The Preparation of Trichloro(phenyl 2-pyridylmethyl sulphoxide)gold(III) and the Kinetics and Equilibria of its Formation and Subsequent Reactions

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In the complex $[Au(N{-}SO)Cl_3]$, formed between $[AuCl_4]^-$ and phenyl 2-pyridylmethyl sulphoxide (N–SO), the ligand is bound only through the nitrogen and all attempts to induce chelation were unsuccessful. The kinetics of the forward and reverse reactions in methanol–water (95:5, v/v) at 25.0 °C are also consistent with the ligand acting as a substituted pyridine with a pK_a of 3.39 (water, 25 °C) and the same steric hindrance as 2-methylpyridine. The behaviour of gold(III) is compared to that of platinum(II).

Sulphoxides (RR′SO) are known[1] to react easily with planar four-co-ordinate tetrachloroplatinate(II) and tetrachloropalladate(II) anions forming complexes such as $[M(RR'SO)Cl_3]^-$ and *cis-* or *trans-*$[M(RR'SO)_2Cl_2]$ where the neutral ligand is S-bonded to the metal (M) *via* σ donation and, possibly, π back donation. Under suitable conditions, $[M(RR'SO)_4]^{2+}$ cations where both S- and O-bonded sulphoxides are present, depending upon the steric congestion, have been obtained also.

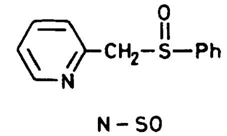
The kinetics of the ligand displacement reactions [equation (1)] and the position of the equilibria in the systems shown by equation (2) with a variety of sulphoxides have been studied in detail.[2,3] On the other hand, little is known about the behaviour of sulphoxides towards the tetrachloroaurate(III) anion, which is isoelectronic with tetrachloroplatinate(II). Gold(III) is an oxidant and easily oxidizes thioethers to sulphoxides;[4] in this way methionine was stereospecifically oxidized to methionine sulphoxide $[MeS(O)CH_2CH_2CH(NH_2)CO_2H]$.[5] However, the oxidation does not proceed to sulphones and therefore, by examining systems containing gold(III) derivatives and sulphoxides, redox processes ought to be absent.

$$[PtCl_4]^{2-} + RR'SO \longrightarrow [Pt(RR'SO)Cl_3]^- + Cl^- \quad (1)$$

$$[PdCl_4]^{2-} + RR'SO \rightleftharpoons [Pd(RR'SO)Cl_3]^- + Cl^- \quad (2)$$

The only report of Au^{III} sulphoxide complexes, to our knowledge, in the literature[6] describes the preparation of $[Au(Me_2SO)Cl_3]$, which was obtained in dry chloroform under an atmosphere of dry nitrogen, and where the dimethyl sulphoxide ligand seems to be very weakly bound to the metal.

In order to study the tendency of the sulphoxide to bind to gold(III) we decided to incorporate the –SO– group into a potentially chelating ligand, as we have recently done with oxygen donors such as carboxylate[7] and alcoholate[8] groups, and for this reason we have synthesized the molecule phenyl 2-pyridylmethyl sulphoxide (N–SO).



N - SO

The ligand N–SO has been shown[9] to react readily with equimolar amounts of the tetrachloroplatinate(II) anion forming, as expected, the neutral complex $[Pt(N{-}SO)Cl_2]$ containing the N,S-bonded chelating group. The kinetic and equilibria aspects of the chemistry of the system involving this ligand and the tetrachloroaurate(III) anion are described in this paper.

Experimental

Phenyl 2-Pyridylmethyl Sulphoxide.—To a solution of 2-[(phenylthio)methyl]pyridine hydrochloride (4 g, 16.8 mmol), obtained by the method reported in the literature,[10] in water (50 cm^3), sodium tungstate dihydrate (50 mg, 0.15 mmol) in water (5 cm^3) and hydrogen peroxide (35% aqueous solution, 1.45 cm^3) in water (5 cm^3) were slowly added, with stirring, at room temperature. The reaction mixture was left at room temperature overnight, then neutralized with solid $NaHCO_3$ and extracted with chloroform. The extract was washed with saturated NaCl solution and dried over magnesium sulphate. Removal of chloroform gave the crude product which was crystallized from diethyl ether–light petroleum (b.p. 40—70 °C). Yield: 3.4 g (94%), m.p. 51—52 °C (Found: C, 66.1; H, 5.1; N, 6.3; S, 14.8. $C_{12}H_{11}NOS$ requires C, 66.3; H, 5.1; N, 6.5; S, 14.7%). The infrared spectrum (Nujol mull between NaCl plates) showed the S=O stretching vibration at 1 045 cm^{-1}. The pK_a, determined with a Beckmann Selection 5000 Ion Analyzer, in water at 25 °C (ionic strength 0.1 mol dm^{-3}) is 3.39 ± 0.01 as an average of three independent measurements.

