New Sulphinate and Sulphonate Complexes of Group 1B Metals

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New sulphinate and sulphonate complexes of the Group 1B metals have been prepared. In the complexes [$ML_2(SO_2Ph)$] (L = PPh_3, M = Cu or Ag) the sulphinate ligand is bonded to the metal through oxygen, whilst in [$AuL(SO_2R)$] [L = PPh_3, R = Ph; L = $P(C_6H_{11})_3$, R = Ph, Me, or Et] the ligand is bonded through sulphur. Sulphonate complexes of stoicheiometry [$ML_2(SO_3Ph)$] (M = Cu, Ag, or Au) and [$AuL(SO_3Ph)$] have been isolated. Infrared spectra and other physical data for the new complexes are reported.

ALTHOUGH a wide range of sulphinate[1,2] and some sulphonate complexes[3-9] of both main-group and transition metals have been prepared, there are few data available on sulphinate[10-13] or sulphonate[3-5] complexes of Group 1B metals. In particular, there have been no previous reports of Group 1B sulphinate or sulphonate complexes containing organophosphine ligands. In this paper we report a number of such complexes together with i.r. data which has enabled the mode of bonding of the RSO_2 or RSO_3 ligands (*O*-,*S*-, or *OO'*-) to the metal to be determined in certain cases. A preliminary account of part of this work has been published.[14]

RESULTS AND DISCUSSION

The new sulphinate and sulphonate complexes (Tables 1 and 2) were prepared by the metathetical reaction of [MClL] (L = organophosphine, M = Group 1B metal) with Ag[SO_2R] or Ag[SO_3R] respectively. For complexes containing 2 mol of the organophosphine, an extra mol of ligand was added after the precipitated AgCl had been filtered off. The silver salts were also prepared by direct addition of ligand to Ag[SO_2R] or Ag[SO_3R], and the gold sulphinates by SO_2 insertion into [AuRL]. An alternative route to [$Cu(PPh_3)_2(SO_3Ph)$] and [$Au(PPh_3)_2(SO_3Ph)$] was the oxygenation of solutions of [$Cu(PPh_3)_2(SO_2Ph)$] or of a 1 : 1 mixture of [$Au(PPh_3)(SO_2Ph)$] and PPh_3.[14]

The complexes are white crystalline solids which are soluble in relatively non-polar solvents such as benzene, chloroform, and tetrahydrofuran (thf) but are insoluble in diethyl ether. The gold complexes are light sensitive both in the solid state and in solution, gradually depositing metallic gold. All the complexes decompose on heating and for this reason they cannot be recrystallised from hot solution. The complex [$Cu(PPh_3)_2(SO_2Ph)$] is oxidised quite rapidly by atmospheric oxygen in $CHCl_3$ or thf solution to the corresponding sulphonate [$Cu(PPh_3)_2(SO_3Ph)$], and [$Au(PPh_3)(SO_2Ph)$] is similarly oxidised to [$Au(PPh_3)_2(SO_3Ph)$] if an extra mol of PPh_3 is added to the solution.[14] The other complexes described are all stable in air, both in the solid state and in solution.

Infrared data for the new sulphinate complexes are presented in Table 2. Only those frequencies which may be assigned to sulphur–oxygen vibrations have been listed. A criterion for distinguishing between the sulphur and oxygen modes of bonding, $M-SO_2R$ and M–OSOR, in sulphinate complexes is based on the observation that the asymmetric and symmetric S–O stretchings occur at higher frequencies for the former bonding mode than for the latter. Thus for sulphur-bonded metal complexes $\nu_{asym}(SO_2)$ is found in the 1 150—1 250 cm^{-1} region and $\nu_{sym}(SO_2)$ in the 1 030—1 100 cm^{-1} region, while for oxygen-bonded complexes these frequencies are in the range 850—1 100 cm^{-1}.[1] Predictions based on this criterion have been confirmed by n.m.r.[2] and *X*-ray data[10] where available. It can be seen from Table 1 that on this basis the copper and silver complexes [$M(PPh_3)_2(SO_2Ph)$] are clearly *O*-bonded, while all the gold complexes are *S*-bonded. This trend is as expected from the application of ' hard ' and ' soft ' acid–base theory.

