

**219.** *Metallic Complexes of Dimethyl-o-(methylthio)phenylarsine.*  
*Part IV.<sup>1</sup> Complexes of Platinum.*

By B. CHISWELL and S. E. LIVINGSTONE.

Complexes formed by platinum with dimethyl-*o*-(methylthio)phenylarsine (As-S) are of several types. In some the platinum atom is quadri-valent; *e.g.*,  $[\text{Pt}(\text{As-S})_2]^{2+}(\text{ClO}_4)_2^{2-}$  and  $[\text{Pt}(\text{As-S})_2]^{2+}[\text{PtCl}_6]^{2-}$  are salts. However,  $\text{Pt}(\text{As-S})\text{I}_2$  is a non-electrolyte and monomeric in nitrobenzene. Conductivity studies and absorption-spectral measurements indicate that in non-aqueous solutions of some complexes there is an equilibrium,  $[\text{Pt}(\text{As-S})_2\text{X}]\text{X} \rightleftharpoons \text{Pt}(\text{As-S})\text{X}_2 + \text{As-S}$ . Further evidence for the existence of the quinquovalent complex ion,  $[\text{Pt}(\text{As-S})_2\text{X}]^+$  is furnished by conductimetric titrations of the diperchlorate,  $[\text{Pt}(\text{As-S})_2](\text{ClO}_4)_2$ , with halide ions and the isolation of the complexes,  $\text{Pt}(\text{As-S})_2\text{XClO}_4$ , which are univalent electrolytes in nitrobenzene and acetone.

In previous papers co-ordination compounds formed by dimethyl-*o*-(methylthio)phenylarsine, *o*-MeS·C<sub>6</sub>H<sub>4</sub>·AsMe<sub>2</sub> (termed here As-S), with nickel and palladium,<sup>2</sup> copper, silver, and gold,<sup>3</sup> and cobalt,<sup>1</sup> have been described. In Part I<sup>2</sup> evidence was adduced from conductivity measurements, molecular-weight determinations, conductimetric titrations, and absorption spectra that the palladium complexes,  $\text{Pd}(\text{As-S})_2\text{X}_2$  (X = Cl, Br, or I), in solution in non-aqueous solvents dissociate  $[\text{Pd}(\text{As-S})_2\text{X}]^+\text{X}^- \rightleftharpoons [\text{Pd}(\text{As-S})\text{X}_2] +$

TABLE 1. *Molecular conductivities of platinum complexes of dimethyl-o-(methylthio)-phenylarsine in nitrobenzene at 25°.*

Compound	Colour	Concn. (10 <sup>-3</sup> M)	Molar condy. (mho)
$[\text{Pt}(\text{As-S})\text{I}_2]$ .....	Deep yellow	2.52	0.9
$[\text{Pt}(\text{As-S})_2](\text{ClO}_4)_2$ .....	White	1.01	56.0
$[\text{Pt}(\text{As-S})_2][\text{PtCl}_4]$	Pale pink	Insol.	
$[\text{Pt}(\text{As-S})_2][\text{PtBr}_4]$	Pale brown	Insol.	
$[\text{Pt}(\text{As-S})_2][\text{PtCl}_6]$	Orange	0.225	57.3
$[\text{Pt}(\text{As-S})_2][\text{PtBr}_6]$	Brownish-orange	Insol.	
$[\text{Pt}(\text{As-S})_2\text{Cl}]\text{Cl}, 2\text{H}_2\text{O}$	Pale yellow	0.92	24.5
$[\text{Pt}(\text{As-S})_2\text{Br}]\text{Br}, 2\text{H}_2\text{O}$	Pale yellow	0.78	19.5
$[\text{Pt}(\text{As-S})_2\text{I}]\text{I}, 2\text{H}_2\text{O}$	Pale yellow	1.00	16.5
$[\text{Pt}(\text{As-S})_2\text{Cl}]\text{ClO}_4$	Cream	1.14	30.3
$[\text{Pt}(\text{As-S})_2\text{Br}]\text{ClO}_4$	Cream	1.00	28.3
$[\text{Pt}(\text{As-S})_2\text{I}]\text{ClO}_4$	Buff	0.99	24.2

As-S. Palladium(II) appears to have a co-ordination number of five in the complexes of the type,  $[\text{Pd}(\text{As-S})_2\text{X}]^+\text{X}^-$ , and the present work was undertaken to see whether platinum(II) would form similar complexes. The compounds prepared are listed in Table 1.