Trichloro(phenyl 2-pyridylmethyl sulphoxide)gold(III).—A solution of phenyl 2-pyridylmethyl sulphoxide (0.217 g, 1 mmol) in water (10 cm^3) was slowly added, with stirring, to a solution of $HAuCl_4{\cdot}3H_2O$ (0.394 g, 1 mmol) in water (20 cm^3), brought to pH 5.5 with 0.1 N $NaHCO_3$ and cooled in an ice-bath. The yellow microcrystalline product, which precipitated within a few minutes, was filtered off, washed with cold water, and dried in vacuum. Yield: 440 mg (85%), m.p. 82 °C (Found: C, 27.8; H, 2.1; Au, 37.6; Cl, 18.7; N, 2.8; S, 6.4. $C_{12}H_{11}AuCl_3NOS$ requires C, 27.7; H, 2.1; Au, 37.8; Cl, 20.4; N, 2.7; S, 6.2%). Infrared (Nujol mull between NaCl plates or polyethylene discs, cm^{-1}) bands: 1 608m [ν(C=N), co-ordinated pyridine ring], 1 045s [ν(S=O)], and 362m,br [ν(Au–Cl)]. Conductivity measurements, carried out in acetone at 25 °C using a Radiometer Copenhagen CDM83 Conductivity Meter, show that the product is non-conducting.

Hydrogen tetrachloroaurate(III) trihydrate, lithium perchlorate, lithium chloride, perchloric acid, and methanol were all reagent-grade products.

Dichlorobis(pyridine)gold(III) *Perchlorate.*—A solution of pyridine (py) (0.79 g, 10 mmol) in water (3 cm^3) was slowly added, with stirring, to a solution of $HAuCl_4{\cdot}3H_2O$ (0.197 g, 0.5

mmol) in water (10 cm^3) at room temperature. The neutral $[Au(py)Cl_3]$ which precipitated within a few minutes, dissolved *after ca.* 3 h and the product, $[Au(py)_2Cl_2]ClO_4$, was then precipitated, by adding a methanolic saturated solution of $LiClO_4$ (50 cm^3), as a pale yellow microcrystalline product. It was washed with cold methanol and diethyl ether, and dried in a vacuum. Yield: 90%, m.p. 180 °C (decomp.) (Found: C, 23.1; H, 1.92, Cl, 20.5; N, 5.4. $C_{10}H_{10}AuCl_3N_2O_4$ requires C, 22.8; H, 1.90; Cl, 20.3; N, 5.35%). Significant infrared bands at 1 608m [ν(C=N)] and 373m cm^{-1} [ν(Au–Cl)].

Kinetics.—The kinetics were studied with a Varian-Cary 219 or with a Perkin-Elmer Coleman 575 UV-V spectrophotometer by periodically scanning the spectrum of the reaction mixture in the range 280—350 nm and/or measuring the changing absorbance at 320 nm, as a function of time. The values of $k_{obs.}$ were determined from the slopes of plots of log $(A_\infty - A_t)$ *vs.* time, A_∞ and A_t being the absorbances at the chosen wavelength at the end of the reaction and at time t respectively, by a weighted non-linear regression analysis.

Estimation of the Equilibrium Constant, K.—The value of K for the reaction $[AuCl_4]^- + \text{N–SO} \rightleftharpoons [Au(\text{N–SO})Cl_3] + Cl^-$ was determined spectrophotometrically by measuring the absorbance variations with time at 320 nm in the period of time during which the isosbestic point at 307 nm is maintained (see below). A small amount (20 μl) of a fresh solution of $[AuCl_4]^-$ in CH_2Cl_2 was introduced into the thermostatted cell of the spectrophotometer (25 °C) containing the appropriate solution of the ligand N–SO in MeOH–H_2O (95:5, v/v), $[H^+] = 1.99 \times 10^{-4}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} ($LiClO_4$). In any case and before the addition of $[AuCl_4]^-$ the absorbance of the solution in the cell was carefully compensated in the blank. The equilibrium constant K was calculated with the expression (3), where x is given by equation (4) and c_0 = initial concentration

