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# Transition Metal S-Sulphinate Complexes

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*This paper reports the preparation and characterisation of sulphinate complexes of palladium and platinum. The structure of the complexes has been investigated using both infrared spectroscopy and chemical reactivity. It is concluded that the sulphinate ligand in all these complexes behaves as a terminal, sulphur bonded ligand. The action of typical halide-bridge breaking reagents has been shown to give rise to a reaction scheme which is satisfactory in interpreting earlier work on these systems.*

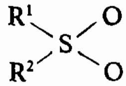
## Introduction

In a recent publication[1] we reported the preparation and characterisation of sulphinate complexes of some transition metals which were anticipated to show class 'a' behaviour, and did, in fact, contain the sulphinate group as an oxygen donor ligand. These complexes were encountered as part of a study of the role of transition metal complexes in polymerization. The means by which these sulphinate complexes initiate polymerization appears to be a free radical mechanism and consequently we have investigated the nature of some other transition metal sulphinate complexes, which might be expected by analogy with the results of other workers,[2] to lose sulphur dioxide and hence provide a possible source of free radicals.

In this paper we wish to report the preparation, characterisation and several reactions of some sulphinate complexes formed by palladium and platinum in which the sulphinate group behaves as a sulphur donor ligand. Such behaviour is in agreement with the general chemistry of palladium and platinum which, under the Arland-Chatt classification, should show class 'b' behaviour.

## Results and Discussion

Using a similar method to that of Venanzi[3] for the preparation of some palladium complexes containing the benzene sulphinate ligand, a series of complexes $[AsPh_4]_2[M_2X_2(RSO_2)_4]$ for M = Pt; Pd: $X = Cl^-$; $Br^-$: $R = C_6H_5$; $CH_3C_6H_4$; have been prepared. These formulae have been derived from analytical, conductivity and molecular weight data. The complexes are soluble in acetone, methylene dichloride, dichloroethane, formamide and methanol. In the latter solvent they appear to behave as 1.2 electrolytes in agreement with our formulation above. Molecular weight measurements in dichloroethane confirm their dimeric nature.

*Infrared Spectra*. The nature of the coordination of the aryl sulphinate group to the metal has been derived from the infrared spectra of these complexes, which show that the ligand is S- bonded in all the systems studied. This is demonstrated by a shift to higher energy of the ν(S–O) absorption bands (Table I) relative to the position of these bands in the corresponding sodium aryl sulphinate.[4] Such behaviour is characteristic of sulphur rather than oxygen coordination of the ligand.[2c,3,5] It is instructive to compare these stretching frequencies to those of organic sulphones  $R^1R^2SO_2$. In these, the ν(S–O) stretching vibrations[6] occur at 1350-1300 cm$^{-1}$ [$\nu(S{-}O)_{asy}$] and 1160-1200 cm$^{-1}$ [$\nu(S{-}O)_{sym}$] which show an even greater shift to higher energy, relative to the S–O stretching vibrations in the aryl sulphinate anion. This difference may be attributed partly to

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[1] C. W. Dudley and C. Oldhan, *Inorg. Chim. Acta*, *2*, 199 (1968).

[2] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, *88*, 180 (1968); C. D. Cook and J. S. Jauhal, *Can. J. of Chem.*, *45*, 303 (1967); G. B. Deacon, *Aust. J. of Chem.*, *20*, 1367 (1967).

[3] B. Chiswell and L. M. Venanzi, *J. Chem. Soc.*, (*A*), 1246 (1966).

[4] S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

[5] F. A. Hartman and A. Wojcicki, *J. Amer. Chem. Soc.*, *88*, 844 (1966); J. P. Bilber and A. Wojcicki, *J. Amer. Chem. Soc.*, *86*, 5051 (1964); J. P. Bilber and A. Wojcicki, *J. Amer. Chem. Soc.*, *88*, 4862 (1966); F. A. Hartman, R. L. Downs, *J. Amer. Chem. Soc.*, *89*, 2493 (1967); P. J. Pollick and A. Wojcicki; F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, 7, 1504 (1968); F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, 2, 289 (1968).

[6] L. J. Bellamy, « *The Infrared Spectra of Complex Molecules* », 2nd edn., Methuen, London, 1958.