<sup>1</sup> Part III, Livingstone, *J.*, 1960, 97.

<sup>2</sup> *Idem*, *J.*, 1958, 4222.

<sup>3</sup> *Idem*, *J.*, 1959, 2931.

Two iodo-complexes,  $\text{Pt}(\text{As-S})\text{I}_2$  and  $\text{Pt}(\text{As-S})_2\text{I}_2 \cdot 2\text{H}_2\text{O}$ , were obtained. The former is a non-electrolyte and is monomeric in freezing nitrobenzene. The latter is a paler yellow and in nitrobenzene solution has a molecular conductivity ( $\Lambda_{1000}$  16.5 mho), which is considerably less than that of a uni-univalent electrolyte (23–30 mho). At further dilution the molecular conductivity ( $\Lambda_{10,000}$ ) is 18.2 mho. However, in nitrobenzene solution containing a fifty-fold excess of the arsine above that contained in the salt, the value of the conductivity ( $\Lambda_{10,000}$ ) is 29.7 mho. Similar chloro- and bromo-complexes,  $\text{Pt}(\text{As-S})_2\text{X}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), were prepared. The water in these compounds is not removed over phosphoric oxide. The chloro-compound has a molecular conductivity ( $\Lambda_{10,000}$ ) in nitrobenzene of 25.5 mho. In the presence of a ten-fold excess of the arsine

FIG. 1. Absorption spectra of iodo-complexes ( $10^{-3}\text{M}$ ) in acetone. A,  $\text{Pt}(\text{As-S})\text{I}_2$ . B,  $\text{Pt}(\text{As-S})_2\text{I}_2$ . C,  $\text{Pt}(\text{As-S})_2\text{I}_2$  with 100-fold excess of As-S. D,  $[\text{Pt}(\text{As-S})_2\text{I}]\text{ClO}_4$ .

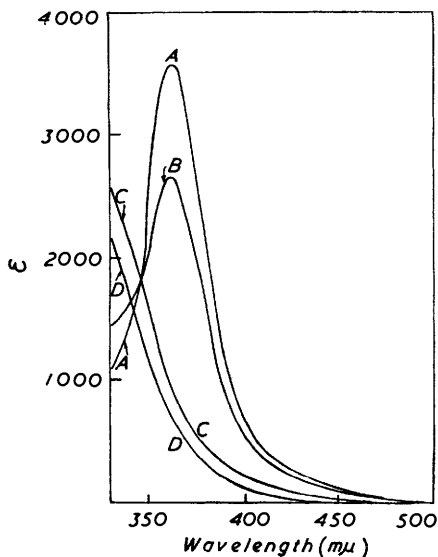
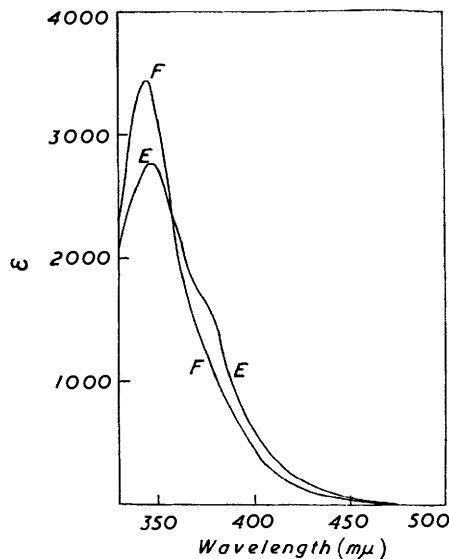


FIG. 2. Absorption spectra of chloro-complexes ( $10^{-3}\text{M}$ ) in acetone. E,  $\text{Pt}(\text{As-S})_2\text{Cl}_2$ . F,  $[\text{Pt}(\text{As-S})_2\text{Cl}]\text{ClO}_4$ .



the conductivity is increased to 26.4 mho, while in the presence of a fifty-fold excess the value is 27.6 mho. These results are consistent with the hypothesis that in nitrobenzene solution the complexes exist principally as the uni-univalent electrolytes,  $[\text{Pt}(\text{As-S})_2\text{X}]\text{X}$ , in equilibrium with the non-electrolytes:  $[\text{Pt}(\text{As-S})_2\text{X}]^+\text{X}^- \rightleftharpoons [\text{Pt}(\text{As-S})_2\text{X}_2] + \text{As-S}$ . This equilibrium lies further to the right for the iodo-complexes. It is similar to that which occurs with the palladium complexes,  $\text{Pd}(\text{As-S})_2\text{X}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ).<sup>2</sup>

TABLE 2. Molecular conductivities ( $\Lambda$ ) in acetone at 25°.