It is less easy from i.r. data alone to determine whether the *O*-bonded sulphinate ligand in the copper and silver complexes is co-ordinated to the metal through one or both oxygen atoms. The preference of

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TABLE 1

Preparation and properties of the new Group 1B sulphinate complexes

Complex	M.p.[a] (θ /°C)	Analysis[b] (%)			M[b]	I.r. spectra (cm^{-1})[c]			Type of bonding
		C	H	P		$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$	ν_{asym}/ν_{sym}	
$Ag[SO_2Ph]$	310—312	29.1 (28.9)	2.4 (2.0)			1 031s (br)	959s (br)	1.08	*OO′*
$[Cu(PPh_3)_2(SO_2Ph)]$	120—124	69.6 (69.7)	4.8 (4.9)	9.0 (8.5)	569[d] (729)	1 018 (sh) 1 020s	964s	1.07	*OO′*
$[Ag(PPh_3)_2(SO_2Ph)]$	125—127	65.1 (65.2)	5.0 (4.6)	7.7 (8.0)	738[e] (773)	1 032 (sh) 1 024s	967s	1.07	*OO′*
$[Au(PPh_3)(SO_2Ph)]$	98—100	48.2 (48.0)	3.4 (3.4)	5.3 (5.2)	588[d] (600)	1 203s	1 049s	1.15	*S*
$[Au\{P(C_6H_{11})_3\}(SO_2Ph)]$	115—120	47.1 (46.6)	6.0 (6.2)			1 197s	1 046s	1.14	*S*
$[Au\{P(C_6H_{11})_3\}(SO_2Me)]$	115	40.6 (41.0)	6.1 (6.5)			1 194s	1 063s	1.12	*S*
$[Au\{P(C_6H_{11})_3\}(SO_2Et)]$	120	42.4 (42.1)	6.6 (6.7)			1 187s	1 060s	1.12	*S*

[a] With decomposition. [b] Calculated values are given in parentheses. [c] In Nujol. [d] In thf. [e] In benzene.

TABLE 2

Preparation and properties of the new Group 1B sulphonate complexes

Complex	M.p. (θ_c/°C)	Analysis[a] (%)			M[a]	Λ[b] S cm^2 mol^{-1}	I.r. spectra (900—1 400 cm^{-1})[c]
		C	H	P			
$Ag[SO_3Me]$	267—270	6.5 (5.9)	1.4 (1.5)			96.1	1 384w, 1 345m, 1 326s, 1 314m, 1 236 (sh), 1 197vs (br), 1 128 (sh), 1 058vs, 1 051 (sh), 964w
$Ag[SO_3Ph]$	313—318	27.1 (27.2)	1.9 (1.9)			88.6	1 236 (sh), 1 217 (sh), 1 195s (br), 1 134s, 1 073m, 1 045s, 1 024s, 999m, 927w
$[Ag(PPh_3)_2(SO_3Me)]$	198—200	60.6 (61.0)	4.5 (4.6)	8.6 (8.5)	717[d] (727)	36.1	1 236m, 1 218s, 1 191s, 1 165s, 1 154m, 1 096s, 1 071w, 1 044s, 1 037 (sh), 1 028m, 998m, 977w, 909m
$[Ag(PPh_3)_2(SO_3Ph)]$	216—218	63.7 (63.9)	4.6 (4.5)	8.1 (7.9)	588[e] (789)	35.8	1 308w, 1 236vs (br), 1 186m, 1 171 (sh), 1 162 (sh), 1 151s, 1 125s, 1 096s, 1 072m, 1 034m, 1 028 (sh), 1 016s, 998s, 976w, 923w
$[Cu(PPh_3)_2(SO_3Ph)]$	191—195	68.0 (67.7)	4.6 (4.7)		736[e] (740)	27.0	1 308w, 1 248vs, 1 236 (sh), 1 184w, 1 154(sh), 1 150s, 1 117s, 1 098s, 1 080w, 1 044m, 1 028 (sh), 1 014s, 998s, 986w, 926w
$[Au(PPh_3)_2(SO_3Ph)]$	207—209	57.2 (57.4)	4.1 (4.0)	7.0 (7.1)	834[e] (878)	53.3	1 311w, 1 215s (br,) 1 188m, 1 163m, 1 124s, 1 101s, 1 068vw, 1 036m, 1 018m, 998m
$[Au(PPh_3)(SO_3Ph)]$	160—161[f]	47.1 (46.7)	3.0 (3.3)	5.1 (5.0)	611[e] (616)	21.8	1 345w, 1 313w, 1 293m, 1 279s, 1 188m, 1 167s, 1 156s, 1 104vs, 1 073w, 1 026m, 1 006s, 1 000 (sh), 987vs, 935w
$[Au\{P(C_6H_{11})_3\}(SO_3Ph)]$	160—162	45.4 (45.5)	6.1 (6.0)				1 340 (sh), 1 295s, 1 282s, 1 274 (sh), 1 176 (sh), 1 166vs, 1 156 (sh), 1 126w, 1 105vs, 1 068w, 1 038w, 1 024w, 1 004s, 972vs (br), 920w
$[Au\{P(C_6H_{11})_3\}(SO_3Me)]$	191—194	40.6 (39.8)	6.1 (6.3)		568[d] (572)	35.8	1 334m, 1 295 (sh), 1 289s, 1 275m, 1 271 (sh), 1 215w, 1 196w, 1 177w, 1 169w, 1 154vs, 1 144 (sh), 1 127w, 1 115w, 1 043w, 1 001 (sh), 990vs, 947s, 921w