$d_\pi$–$d_\pi$ back donation from filled orbitals of the metal to empty orbitals of the sulphur (which is also indicated by the infrared spectra of some of the reaction products of these complexes to be discussed later) and partly in the difference between the metal-sulphur $\sigma$ bond in the complex and the corresponding sulphur-carbon $\sigma$ bond in the sulphones.

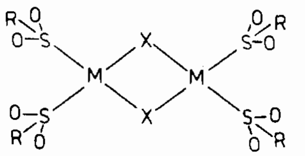
**Table I.** Infrared Data

| Compound | $\nu(S—O)_{asy}$ in $cm^{-1}$ | $\nu(S—O)_{sym}$ in $cm^{-1}$ | $\delta(S—O)$ in $cm^{-1}$ |
|---|---|---|---|
| $[AsPh_4]_2[Pt_2Cl_2(BSO_2)_4]$ | 1235, 1220 | 1059 | 587 |
| $[AsPh_4]_2[Pt_2Cl_2(TSO_2)_4]$ | 1225 | 1060 | 584 |
| $[AsPh_4]_2[Pt_2Br_2(BSO_2)_4]$ | 1224, 1210 | 1051 | 580 |
| $[AsPh_4]_2[Pt_2Br_2(TSO_2)_4]$ | 1229, 1208 | 1050 | 583 |
| $[AsPh_4]_2[Pd_2Cl_2(BSO_2)_4]$ | 1221, 1207 | 1048 | 573 |
| $[AsPh_4]_2[Pd_2Cl_2(TSO_2)_4]$ | 1222 | 1057 | 578 |
| $[AsPh_4]_2[Pd_2Br_2(BSO_2)_4]$ | 1218, 1205 | 1047 | 592 |
| $[AsPh_4]_2[Pd_2Br_2(TSO_2)_4]$ | 1220 | 1046 | 582 |

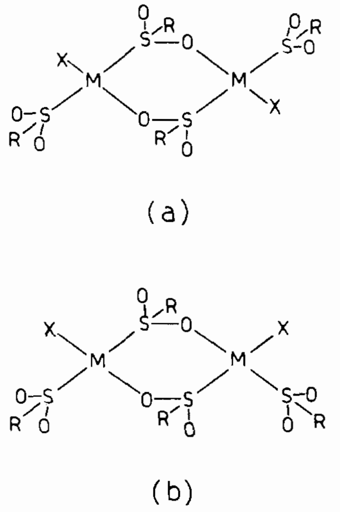
$BSO_2H = C_6H_5SO_2H$ $TSO_2H = pCH_3C_6H_4SO_2H$

For those complexes in which S–O stretching vibrations show the presence of a metal-sulphur bond, bands are observed in the region 570-600 $cm^{-1}$ in agreement with the assignments made by Deacon[2c] for $SO_2$ bending modes in some mercury(II) sulphinate complexes. This region appears to be a valuable diagnostic one for sulphur bonded entities in molecules of this type.

It is therefore possible to discuss the infrared data for these compounds in terms of the two structures I and II, *i.e.* with either the halide atom or the sulphinate group serving as a bridging ligand. For a structure of type II, the infrared spectra particularly in the S–O stretching region might be anticipated to be complex but such a mode of coordination, although unlikely, cannot be eliminated on this basis.



Structure I



Structure II

In order to distinguish further between these structures we have reacted the dimeric species, with some typical halide bridge breaking reagents, *i.e.* a series of nitrogen bases including *p*-toluidine, pyridine and 2,2'-bipyridyl. Analyses of the products show that these are bes tinterpreted in terms of a halide bridging atom but depending upon reaction conditions, two different products are obtained, *i.e.*

$(Sulphinate)_2 M(Base)_2$ and $(Sulphinate) MX(Base)_2$ where M = Pd, Pt and X = Cl, Br.

The infrared spectra of these complexes are summarised in Table II.