$$K = \frac{c_0 x^2}{(1 - x)(c_1 - c_0 x)} \quad (3)$$

$$x = \frac{D_\infty - D_0}{c_0\{\varepsilon[Au(\text{N–SO})Cl_3] - \varepsilon[AuCl_4]^-\}} \quad (4)$$

of $[AuCl_4]^-$, c_1 = initial concentration of unprotonated N–SO, $\varepsilon[Au(\text{N–SO})Cl_3] = 2\,534$ and $\varepsilon[AuCl_4]^- = 4\,622$ (molar absorption coefficients at 320 nm), D_∞ = absorbance of the equilibrium mixture at 320 nm, and D_0 = absorbance of $[AuCl_4]^-$ at time $t = 0$ and 320 nm.

The molar absorption coefficients of the species $[Au(\text{N–SO})Cl_3]$ and $[AuCl_4]^-$ (supplied as $[NEt_4][AuCl_4]$) were determined using freshly prepared solutions of known concentration of pure, fully characterized samples.

Results and Discussion

The product of the reaction between $[AuCl_4]^-$ and phenyl 2-pyridylmethyl sulphoxide, (N–SO), is the non-electrolyte $[Au(\text{N–SO})Cl_3]$, with the ligand monodentate. The absence of any shift in ν(S=O) from that of the free ligand suggests that binding is through nitrogen. In the product of the reaction between $[PtCl_4]^{2-}$ and the same ligand, $[Pt(\text{N–SO})Cl_2]$, where chelation is observed,[9] ν(S=O) shifts from 1 045 to 1 150 cm^{-1} (indicative of Pt–S binding) and in the only reported Au^{III}–Me_2SO complex, $[Au(Me_2SO)Cl_3]$, a similar shift (1 053 to 1 198 cm^{-1}) is also observed.[6] The kinetic evidence below also strongly supports bonding through nitrogen only. All attempts to form the chelate complex failed and were generally accompanied by reduction of the complex to metallic gold.

The kinetics of the reaction (5) have been studied spectrophotometrically at 25 °C in methanol–water (95:5, v/v). In order to avoid the formation of $[AuCl_3(H_2O)]$ and $[AuCl_3(OH)]^-$ while the solutions were being brought to thermal equilibrium before starting the reaction, a sufficient excess of acid was used and the process was initiated by adding the solid substrate $[AuCl_3(\text{N–SO})]$ or a small quantity of a concentrated solution of the substrate in HCl-free chloroform. The solid added directly with the aid of a capillary tube in the spectrophotometric cell containing a thermostatted solution of the reagents dissolves immediately and there is no interference in the kinetic run. The chloroform solution (20 μl) was added with a micropipette to the solution of the other reagents (3 cm^3) in the spectrophotometric cell. Both procedures led to exactly the same results. Chloroform solutions which have not been freed from HCl will deposit, in a few days, very well formed crystals of $[\text{HN–SO}]^+[AuCl_4]^-$.

$$[Au(\text{N–SO})Cl_3] + Cl^- \longrightarrow [AuCl_4]^- + \text{N–SO} \quad (5)$$

The spectrum of the reacting mixture, recorded in the range 280—350 nm with time, is consistent with a single stage characterized by the presence of an isosbestic point at 307 nm. The spectrum at the end of the reaction corresponds exactly to that of a mixture of $[AuCl_4]^-$ (absorbance maximum at 320 nm) and the free ligand measured in the same solvent and at the same hydrogen-ion concentration. The absorbance at the isosbestic point (307 nm) allows the concentration of the complex in each kinetic run to be calculated using the independently measured molar absorption coefficient. The added chloride was always present in sufficient excess for its concentration to be unaffected by the reactions whose kinetics were shown to be strictly first order.

The first-order rate constants, $k_{obs.}{}^r$ summarized in Table 1, refer to three sets of experiments carried out at different hydrogen-ion concentrations.

In each set of experiments the kinetics obey the two-term rate law, $k_{obs.}{}^r = k_1{}^r + k_2{}^r[Cl^-]$ which is usual for nucleophilic substitution at planar four-co-ordinate substrates.[11] The values of $k_1{}^r$ and $k_2{}^r$ are summarized in Table 2.

