Di-iodobis(dimethyl-*o*-methylthiophenylarsine)rhodium*(III) *Tetraiodo(dimethyl-*o*-methylthiophenylarsine)rhodate*(III).—The arsine (0·5 g.) in alcohol (10 ml.) was added to a solution of sodium hexachlororhodate(III) (0·3 g.) and lithium iodide (0·4 g.) in water (10 ml.). The solution was heated on the water-bath for 20 min. and, on cooling, gave the *iodo-complex*, which was recrystallized from alcohol (yield, 0·5 g.) (Found: C, 19·75; H, 2·5; I, 46·1; Rh, 12·4. $C_{27}H_{39}I_6S_3As_3Rh_2$ requires C, 19·6; H, 2·4; I, 46·1; Rh, 12·5%).

*Di-iodobis(dimethyl-*o*-methylthiophenylarsine)rhodium*(III) *Pentaiodide*.—Sodium hexachlororhodate(III) (0·5 g.) in water (5 ml.) was treated with 66% hydriodic acid (5 ml.) containing iodine and then with the arsine in alcohol (25 ml.). The solution was refluxed for 2 hr. and cooled, and the *complex* (0·5 g.) filtered off (Found: C, 14·4; H, 2·5; I, 61·5; Rh, 7·6. $C_{18}H_{26}I_7S_2As_2Rh$ requires C, 14·9; H, 1·8; I, 61·3; Rh, 7·1%).

*Trichlorobis(dimethyl-*o*-methylthiophenylarsine)iridium*(III).—The arsine (0·5 g.) in alcohol (10 ml.) was added to a solution of ammonium hexachloroiridate(III) (0·4 g.) in water (10 ml.), containing 10N-hydrochloric acid (2 drops). The solution was heated on the water-bath for 30 min., then cooled. Addition of water (10 ml.) precipitated a red oil, which was separated and heated with alcohol (20 ml.). The mixture, upon cooling, deposited the crystalline *compound*, which was filtered off and washed with a little alcohol (yield, 0·4 g.) (Found: C, 28·8; H, 3·4; Cl, 14·0; Ir, 25·2%; *M*, cryoscopically in 0·54% nitrobenzene, 870. $C_{18}H_{26}Cl_3S_2As_2Ir$ requires C, 28·6; H, 3·5; Cl, 14·1; Ir, 25·5%; *M*, 756).

*Tribromobis(dimethyl-*o*-methylthiophenylarsine)iridium*(III).—In a similar manner a solution of ammonium hexachloroiridate(III) (0·4 g.) in 34% hydrobromic acid (10 ml.) gave the monosolvated *bromo-compound* (yield, 0·45 g.) (Found: C, 25·5; H, 2·9; Br, 25·8; Ir, 20·8.

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[8] Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1945, **79**, 121.

[9] Ray and Adhikari, *J. Indian Chem. Soc.*, 1932, **9**, 251.

[10] Lord, Lynch, Schumb, and Slowinski, *J. Amer. Chem. Soc.*, 1950, **72**, 522.

[11] Hampson and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 2702; Zachariasen, *Acta Cryst.*, 1954, **7**, 792.

[12] Hoard, *Acta Cryst.*, 1939, **61**, 1252.

[13] Sharpe, *J.*, 1950, 3444.

$C_{18}H_{26}Br_3S_2As_2Ir,C_2H_5{\cdot}OH$ requires C, 25·7; H, 3·4; Br, 25·7; Ir, 20·7%). When heated to decomposition the compound gave a colourless condensate.

*Tri-iodobis(dimethyl-*o*-methylthiophenylarsine)iridium*(III).—In a similar manner a solution of ammonium hexachloroiridate(III) (0·4 g.) and sodium iodide (2 g.) in water (10 ml.) yielded the crystalline *iodo-complex* (0·4 g.) (Found: C, 21·1; H, 2·3; I, 37·3; Ir, 18·8%; *M*, cryoscopically in 0·27% nitrobenzene, 960. $C_{18}H_{26}S_2As_2I_3Ir$ requires C, 21·0; H, 2·5; I, 37·4; Ir, 18·8%; *M*, 1030).

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