Using similar reasoning to the above, the presence of an aryl sulphinate ligand coordinated to the metal via its sulphur atom can readily be seen. However, the symmetric and assymmetric S–O stretching vibrations merit further comment. Although these show the anticipated rise with respect to the free ligand there is a significant decrease relative to the initial dimeric species. Comparison of these results with published data[3] for some palladium sulphinate complexes containing other ligands show that there appear to be several factors to be considered in discussing the position of $\nu(S—O)_{asy}$, the more sensitive of the S–O stretching modes. For those compounds in which the sulphinate group is thought to be *trans* to the following ligands: bridging chlorine, terminal chlorine, water, piperidine and *p*-toluidine there is a gradual decrease in $\nu(S—O)_{asy}$ from 1220 $cm^{-1}$ to 1155 $cm^{-1}$ This gradual decrease is almost certainly related to the donor ability of this *trans* ligand.

However, whilst recognising that other factors such as stereochemistry of the ligand may modify this conclusion, we feel that another feature which has to be considered in a discussion of these S–O stretching frequencies is the possibility of hydrogen bonding between the sulphinate oxygen atom and the amine hydrogen atoms. This is readily shown by a comparison of $\nu(S—O)_{asy}$ with the $pK_a$ of the amine in the series $Cl(BSO_2)Pd(A)_2$ where A = pyridine and *p*-toluidine. These ligands have $pK_a$ values of 5.3 and 5.1 respectively and thus if only electronic effects were important it would be expected that $\nu(S—O)_{asy}$ would be higher in the *p*-toluidine complex. Experimentally, however, the reverse is observed with the lower S–O stretching frequency occuring for the *p*-toluidine complex (*i.e.* with a hydrogen atom directly attached to the nitrogen). Further indication that hydrogen bonding is occurring in these complexes is suggested by the broadening of the S–O stretching vibrations. A similar conclusion has been made by earlier workers[7] from comparisons of N–H stretching vibrations.

In deriving a stereochemistry for the mononuclear species, recourse to their infrared spectra is useful. For complexes containing one or two sulphinate groups, the spectra in the (S–O) stretching region are

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[7] L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 3841 (1960), and references therein.

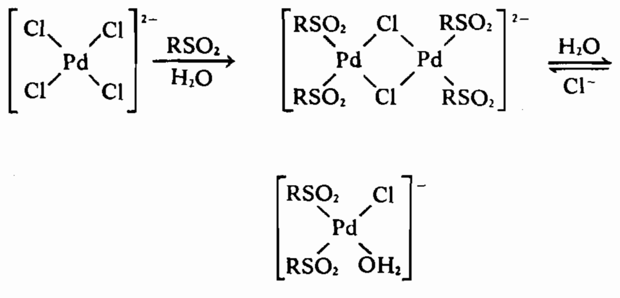
identical and from this one may conclude that the sulphinate group is *trans* to the same ligand in both compounds. Consequently we favour a *cis* configuration of the amine.

We have also unsuccessfully attempted to prepare complexes of the type $[(RSO_2)_2PdCl\,(p\text{-toluidine})]^-$ by reaction of the dimeric halogen bridged species with two equivalents of *p*-toluidine. The product of this reaction in methanol solution is the insoluble $(RSO_2)_2Pd(p\text{-toluidine})_2$. We attribute this to the fact that even in the presence of a small amount of amine, an equilibrium is set up

$$[Pd_2Cl_2(RSO_2)_4]^{2-} + 2am \overset{\text{fast}}{\rightleftharpoons} 2[(RSO_2)_2PdClam]^- \overset{\text{fast}}{\rightleftharpoons} [(RSO_2)_2Pd(am)_2]$$

and the product isolated under the condition of our experiment is the insoluble $(RSO_2)_2Pd(p\text{-toluidine})_2$. Venanzi[3] suggested that a species $(BSO_2)_2Pd(\text{piperidine})_2$, which he was unable to isolate, was an intermediate in the reaction of piperidine with $PdCl(BSO_2)_2(H_2O)$ and in order to explain the formation of the product, *i.e.* $Pd(BSO_2)Cl(\text{piperidine})_2$, it was necessary to assume that such an intermediate species loses sulphinate in the presence of chloride ions. As we have been able to isolate a diammine disulphinate species we have a system where this assumption may be tested. We do in fact find that $(\text{sulphinate})_2Pd(p\text{-toluidine})_2$, when suspended in methanol, will react with added halide ion with loss of sulphinate to give $(\text{sulphinate})(\text{halide})Pd(p\text{-toluidine})_2$.