The discrepancy among the three sets of values is comparable

Table 1. First-order rate constants for the reactions of $[Au(\text{N–SO})Cl_3]$ with chloride ion at 25 °C in MeOH–H_2O (95:5, v/v); $I = 0.1$ mol dm^{-3} ($LiClO_4$)*

$10^4[H^+]$	$10^4[Cl^-]$	$10^4 k_{obs.}{}^r/s^{-1}$
mol dm^{-3}		
1.99	6	64 ± 2
	8	79 ± 5
	10	104 ± 6
	12	108 ± 6
	14	121 ± 1
	16	133 ± 4
	20	155 ± 5
5.75	7.93	90 ± 3
	9.91	99 ± 4
	11.9	116 ± 6
	13.88	125 ± 5
	15.86	131.5 ± 2
57.5	7.93	74 ± 3
	9.91	92 ± 3
	11.9	100.5 ± 4
	13.88	112 ± 6
	15.86	119 ± 2

* Substrate concentration always less than 10^{-4} mol dm^{-3}.

Table 2. Specific rate constants, k_1^r and k_2^r, for reaction (5) at 25 °C in MeOH–H_2O (95:5, v/v); I = 0.1 mol dm^{-3} ($LiClO_4$)

$[H^+]$/mol dm^{-3}	$10^3k_1^r$/s^{-1}	k_2^r/dm^3 mol^{-1} s^{-1}
1.99×10^{-4}	3.03 ± 0.55	6.42 ± 0.46
5.75×10^{-4}	4.52 ± 0.38	5.69 ± 0.32
5.75×10^{-3}	3.54 ± 0.55	5.32 ± 0.37

with the experimental errors, which are relatively high due to the lability of the system. We can therefore deduce that both pathways are unaffected by acid and the first-order rate constant k_1^r refers to the solvolytic process shown by equation (6) (S being a solvent molecule), followed by the fast reaction (7), whereas the second-order rate constant k_2^r refers to the

$$[Au(N\text{–}SO)Cl_3] + S \longrightarrow [AuSCl_3] + N\text{–}SO \quad (6)$$

$$[AuSCl_3] + Cl^- \longrightarrow [AuCl_4]^- + S \quad (7)$$

direct associative displacement of the ligand N–SO by the entering chloride ion [equation (8)].

$$[Au(N\text{–}SO)Cl_3] + Cl^- \longrightarrow [AuCl_4]^- + N\text{–}SO \quad (8)$$

The assignment of the k_1^r term to the solvolytic process is consistent with the observed decay of the substrate in methanol–water in the absence of chloride, even though, in that case, the reaction is complicated by equilibria and further solvolysis. The assignment of the k_2^r term to the direct displacement of the N-bonded phenyl 2-pyridylmethyl sulphoxide by chloride ion can be independently confirmed. It is known[12] that in the displacement by chloride of heterocyclic nitrogen donors (N) from complexes of the type $[AuCl_3(N)]$ there is a linear free-energy relationship of the type $\log k_2 = a(pK_a) + b$, independent of the steric hindrance of the ring substituents, where pK_a is that of HN^+ in water. In the mixture methanol–water (95:5, v/v) this relationship is also obeyed and the values of the parameters a and b, already measured,[7] are 0.67 and 2.81 respectively. A k_2^r value of 6.42 dm^3 mol^{-1} s^{-1} leads therefore to an expected pK_a of 3.03 which can be compared with the value of 3.39 measured directly.

The study of the reverse process, *i.e.* the reaction between $[AuCl_4]^-$ and the ligand N–SO, under the same experimental conditions, is more complicated. By examining the changing absorbance of a mixture of $[AuCl_4]^-$ and excess N–SO one can observe, for a limited period of time, the expected decrease of the maximum at 320 nm with the maintenance of an isosbestic point at 307 nm, *i.e.* it follows the reverse pathway to that of the forward reaction. However this process does not go to completion, the chloride released becoming sufficient to make the reaction reversible. Attempts to study this under first-order conditions failed because the excess of chloride needed to cause this shifts the equilibrium completely in the direction of $[AuCl_4]^-$ + N–SO. A compensating increase in the amount of N–SO present was ruled out because of the high absorbance of this species in the relevant region of the spectrum. As the reaction proceeds the isosbestic point at 307 nm is no longer maintained and, over a longer period of time, a second isosbestic point develops at 314 nm, indicating a second stage of the reaction. This second stage, with the same isosbestic point, can be observed independently when the complex $[Au(N\text{–}SO)Cl_3]$ is reacted with excess N–SO under the same experimental conditions. It corresponds to a relatively small change in absorbance and consequently, the derived rate constants have a large experimental error. Preliminary studies indicate that the rate, within the large limit of experimental error, is insensitive to [N–SO] with the first-order rate constant in the range (1.5—2) × 10^{-4} s^{-1}. It is suggested that this can be attributed to the displacement of a second chloride, leading to the formation of the bisubstituted complex $[Au(N\text{–}SO)_2Cl_2]^+$. Attempts to prepare the bis species $[Au(N\text{–}SO)_2Cl_2]^+$ have so far been unsuccessful, the complex eventually being reduced to metallic gold, but the much more stable pyridine complex $[Au(py)_2Cl_2]^+$ has been prepared as its perchlorate which is a pale yellow 1:1 electrolyte (CH_3NO_2), by reaction between $[Au(py)Cl_3]$ and a ten-fold excess of pyridine in the presence of $LiClO_4$ in methanol–water (95:5, v/v). The spectrum of this complex in the range 290—350 nm is qualitatively similar to that of the final spectra of the reaction of N–SO and $[Au(N\text{–}SO)Cl_3]$. In particular, the shoulder at 320 nm observed in the monosubstituted complex has completely disappeared. The absence of a measurable second-order contribution in this process is likely to be due to the fact that both the substrate and the nucleophile N–SO are sterically hindered.