Compound	Concn. ( $10^{-3}\text{M}$ )	$\Lambda$ (mho)	Compound	Concn. ( $10^{-3}\text{M}$ )	$\Lambda$ (mho)
$[\text{Pt}(\text{As-S})_2\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$	1.05	61	$[\text{Pt}(\text{As-S})_2\text{I}]\text{ClO}_4$	1.05	149
$[\text{Pt}(\text{As-S})_2\text{Br}]\text{Br} \cdot 2\text{H}_2\text{O}$	0.99	51	$[\text{Pt}(\text{As-S})_2](\text{ClO}_4)_2$	1.01	291
$[\text{Pt}(\text{As-S})_2\text{I}]\text{I} \cdot 2\text{H}_2\text{O}$	1.02	46	$\text{NaClO}_4$	1.00	146
$[\text{Pt}(\text{As-S})_2\text{Cl}]\text{ClO}_4$	1.04	142	$\text{LiI}$	1.00	135
$[\text{Pt}(\text{As-S})_2\text{Br}]\text{ClO}_4$	1.02	142			

The perchlorates of the ions,  $[\text{Pt}(\text{As-S})_2\text{X}]^+$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ), are uni-univalent electrolytes in nitrobenzene solution (see Table 1). In Table 2 are listed the conductivities in acetone solution of the complexes containing the cations,  $[\text{Pt}(\text{As-S})_2\text{X}]^+$ ; the conductivities of the diperchlorate,  $[\text{Pt}(\text{As-S})_2](\text{ClO}_4)_2$ , sodium perchlorate, and lithium iodide are

given for comparison. Whereas the perchlorates are uni-univalent electrolytes in acetone solution, the halides have conductivities less than that expected for uni-univalent electrolytes in this solvent (approx. 145 mho). It appears that the equilibrium written above lies more in favour of the quadricovalent non-electrolytes in acetone than in nitrobenzene solution. Additional evidence of this equilibrium is furnished by the absorption spectra shown in Fig. 1. An acetone solution of the compound,  $\text{Pt(As-S)}_2\text{I}_2 \cdot 2\text{H}_2\text{O}$ , displays an absorption maximum at the same wavelength ( $\lambda_{\text{max}}$ , 362  $\text{m}\mu$ ) as a solution of the non-electrolyte,  $\text{Pt(As-S)}_2\text{I}_2$ , but with a lower molar extinction coefficient. However, the spectrum of the former compound in acetone solution, containing a large excess of the arsine, exhibits no peak above 330  $\text{m}\mu$ , but closely resembles that of the perchlorate,  $[\text{Pt(As-S)}_2\text{I}]\text{ClO}_4$ . Fig. 2 shows the spectra of the complexes  $\text{Pt(As-S)}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $[\text{Pt(As-S)}_2\text{Cl}]\text{ClO}_4$ . The former has an absorption maximum at 347  $\text{m}\mu$  and the latter at 345  $\text{m}\mu$ .

The formation of the quinquivalent complexes is demonstrated by conductimetric titrations of the diperchlorate,  $[\text{Pt(As-S)}_2](\text{ClO}_4)_2$ , with halide ions in nitrobenzene solution. A sharp end-point occurs after the addition of one equivalent of halide ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ). There is no inflection after the addition of two equivalents of halide ion. The quinquivalent complex ions of platinum with our ligand are more stable than the corresponding palladium complex ions,  $[\text{Pd(As-S)}_2\text{X}]^+$ , which are stable in non-aqueous solvents only in the presence of a large excess of the ligand.<sup>2</sup> As was mentioned in the discussion of the palladium complexes in Part I of this series,<sup>2</sup> the metal atom in these complex ions is not necessarily quinquivalent in solution in non-aqueous ionising solvents, since it is possible that a molecule of the solvent is co-ordinated in the remaining octahedral position. Evidence for the solvation of halogenopalladate(II) ions,  $[\text{PtX}_4]^{2-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and  $[\text{Pd}_2\text{X}_6]^{2-}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ), has been published recently.<sup>4</sup> However, solvation appears to be much less for the chloroplatinate(II) ion,  $[\text{PtCl}_4]^{2-}$ .<sup>4,5</sup>