It should be noted that the aquo complex, first reported by Venanzi,[3] was prepared by direct reaction, in aqueous solution, of the tetrachloropalladite ion with sodium sulphinate. We similarly obtained the aquo complex but also from the same reaction mixture, by addition of a large counter ion, $Ph_4As^+$, we isolated the halogen bridged species. Thus as not all the palladium is precipitated as the aquo complex and as there are also chloride ions in the reaction mixture from the $[PdCl_4^-]^{2-}$ there appears to be an equilibrium set up:

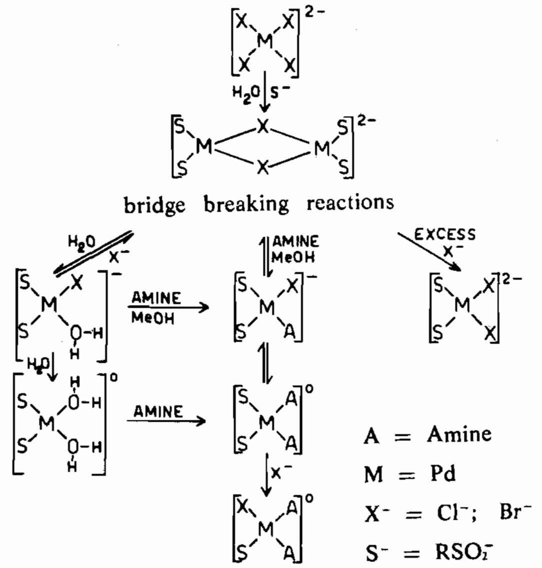


Further proof of this is provided by the fact that a freshly filtered sample of the aquo complex (*i.e.* damp with $Cl^-$) is cold water soluble, in contrast to the sparing solubility of a purified sample, and from this solution again the halogen bridged species can be isolated.

Now Venanzi[3] also reports two further reactions of the mono aquo complex.

(a) With a 100 fold excess of chloride ions $[(BSO_2)_2PdCl_2]^{2-}$ is formed. A satisfactory explanation of this would be, firstly, reaction with part of this chloride ion to form the dimeric species and then cleavage of this chlorine bridged dimer by the remaining excess chloride ion, a bridge breaking reaction previously observed[8] in some organometallic halogen bridged species.

(b) Recrystallization of the complex from water yields a diaquo complex, *i.e.* substitution of the halide atom. Thus we envisage an overall reaction scheme:



A consequence of such a scheme is that in order to explain the reaction of the monoaquo complex with amine it is necessary to postulate that the co-ordinated water is first removed in preference to the co-ordinated chlorine. Such a suggestion is in agreement with the observation[3] that $(\text{sulphinate})_2Pd(H_2O)_2$ with amine yields metallic palladium.

Thus (i) from the work reported here; (ii) from a knowledge that sulphur bridged structures, *e.g.* bridging thiols, are stable to bridge breaking by *p*-toluidine.[9] (iii) from the ready fission of halide bridged complexes by amine[10] it would apear that the halide atom serves as the bridging species in these complexes and the sulphinate group as a terminal S-bonded species.

## Experimental Section

*Preparation. Method A* (ref. Table III). To a solution of 5 mmole of potassium tetrahaloplatinite in 5 ml of water was added a solution of 10 mmole of sodium aryl sulphinate hydrate in 5 ml of water. The temperature was kept at 40°C for 3-4 hours whereupon the initial red solution gradually became

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(8) E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 434 (1964); L. M. Vallarino, *Inorg. Chem.*, *4*, 161 (1965).

(9) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953); J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1949 (1938).

(10) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1622 (1939); J. Chatt, *J. Chem. Soc.*, 652 (1951); J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955); J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2445 (1957).