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm^{-3} solutions in nitromethane. [c] In Nujol. [d] In chloroform. [e] In thf. [f] With decomposition.

Cu^I and Ag^I for four-co-ordination in complexes with organophosphine ligands,[15,16] however, suggests that the latter is more likely, in which case either intra- or intermolecular binding is possible.

The postulate of M–S bonding in the gold sulphinates is supported by the $\nu_{asym}(SO_2) : \nu_{sym}(SO_2)$ ratios, which are in the range 1.10—1.18 : 1 as expected for this type of complex.[17] For an *S*-bonded complex either structure (*a*) or (*b*) is possible, but we prefer (*b*), at least for R = Ph, since the structure of $Na[SO_2Ph]$ {from which $Ag[SO_2Ph]$ and hence the $[Au(PR_3)(SO_2Ph)]$ complexes were prepared} is known to contain an *S*-bonded phenyl group.[18]

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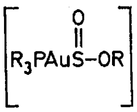
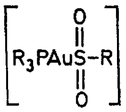
The reaction of SO_2 with $[AuPh(PPh_3)]$ gave an identical product to that obtained from the metathetical reaction of $[AuCl(PPh_3)]$ with $Ag[SO_2Ph]$, except that an i.r. spectrum of a freshly prepared sample in Nujol exhibited two additional bands at 1 324 and 1 148 cm^{-1} and a more intense band at 524 cm^{-1}. These might be due to the presence of loosely bound SO_2 since they disappear after *ca.* 0.5 h.[15] The complex $[Au(PPh_3)(SO_2Ph)]$ took up an additional mol of phosphine to give a complex the i.r. spectrum of which is similar to those of $[M(PPh_3)(SO_2Ph)]$ (M = Cu or Ag). Satisfactory analytical data for this complex could not be obtained, however, due to phosphine dissociation on attempted recrystallisation.



$$\left[R_3PAu\overset{\overset{O}{\|}}{S}{-}OR\right]$$

(*a*)



$$\left[R_3PAu\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R\right]$$

(*b*)

The i.r. spectra of the new sulphonate complexes are more difficult to interpret than those of the sulphinates, since there are a large number of bands in the 900—1 300 cm^{-1} region (Table 2). We therefore did not attempt specific assignments. The i.r. spectrum of $Ag[SO_3Me]$ is very similar to those of $K[SO_3Et]$ [19] and $Na[SO_3Me]$.[3,4] Coupled with conductivity measurements in aqueous solution, which show that the complexes $Ag[SO_3R]$ (R = Me or Ph) are strong electrolytes, the above evidence leads us to suggest that these complexes are ionic both in the solid state and in aqueous solution. The complexes containing co-ordinated phosphine ligands exhibit lower conductivities in nitromethane than $Ag[SO_3R]$ in this solvent, but are clearly dissociated to a significant extent. It seems likely that several different species are present [16] in equilibrium. Molecular-weight measurements in chloroform and thf, however, gave values which, for most of the complexes, are close to those required for a monomeric formulation. In the solid state, i.r. spectra of the phosphine-containing salts in Nujol clearly indicate that the sulphonate ligands are co-ordinated to the metal. Since there is good evidence that the R group (R = Ph or Me) in metal sulphonate complexes is attached to the sulphur atom,[20] co-ordination to the metal must be through one or more of the oxygen atoms. *X*-Ray data are required, however, before any firm conclusion can be reached as to how many oxygen atoms are involved.

EXPERIMENTAL

All the preparations of the sulphinate complexes were carried out under nitrogen or in a conventional Pyrex vacuum line. Dry solvents were deaerated before use. Light petroleum had b.p. 30—40 °C. Triphenylphosphine was freshly recrystallised from absolute alcohol. Infrared spectra were recorded between CsBr plates on a Perkin-Elmer 257 spectrometer with CO as calibrant. Solid-state Raman spectra were obtained on a Coderg PHO instrument.