*o*-Phenylenebisdimethylarsine,  $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ , also forms complexes in which platinum is apparently quinquivalent in solution in non-aqueous polar solvents.<sup>6</sup> The complex,  $\text{Pt(As-As)}_2\text{I}_2$  ( $\text{As-As} = o\text{-phenylenebisdimethylarsine}$ ), has been shown to possess a distorted octahedral configuration in the solid state.<sup>7</sup> The structure of the corresponding complex with our ligand, *viz.*,  $\text{Pt(As-S)}_2\text{I}_2$ , in the solid state is being investigated. The bonding present in the hexicovalent palladium complexes has been discussed.<sup>2,8</sup> It seems most likely that the bonding in the analogous platinum complexes of the ligand  $\text{As-S}$  is similar, involving the use by the platinum atom of two  $6p6d$ -bonds normal to the plane of the four  $5d6s6p^2$ -hybrid bonds.

#### EXPERIMENTAL

Analyses were made on material dried over phosphoric oxide.

*Bis*[dimethyl-*o*-(methylthio)phenylarsine]platinum(II) Chloroplatinate(II).—An aqueous solution of potassium chloroplatinate(II) (1.8 g.) was added to a solution of the arsine (1 g.) in acetone (20 ml.). The precipitated complex was filtered off and washed with water, then with acetone (yield, 2.15 g.) (Found: C, 21.5; H, 2.7; Pt, 39.2.  $\text{C}_{18}\text{H}_{26}\text{Cl}_4\text{S}_2\text{As}_2\text{Pt}_2$  requires C, 21.9; H, 2.7; Pt, 39.4%).

*Bis*[dimethyl-*o*-(methylthio)phenylarsine]platinum(II) Bromoplatinate(II).—By a similar procedure to the above the bromoplatinate(II) complex was prepared from potassium bromoplatinate(II) (0.5 g.) and the arsine (0.5 g.) (yield, 0.4 g.) (Found: C, 18.5; H, 2.3; Br, 26.8; Pt, 33.4.  $\text{C}_{18}\text{H}_{26}\text{Br}_4\text{S}_2\text{As}_2\text{Pt}_2$  requires C, 18.5; H, 2.3; Br, 27.4; Pt, 33.3%).

*Bis*[dimethyl-*o*-(methylthio)phenylarsine]platinum(II) Chloroplatinate(IV).—In a similar manner the chloroplatinate(IV) was obtained from potassium chloroplatinate(IV) (0.4 g.) and the arsine

<sup>4</sup> Harris, Livingstone, and Reece, *J.*, 1959, 1505.

<sup>5</sup> Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

<sup>6</sup> Harris, Nyholm, and Phillips, unpublished work.

<sup>7</sup> Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

<sup>8</sup> Harris and Nyholm, *J.*, 1956, 4375.

(0.5 g.) (yield, 0.6 g.) (Found: C, 20.2; H, 2.4; Pt, 35.8.  $C_{18}H_{26}Cl_6S_2As_2Pt_2$  requires C, 20.4; H, 2.5; Pt, 35.8%).

*Bis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Bromoplatinate*(IV).—The bromoplatinate(IV) was obtained as described above from potassium bromoplatinate(IV) (1 g.) and the arsine (0.3 g.) (yield, 0.5 g.) (Found: C, 16.5; H, 2.1; Pt, 29.2.  $C_{18}H_{26}Br_6S_2As_2Pt_2$  requires C, 16.3; H, 2.0; Pt, 29.4%).

*Di-iododimethyl-o-(methylthio)phenylarsineplatinum*(II).—The arsine (0.5 g.) in alcohol (20 ml.) was added slowly, with stirring, to a solution containing potassium chloroplatinate(II) (1 g.) and potassium iodide (2 g.) in water (50 ml.). The precipitated *iodo-complex* was filtered off and washed with water, then with a few drops of acetone (yield, 0.6 g.) (Found: C, 16.0; H, 1.7; Pt, 28.9%; *M*, cryoscopically in 0.40% nitrobenzene solution, 650.  $C_9H_{13}I_2SAsPt$  requires C, 16.0; H, 1.9; Pt, 28.8%; *M*, 677).