**Table II.** Infrared Data ($cm^{-1}$)

| Compound | $\nu(S{-}O)_{asy}$ | $\nu(S{-}O)_{sym}$ | $\delta(S{-}O)$ | $\nu(N{-}H)_{asy}$ | $\nu(N{-}H)_{sym}$ | $\delta(N{-}H)$ |
|---|---|---|---|---|---|---|
| $[(CH_3C_6H_4NH_2)_2Pt(BSO_2)_2]$ | | | | | | |
| from µ-dichloro complex | 1164 | 1040 | 588 | 3160 | 3080 | 1511 |
| from µ-dibromo complex | 1166 | 1042 | 586 | 3163 | 3082 | 1511 |
| $[(CH_3C_6H_4NH_2)_2Pt(TSO)_2)_2]$ | | | | | | |
| from µ-dichloro complex | 1165 | 1040 | 584 | 3162 | 3081 | 1513 |
| from µ-dibromo complex | 1165 | 1041 | 585 | 3163 | 3082 | 1512 |
| $[(CH_3C_6H_4NH_2)_2Pd(BSO_2)_2]$ | | | | | | |
| from µ-dichloro complex | 1145 | 1032 | 583 | 3197 | 3100 | 1511 |
| from µ-dibromo complex | 1148 | 1035 | 582 | 3198 | 3100 | 1511 |
| $[(CH_3C_6H_4NH_2)_2Pd(TSO_2)_2]$ | | | | | | |
| from µ-dichloro complex | 1140 | 1033 | 581 | 3195 | 3105 | 1512 |
| from µ-dibromo complex | 1142 | 1037 | 583 | 3198 | 3100 | 1512 |
| $[(CH_3C_6H_4NH_2)_2PdCl(BSO_2)]$ [a] | 1145 | 1034 | 582 | 3196 | 3100 | 1511 |
| $[(CH_3C_6H_4NH_2)_2PdBr(BSO_2)]$ [b] | 1140 | 1034 | 582 | 3199 | 3101 | 1511 |
| $[(CH_3C_6H_4NH_2)_2PdCl(TSO_2)]$ [c] | 1140 | 1037 | 581 | 3200 | 3110 | 1510 |
| $[(C_5H_5N)_2Pd(BSO_2)Cl]$ | 1184 | 1032 | 587 | — | — | — |
| $[(2,2'\text{-Bipy})Pd(BSO_2)Cl]$ | 1198 | 1048 | 589 | — | — | — |

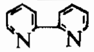
$BSO_2H = C_6H_5SO_2H$ $TSO_2H = pCH_3C_6H_4SO_2H$

[a] Prepared from $[(CH_3C_6H_4NH_2)_2Pd(BSO_2)_2]$; [b] prepared from $[AsPh_4]_2[Pd_2Br_2(BSO_2)_4]$; [c] prepared from $[AsPh_4]_2[Pd_2Cl_2(TSO_2)_4]$.