Silver(I) *Benzenesulphinate*.—An ethanolic solution of $Na[SO_2Ph]\cdot 2H_2O$ (0.86 g, 4.3 mmol) was treated with a warm aqueous solution of $Ag[NO_3]$ (0.72 g, 4.3 mmol). The white precipitate produced was filtered off, washed with water and acetone, and dried under reduced pressure over P_4O_{10}, yield 70%.

(*Benzenesulphinato*)*bis*(*triphenylphosphine*)*silver*(I).—

(*i*) Triphenylphosphine (0.23 g, 0.88 mmol) and $Ag[SO_2Ph]$ (0.2 g, 0.81 mmol) in deaerated thf (30 cm^3) were shaken overnight. The remaining solid was centrifuged off and light petroleum was added to the supernatant liquid to effect precipitation. The product was dissolved in benzene and reprecipitated with diethyl ether, yield 80%.

(*ii*) Chloro(triphenylphosphine)silver(I) (0.2 g, 0.5 mmol) in deaerated thf (10 cm^3) was stirred for 1.5 h with $Ag[SO_2Ph]$ (0.12 g, 0.5 mmol). The precipitated AgCl was centrifuged off and the supernatant liquid was added to freshly recrystallised PPh_3 (0.13 g, 0.5 mmol). Light petroleum was used to effect precipitation. The product was dissolved in thf and reprecipitated by addition of light petroleum and cooling, yield 75%. (*Benzenesulphinato*)*bis*(*triphenylphosphine*)*copper*(I) was prepared similarly by this method, yield 70%.

(*Benzenesulphinato*)(*triphenylphosphine*)*gold*(I).—(*i*) A suspension of $[AuCl(PPh_3)]$ (0.2 g, 0.4 mmol) and $Ag[SO_2Ph]$ (0.1 g, 0.4 mmol) in thf (10 cm^3) was stirred for 2 h. The precipitated AgCl was centrifuged off and the supernatant liquid was evaporated to dryness. Diethyl ether (100 cm^3) was added and the mixture was stirred for 1.5 h. The product was filtered off and purified by dissolving in thf and reprecipitating with light petroleum, yield 75%.

(*ii*) The complex $[AuPh(PPh_3)]$ was treated with an excess of SO_2 which was condensed on to the complex in an ampoule at −196 °C. The mixture was allowed to warm to room temperature and left for 0.75 h. The excess of SO_2 was then allowed to evaporate off, when the product was obtained in near quantitative yield. Mass spectrum (source temperature, 95 °C): no molecular ion, $[Au(PPh_3)(SO_2Ph)]^+$, but peaks attributable to $[AuPh(PPh_3)]^+$ (*m*/*e* 534), $[Au(PPh_3)]^+$ (477), and $[PPh_3]^+$ (262).

(*Benzenesulphinato*)(*tricyclohexylphosphine*)*gold*(I).— A suspension of $[AuCl\{P(C_6H_{11})_3\}]$ (0.2 g, 0.39 mmol) and $Ag[SO_2Ph]$ (0.1 g, 0.39 mmol) in thf (15 cm^3) was stirred overnight. The precipitated AgCl was centrifuged off and the supernatant liquid was evaporated to *ca.* 5 cm^3. Light petroleum was added to effect precipitation, yield 70%. Mass spectrum (source temperature, 140 °C): no molecular ion, $[Au\{P(C_6H_{11})_3\}(SO_2Ph)]^+$, but peaks attributable to $[AuPh\{P(C_6H_{11})_3\}]^+$ (*m*/*e* 554), $[Au\{P(C_6H_{11})_3\}]^+$ (477), and $[Au\{P(C_6H_{11})_2\}]^+$ (394).

(*Methanesulphinato*)- and (*ethanesulphinato*)-(*tricyclohexylphosphine*)*gold*(I) were prepared analogously to $[Au(PPh_3)(SO_2Ph)]$ [method (*ii*)] from methyl- and ethyl-tricyclohexylphosphine)gold respectively.[20]

Silver(I) *Methanesulphonate*.—An aqueous solution of $Ag[NO_3]$ (5.0 g, 29.1 mmol) was added to $MeSO_3H$ (2.8 g, 29.1 mmol). Slow evaporation of water gave a mixture of a white powder and colourless needles. The needles were manually separated, washed with acetone and diethyl ether, and dried at reduced pressure over P_4O_{10}, yield 25%. Hydrogen-1 n.m.r. spectrum in D_2O: τ 7.26 (s). Raman spectrum (solid): 1 053m, 1 039w, 735s, 654m, 573w, 560m, 549w, 528s, and 351s cm^{-1}.