Table 3. Pseudo-first-order rate constants calculated from the initial rate, $k_{obs.}^r$ for the reactions of N–SO with $[AuCl_4]^-$ at 25 °C in MeOH–H_2O (95:5, v/v); $[H^+] = 1.99 \times 10^{-4}$ mol dm^{-3}, I = 0.1 mol dm^{-3} ($LiClO_4$)

$10^4[AuCl_4]^-$ mol dm^{-3}	10^3[N–SO] mol dm^{-3}	D_0	D_{comp}	$10^3k_{obs.}^r$/s^{-1}
2.46	3.63	1.139	0.624	0.77
2.39	5.69	1.107	0.607	0.96
2.35	7.82	1.085	0.595	1.25
2.44	9.33	1.129	0.619	1.37
2.49	11.23	1.149	0.623	1.62

A significant observation is that on mixing a solution of $[Au(N\text{–}SO)Cl_3]$ with an excess of both Cl^- and N–SO the first reaction is identical to that in the absence of N–SO (*i.e.*, the formation of $[AuCl_4]^-$ and free N–SO in solution) but at later times the characteristic maximum of $[AuCl_4]^-$ at 320 nm slowly disappears and the final spectrum is identical to that observed at the end of the reaction between $[AuCl_4]^-$ and excess N–SO. This behaviour can be explained if the initial formation of $[AuCl_4]^-$ is kinetically favoured {the substitution of a chloride in $[Au(N\text{–}SO)Cl_3]$ by N–SO is slow}, but the presence of a significant amount of the bisubstituted complex is finally required by the thermodynamics of the system.

The complications encountered in the reaction between $[AuCl_4]^-$ and excess N–SO prevent a complete study of the kinetics but a reasonable estimate of the rate constant was made by plotting $\ln (D_t - D_{comp})$ against time, where D_t is the absorbance at time t during the period when the isosbestic point at 307 nm is maintained and D_{comp} is the calculated absorbance of a solution of $[Au(N\text{–}SO)Cl_3]$ at the same concentration as that of the starting material. Such a plot is curved but the initial slope was taken as $k_{obs.}^r$ and values are reported in Table 3. A plot of $k_{obs.}^r$ against [N–SO] is linear with slope (11.2 ± 0.5) × 10^{-2} dm^3 mol^{-1} s^{-1} and intercept (3.5 ± 0.4) × 10^{-4} s^{-1}. The first-order rate constant compares well with that (5 × 10^{-4} s^{-1}) obtained in the reaction between $[AuCl_4]^-$ and pyridine-2-methanol.[8] Since it is known[13] that the discrimination of $[AuCl_4]^-$ between substituted pyridines does not depend upon the nature of the solvent [and in any case the change from methanol–water (95:5, v/v) to dry methanol is not very great] it is possible to use the relationship derived therein to calculate a value for k_2^r of a substituted pyridine with a pK_a of 3.39 and a steric hindrance similar to 2-methylpyridine attacked only through nitrogen. The value obtained, 0.093 dm^3 mol^{-1} s^{-1}, compares well with the experimental value (0.112 ± 0.005 dm^3 mol^{-1} s^{-1}).