**Table III.** Physical Data

| Compound | Colour | Decomp. Point °C | Method of prep. | Found %C | Found %H | Found %X | Calculated %C | Calculated %H | Calculated %X |
|---|---|---|---|---|---|---|---|---|---|
| $[AsPh_4]_2[Pt_2Cl_2(BSO_2)_4]$ [g] | cream | >300 | A | 48.3 | 3.5 | 21.6 [a] | 48.3 | 3.4 | 21.8 |
| $[AsPh_4]_2[Pt_2Cl_2(TSO_2)_4]$ [h] | cream | — | A | 49.3 | 3.9 | 21.5 [a] | 49.4 | 3.7 | 21.1 |
| $[AsPh_4]_2[Pt_2Br_2(BSO_2)_4]$ | white | — | A [l] | 45.7 | 3.3 | 21.3 [a] | 45.9 | 3.2 | 20.7 |
| $[AsPh_4]_2[Pt_2Br_2(TSO_2)_4]$ | white | — | A [l] | 46.8 | 3.6 | 7.9 [b] | 47.1 | 3.5 | 8.3 |
| $[(CH_3C_6H_4NH_2)_2Pt(BSO_2)_2]$ | creamy/ yellow | — | D | | | | | | |
| from µ-dichloro complex | | | | 45.3 | 4.1 | 4.1 [c] | 45.1 | 4.1 | 4.1 |
| from µ-dibromo complex | | | | 45.0 | 3.9 | 9.7 [d] | 45.1 | 4.1 | 9.3 |
| $[(CH_3C_6H_4NH_2)_2Pt(TSO_2)_2]$ | creamy/ yellow | — | D | | | | | | |
| from µ-dochloro complex | | | | 46.8 | 4.5 | 0.0 [e] | 46.7 | 4.5 | 0.0 |
| from µ-dibromo complex | | | | 46.3 | 4.4 | 3.7 [c] | 46.7 | 4.5 | 3.9 |
| $[AsPh_4]_2[Pd_2Cl_2(BSO_2)_4]$ [i,m] | canary yellow | 120-130 | C | 53.7 | 3.6 | 13.3 [f] | 53.6 | 3.7 | 13.2 |
| $[AsPh_4]_2[Pd_2Cl_2(TSO_2)_4]$ | canary yellow | — | C | 54.8 | 4.2 | — | 54.6 | 4.1 | — |
| $[AsPh_4]_2[Pd_2Br_2(BSO_2)_4]$ | yellow/ orange | 135-140 | C | 50.2 | 3.8 | 12.4 [f] | 50.8 | 3.6 | 12.5 |
| $[AsPh_4]_2[Pd_2Br_2(TSO_2)_4]$ | yellow/ orange | — | C | 51.6 | 4.0 | 12.3 [f] | 51.9 | 3.9 | 12.1 |
| $[(CH_3C_6H_4NH_2)_2Pd(BSO_2)_2]$ | creamy/ yellow | 172-177 | D | | | | | | |
| from µ-dichloro complex [j] | | | | 51.6 | 4.5 | 5.1 [c] | 51.8 | 4.7 | 4.7 |
| from µ-dibromo complex | | | | 51.7 | 4.7 | 4.5 [c] | 51.8 | 4.7 | 4.7 |
| $[(CH_3C_6H_4NH_2)_2Pd(TSO_2)_2]$ | creamy/ yellow | — | D | | | | | | |
| from µ-dichloro complex | | | | 52.9 | 5.2 | 4.6 [c] | 53.3 | 5.1 | 4.5 |
| from µ-dibromo complex | | | | 52.9 | 5.2 | 4.3 [c] | 53.3 | 5.1 | 4.5 |
| $[(CH_3C_6H_4NH_2)_2PdCl(BSO_2)]$ | pale yellow | 175-180 | F | 48.8 | 4.9 | 7.1 [e] | 48.3 | 4.7 | 6.7 |
| $[(CH_3C_6H_4NH_2)_2PdBr(BSO_2)]$ [k] | pale yellow | 180-188 | E | 44.8 | 4.1 | 4.7 [c] | 44.3 | 4.3 | 5.2 |
| $[(CH_3C_6H_4NH_2)_2PdCl(TSO_2)]$ | pale yellow | 165-170 | E | 49.5 | 5.0 | 5.6 [c] | 49.3 | 4.9 | 5.5 |
| $[(22'\text{Bipy})Pd(BSO_2Cl]$ | pale yellow | 195-200 | G | 43.4 | 3.0 | 6.7 [c] | 43.8 | 3.0 | 6.4 |
| $[(C_5H_5N)_2Pd(BSO_2)Cl]$ | yellow | — | G | 43.6 | 3.1 | 6.1 [c] | 43.8 | 3.0 | 6.4 |

$BSO_2H = C_6H_5SO_2H$ $TSO_2H = p\text{-}CH_3C_6H_4SO_2H$ 2,2'-Bipy =



[a] X = Pt; [b] X = Br; [c] X = N; [d] X = S; [e] X = Cl; [f] X = Pd; [g] %Cl, found 4.5, calc. 4.0; [h] %S, found 6.8, calc. 6.9; [i] %Cl found 4.9, calc. 4.4; [j] %Cl found 0.0, calc. 0.0; [k] %Br found 14.3, calc. 14.8; [l] The bromo platinite was prepared in situ as described in experimental method B; [m] Apparent molecular weight in dichloroethane 694, calculated molecular weight assuming 100% dissociation 2082; theoretical 1615.

brown and finally pale yellow. After cooling and allowing to stand for 24 hours a solution of 5 mmoles of tetraphenylarsonium chloride in 10 ml of water was added. The solid which precipitated was recrystallized from methanol.

*Method B.* Potassium bromo platinate (1.78 mmole) was dissolved in 20 ml of water and carefully reduced by the dropwise addition, whilst stirring, of a saturated solution of sulphur dioxide. Nitrogen was continually bubbled through the solution to prevent local high concentrations of sulphur dioxide developing. This process was repeated until, after warming to 30°C and bubbling nitrogen vigorously through the solution to expel any excess sulphur dioxide, no precipitate was formed when one drop of the solution was tested with three drops of a saturated solution of ammonium chloride.