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Silver(I) *Benzenesulphonate*.—Benzenesulphonic acid solution (33% w/w; 3 g, 6.3 mmol) was treated with Ag[NO$_3$] (1.08 g, 6.4 mmol) in water (10 cm^3). The solution was evaporated on a water-bath until a crust appeared. The mixture was then allowed to cool. The white solid was filtered off and then dried over P_4O_{10}, yield 65%. Raman spectrum (solid): 1 053m, 1 039w, 735s, 654m, 573w, 560m, 549w, 528s, and 351s cm^{-1}.

(*Methanesulphonato*)*bis*(*triphenylphosphine*)*silver*(I).— A suspension of Ag[SO$_3$Me] (0.24 g, 1.2 mmol) in thf (15 cm^3) was treated with PPh$_3$ (0.63 g, 2.4 mmol) and the mixture was stirred until a colourless solution was obtained. The solution was evaporated to *ca.* 5 cm^3 and light petroleum was added to effect precipitation. The white solid was dissolved in MeOH and reprecipitated with diethyl ether.

(*Benzenesulphonato*)*bis*(*triphenylphosphine*)*silver*(I).—(*i*) A suspension of [AgCl(PPh$_3$)$_3$] (0.3 g, 0.28 mmol) and Ag[SO$_3$Ph] (0.071 g, 0.28 mmol) in thf (15 cm^3) was stirred overnight. The precipitated AgCl was filtered off and light petroleum was added to the filtrate to effect precipitation. The precipitate was dissolved in CHCl$_3$ and reprecipitated with light petroleum, yield 80%.

(*ii*) A suspension of Ag[SO$_3$Ph] (0.2 g, 7.5 mmol) in absolute EtOH (5 cm^3) was treated with PPh$_3$ (0.4 g, 15 mmol) in acetone. Addition of light petroleum precipitated a white solid, yield 85%.

(*Benzenesulphonato*)*bis*(*triphenylphosphine*)*copper*(I).— A suspension of [CuCl(PPh$_3$)] (0.4 g, 1.1 mmol) and Ag[SO$_3$Ph] (0.29 g, 1.1 mmol) in thf was stirred vigorously overnight. The precipitated AgCl was centrifuged off and the supernatant liquid was added to PPh$_3$ (0.29 g, 1.1 mmol) in EtOH (2 cm^3). Light petroleum was added to the yellow solution to effect precipitation. The solid collected was dissolved in benzene and reprecipitated with diethyl ether, yield 70%. (*Benzenesulphonato*)*bis*(*triphenylphosphine*)*gold*(I) was prepared analogously but was recrystallised by dissolving the product in thf, adding light petroleum, and then cooling.

(*Benzenesulphonato*)(*triphenylphosphine*)*gold*(I).—A suspension of [AuCl(PPh$_3$)] (0.20 g, 0.4 mmol) and Ag[SO$_3$Ph] (0.13 g, 0.49 mmol) in thf (10 cm^3) was stirred overnight. The precipitated AgCl was centrifuged off and the supernatant liquid was evaporated to dryness. Diethyl ether (100 cm^3) was added to the solid residue and the mixture was stirred for several hours. The remaining solid was filtered off, dissolved in benzene, and reprecipitated with diethyl ether.

(*Benzenesulphonato*)(*tricyclohexylphosphine*)*gold*(I).— A suspension of [AuCl{P(C$_6$H$_{11}$)$_3$}] (0.2 g, 0.39 mmol) and Ag[SO$_3$Ph] (0.11 g, 0.43 mmol) in thf (20 cm^3) was stirred overnight at ambient temperature. The precipitated AgCl was centrifuged off and the product was precipitated from the supernatant liquid by addition of light petroleum, yield 85%.

(*Methanesulphonato*)(*tricyclohexylphosphine*)*gold*(I) was prepared analogously from [AuI{P(C$_6$H$_{11}$)$_3$}] (0.2 g, 0.33 mmol) and Ag[SO$_3$Me] (0.07 g, 0.35 mmol). The product was dissolved in methanol and reprecipitated with diethyl ether, yield 75%.

One of us (J. B.) thanks the S.R.C. for the award of a maintenance grant.

[6/1541 *Received, 6th August,* 1976]