Table 4. Equilibrium constants calculated from the rate of approach to equilibrium for the processes $[AuCl_4]^- + N\text{-}SO \rightleftharpoons [Au(N\text{-}SO)Cl_3] + Cl^-$ in MeOH–H_2O (95:5, v/v); $[H^+] = 1.99 \times 10^{-4}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} ($LiClO_4$)

$10^4[AuCl_4]^-$	10^3[N-SO]			$10^3k_{obs.}$*/	
mol dm^{-3}		D_0	D_∞	s^{-1}	10^2K
2.46	3.63	1.139	0.920	2.4	2.2 ± 0.2
2.39	5.69	1.107	0.872	2.15	1.80 ± 0.07
2.35	7.82	1.085	0.862	3.00	1.16 ± 0.03
2.44	9.33	1.129	0.823	2.82	2.4 ± 0.5
2.49	11.23	1.149	0.844	3.07	1.9 ± 0.3
				average	1.88 ± 0.13

From the kinetic data it is possible to estimate a value for the equilibrium constant for the process, $K = k_2^f/k_2^r = (11.2 \pm 0.5) \times 10^{-2}/(6.42 \pm 0.46) = 0.0174 \pm 0.0015$.

It was also observed that the absorbance changes with time could be fitted to an exponential curve over the whole of the time period when the isosbestic point was maintained, provided a different value for the final absorbance was used. Using D_∞ and $k_{obs.}$* as variable parameters the data were fitted to the curve given by $(D_t - D_\infty) = (D_0 - D_\infty)\exp(-k_{obs.}{*}t)$. Assuming that D_∞ could be identified as the absorbance of an equilibrium mixture of $[AuCl_4]^-$ and [Au(N-SO)Cl_3] under the experimental conditions, unaffected by any subsequent change, the fraction of reaction was calculated and the equilibrium constant, K, determined as outlined in the Experimental section. The values are included in Table 4. Bearing in mind the experimental problems the agreement between the values of K determined by the two methods is reasonably good.

All the results reported above are fully consistent with a reaction scheme in which phenyl 2-pyridylmethyl sulphoxide binds to gold(III) only through the heterocyclic nitrogen donor and interaction, if any, through the sulphoxide group cannot be detected either by kinetic or equilibria measurements. It remains therefore to be discussed why $[PtCl_4]^{2-}$ and $[AuCl_4]^-$ behave in such a different way towards sulphoxides.

A first consideration to be pointed out is that while stable and inert sulphoxide complexes of platinum(II) are well known, the lability and stability of such sulphoxide complexes is strongly dependent upon the nature of the substrate. Dimethyl sulphoxide in the anionic complex $[Pt(Me_2SO)Cl_3]^-$ is thermodynamically stable and kinetically inert and the reaction of this substrate with a variety of nucleophiles leads to the substitution of the chloride *trans* to the neutral ligand.[14] The kinetic *trans* effect of Me_2SO in this complex is larger than that of dimethyl sulphide in $[Pt(Me_2S)Cl_3]^-$. The kinetic inertness of a single Me_2SO bound through sulphur to platinum is maintained in many neutral and monocationic complexes provided significant steric hindrance is absent. However, the displacement of Me_2SO from the dication $[Pt\{NH(CH_2CH_2NH_2)_2\}(Me_2SO)]^{2+}$ has been observed and studied, suggesting that the stability and inertness is reduced when the charge of the complex is high enough. The lack of lability of a single sulphoxide is to be contrasted with the enormous mutual labilization of a pair of *cis* dimethyl sulphoxides in neutral *cis*-$[Pt(Me_2SO)_2Cl_2]$[15] as well as cationic $[Pt(NH_2CH_2CH_2NH_2)(Me_2SO)_2]^{2+}$ species.[16] It can also be contrasted to the fact that dimethyl sulphoxide has frequently been used as a solvent[17] for square-planar substitution reactions and there has never been any suggestion that the solvolytic pathway, which frequently offers a major route for substitution, presents anything other than a typical labile solvento-intermediate. In a number of respects Me_2SO resembles ethene in (*a*) its absence of *trans* influence to accompany its strong *trans* effect, (*b*) the great instability of the bis complexes compared to the mono-species and, (*c*) the low nucleophilicity. The observation that Au^{III} does not form stable sulphoxide complexes is therefore another point of resemblance and suggests, possibly, that the π-acceptor properties of sulphoxides play a significant part in the stabilization of these Pt–S bonded species as well as contributing to the *trans* effect. The greater effective nuclear charge on Au^{III} as compared to that of Pt^{II}[18] will reduce its ability to act as a π donor and consequently its ability to satisfy the back donation needs of S-bonded sulphoxide will be less than that of Pt^{II}.

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