*Method C.* When a solution of 2.5 mmole of potassium tetrahalopalladite in 5 ml of water was treated with a solution of potassium aryl sulphinate, 5 mmole in 6 ml of water, a bright orange precipitate formed over a period of 10 minutes. This was filtered and identified by elemental analysis and infrared spectroscopy[3] as potassiumbis(aryl sulphinate)haloaquopalladium(II); for example using potassium bromo palladite and potassium p-toluene sulphinate, the product isolated was $K[Pd(C_7H_7SO_2)_2Br(H_2O)]$, found C = 30.9, H, = 3.1; Pd = 19.7, calculated for $KPdC_{14}H_{16}S_2O_5Br$, C = 30.4, H = 2.9, Pd = 19.2.

The filtrate from this reaction was warmed to 30°C for 3-4 hours and allowed to stand for 24 hours. Treatment, slowly, with stirring, with a 10% solution of tetraphenylarsonium chloride in water resulted in a canary yellow precipitate which was recrystallized from dichloromethane.

*Method D.* When a solution of the dimeric species in methanol was treated with either 2 equivalents, 4 equivalents or excess *p*- toluidine dissolved in methanol, precipitation of the product occurred.

*Method E.* When the dimeric species dissolved in methanol were treated with 4 equivalents of *p*-toluidine in methanol and allowed to react for 24-36 hours, the initial heavy granular precipitate slowly changed appearance to a very bulky precipitate which was isolated and washed with methanol.

*Method F.* When finely ground bis(*p*-toluidine)bis(benzene-S-sulphinate)palladium(II) was suspended in methanol and treated with an aqueous solution of sodium chloride, a chlorine containing product was isolated after 36 hours.

*Method G.* When the dimeric species dissolved in methanol were treated with 4 equivalents of amine dissolved in methanol the colour of the solution was immediately changed from canary yellow to very pale yellow. After several days a white precipitate appeared which was isolated and washed with methanol.

*Analises.* Carbon, hydrogen, nitrogen, sulphur and halogen were determined by Weiler and Strauss, Oxford.

Platinum was determined, after removal of arsenic as tetraphenylarsonium tetraphenylboron, by reduction using formic acid and sodium acetate and was weighed as metallic platinum. Palladium was determined as palladiumbis(dimethylglyoximate), the complexes having first been oxidized using fuming sulphuric acid and 70% perchloric acid. Results are shown in Table III.

*Spectroscopic measurements.* Infrared spectra were recorded as nujol mulls on a Perkin Elmer 457 spectrophotometer using Caesium Iodide optics.

Electrical conductivities (Table IV) were measured on a Wayne Kerr conductivity bridge using a Pye Instruments conductivity cell with methanol as solvent.

**Table IV.**

| Compound | | ΛM (in MeOH) ($\Omega^{-1}$ at 25°C) |
|---|---|---|
| $[AsPh_4]_2[Pt_2Cl_2(BSO_2)_4]$ | | 138.7 |
| $[AsPh_4]_2[Pt_2Cl_2(TSO_2)_4]$ | | 141.5 |
| $[AsPh_4]_2[Pt_2Br_2(BSO_2)_4]$ | | 171.2 |
| $[AsPh_4]_2[Pt_2Br_2(TSO_2)_4]$ | | 181.4 |
| $[AsPh_4]_2[Pd_2Cl_2(BSO_2)_4]$ | | 118.9 |
| $[AsPh_4]_2[Pd_2Cl_2(TSO_2)_4]$ | | 125.9 |
| $[AsPh_4]_2[Pd_2Br_2(BSO_2)_4]$ | | 137.7 |
| $[AsPh_4]_2[Pd_2Br_2(TSO_2)_4]$ | | 146.2 |
| | $[AsPh_4]_2[PtCl_4]$ [a] | 181.4 |
| comparison | 1:1 electrolytes [b] | ≃ 80 |
| | 1:2 electrolytes [b] | ≃ 180 |

[a] Determined experimentally; [b] R. A. Krause and D. H. Busch, *J. Amer. Chem. Soc., 82,* 1960, 4830.

Molecular weights (Table III) were determined using a vapour pressure method on a Mechrolab Vapour Pressure Osmometer.

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