*Chlorobis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Chloride Dihydrate*.—Bis[di-methyl-o-(methylthio)phenylarsine]platinum(II) chloroplatinate(II) (0.4 g.) was refluxed for 48 hr. with the arsine (0.4 g.) in 3:1 acetone-water (40 ml.). The insoluble starting material (0.05 g.) was filtered off and the solution was evaporated to approx. 10 ml. The solution, on cooling, deposited the crystalline *compound*, which recrystallized from acetone (yield, 0.4 g.) (Found: C, 28.8; H, 4.0; Cl, 9.6; Pt, 25.7.  $C_{18}H_{30}O_2Cl_2S_2As_2Pt$  requires C, 28.5; H, 4.0; Cl, 9.4; Pt, 25.8%). The compound when heated in a closed tube gives a positive test for water.

*Bromo*[bisdimethyl-o-(methylthio)phenylarsine]platinum(II) *Bromide Dihydrate*.—This *compound* was prepared in a similar manner by refluxing bromoplatinate(II) (0.4 g.) for 30 min. with the arsine (1.7 g.) (yield, 0.4 g.) (Found: C, 26.1; H, 4.0; Pt, 23.5.  $C_{18}H_{30}O_2Br_2S_2As_2Pt$  requires C, 25.5; H, 3.6; Pt, 23.0%). When heated in a closed tube it gives a positive test for water.

*Iodobis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Iodide Dihydrate*.—Potassium chloroplatinate(II) (0.4 g.) and potassium iodide (2 g.) in water (40 ml.) were added slowly, with stirring, to the arsine (0.5 g.) in acetone (20 ml.). The precipitated *iodo-complex* was filtered off and washed with water and then with a few drops of acetone (yield, 0.6 g.) (Found: C, 22.8; H, 3.2; I, 26.3; Pt, 20.8.  $C_{18}H_{30}O_2I_2S_2As_2Pt$  requires C, 23.0; H, 3.2; I, 27.0; Pt, 20.8%). The compound when heated in a closed tube gives a positive test for water.

*Chlorobis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Perchlorate*.—Treatment of a solution of the above chloride (0.2 g.) in alcohol (10 ml.) with 60% perchloric acid (4 drops) gave the crystalline *perchlorate* (0.2 g.) (Found: C, 27.1; H, 3.0; Pt, 24.7.  $C_{18}H_{26}O_4Cl_2S_2As_2Pt$  requires C, 27.5; H, 3.3; Pt, 24.8%).

*Bromobis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Perchlorate*.—In a similar manner the bromide (0.3 g.) gave the *bromo-complex perchlorate* (0.2 g.) (Found: C, 26.9; H, 3.9; Pt, 23.1.  $C_{18}H_{26}O_4ClBrS_2As_2Pt$  requires C, 26.2; H, 3.2; Pt, 23.2%).

*Iodobis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Perchlorate*.—In a similar manner the iodide (0.3 g.) gave the *iodo-complex perchlorate* (0.3 g.) (Found: C, 24.3; H, 3.3; Pt, 22.4.  $C_{18}H_{26}O_4ClIS_2As_2Pt$  requires C, 24.6; H, 3.0; Pt, 22.2%).

*Bis*[dimethyl-o-(methylthio)phenylarsine]platinum(II) *Perchlorate*.—The *iodo-complex perchlorate* (0.3 g.) in alcohol (20 ml.) was treated with silver perchlorate (1.0 g.) in water (20 ml.), and the solution was heated on the water-bath for 4 hr. to ensure complete precipitation of silver iodide. The solution was filtered and the filtrate was evaporated to approx. 25 ml.; it then gradually deposited the *compound*, which was filtered off and washed with water, then with saturated potassium iodide solution, and finally with water (yield, 0.2 g.) (Found: C, 25.4; H, 3.1; Pt, 22.8.  $C_{18}H_{26}O_8Cl_2S_2As_2Pt$  requires C, 25.4; H, 3.1; Pt, 22.8%).

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