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A Comparison of the *Trans*-Effects of Dimethyl- and Diethylsulphide in Platinum(II) Complexes

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The kinetics of the replacement of chloride trans *to diethylsulphide in* $[Pt(SEt_2)Cl_3]^-$ *by a variety of amines have been studied in methanol at 30 °C. The reverse reaction has been studied with 3-chloropyridine as leaving group. The rate constants are compared with those of the corresponding reactions of the dimethylsulphide analogue. In general, the* Et_2S *complexes are more reactive but the reactivity ratio depends upon the nature of the complex and of the entering group.*

Introduction

In recent years we have been making a systematic study of the kinetics and equilibria of reactions of the type,

$$[PtLCl_3]^- + am \rightleftarrows trans\text{-}[PtL(am)Cl_2] + Cl^-$$

(am = amine) in order to examine, in depth, the kinetic *trans*-effect of the neutral ligands, L, with particular reference to the ways in which the donor atom and the substituents on it affect the reactivities and the equilibria. We have already reported the results for the two sulfur donors, $(CH_3)_2SO$ [1] and $(CH_3)_2S$ [2] and have shown that, in general, the sulfoxide exerts a greater *trans*-effect than the thioether but the extent of the difference depends upon the substrate and the nature of the reaction being studied. The work has been extended to a systematic study of ligands containing phosphorus and arsenic donors and the extent to which their *trans* effects depend upon the nature of the substituents attached to the donor atom and this work will be published elsewhere [3]. This paper reports a comparison of the *trans* effects of diethyl- and dimethylsulphide in order to evaluate the relative importance of electronic and steric effects and to provide the required background for the study of the phosphorus and arsenic compounds.

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Experimental

Preparation of Compounds

Tetraethylammonium trichlorodiethylsulphideplatinate(II)

$Et_4NCl \cdot H_2O$ (1.03 g; 5.6 mmol) was added to a solution of $[Pt_2Cl_4(SEt_2)_2]$ (2.00 g; 2.8 mmol) (prepared from *cis*-dichlorobis(diethylsulphide)platinum(II) [4] by the method of Chatt and Venanzi [5, 6]) in dichloromethane (100 cm^3). The mixture was stirred at room temperature overnight and the crude product precipitated by carefully adding diethylether and then recrystallised from dichloromethane–diethylether as yellow crystals (2.1 g). *Anal.* Calcd. for $C_{12}H_{30}Cl_3NPtS$: C, 27.6; H, 5.8; N, 2.7; Cl, 20.4. Found: C, 27.2; H, 5.7; N, 2.6; Cl, 20.5.

trans-*Dichloro(pyridino)(diethylsulphide)platinum-(II)*

This complex was prepared by a modification of Chatt's method [7]. The dimer, $Pt_2Cl_4(SEt_2)_2$ (0.1 g; 0.14 mmol) was dissolved in dichloromethane (50 cm^3) and a solution of pyridine (0.024 g; 0.30 mmol) in dichloromethane (25 cm^3) was slowly added to the stirred solution over a period of 30 min. The yellow solution was filtered and the solvent removed on a rotary evaporator. The brown oil which remained was dissolved in methanol which was then removed in a rotary evaporator until the solution started to deposit the product as yellow crystals which were eventually filtered off (0.042 g). *Anal.* Calcd. for $C_9H_{15}Cl_2NPtS$; C, 24.8; H, 3.5; N, 3.2. Found: C, 24.7; H, 3.5; N, 3.2.

Reagents and Kinetics

The reagents were prepared and purified by methods previously described [2]. The reactions were started and followed in the ways described elsewhere [2] except that the bulk of the spectrophotometric measurements were made with a Pye Unicam SP 1750 spectrophotometer fitted with a Unicam SP 1805 programme controller and a Unicam

TABLE I. Rate Constants for the Reaction, $[Pt(SR_2)Cl_3]^- + am \xrightarrow{k_1^f + k_2^f[am]} trans\text{-}[Pt(SR_2)(am)Cl_2] + Cl^-$.

am	pK_a[c]	R = Et[a,b]		R = Me[a]		$k_2^f(SEt_2)/k_2^f(SMe_2)$
		$10^3k_1^f/s^{-1}$	$10^2k_2^f/M^{-1}\,s^{-1}$	$10^3k_1^f/s^{-1}$	$10^2k_2^f/M^{-1}\,s^{-1}$	
piperidine	11.12	0.97 ± 0.24	17.9 ± 1.0	1.26 ± 0.88[e]	19.8 ± 1.5[e]	0.90
cyclo-hexylamine	10.66	1.65 ± 0.18	8.0 ± 0.5	0.94 ± 0.07[e]	10.9 ± 0.3[e]	0.73
morpholine	8.33	2.53 ± 0.64	57.6 ± 3.7	1.07 ± 0.18[f]	67.8 ± 1.6[f]	0.85
3,4-dimethylpyridine	6.50	2.00 ± 0.05	8.2 ± 0.02	1.22 ± 0.03[e]	6.6 ± 0.2[e]	1.24
4-methylpyridine	6.02	2.04 ± 0.11	8.8 ± 0.7	1.21 ± 0.02[f]	6.5 ± 0.1[f]	1.35
pyridine	5.25	2.08 ± 0.14	10.1 ± 0.4	1.33 ± 0.04[e]	6.2 ± 0.2[e]	1.63
3-chloropyridine	2.84	2.23 ± 0.13	21.4 ± 0.8	1.14 ± 0.03[f]	13.0 ± 0.2[f]	1.65
3-bromopyridine	2.84	1.98 ± 0.23	25.7 ± 1.3	1.12 ± 0.02[f]	14.2 ± 0.1[f]	1.81
4-cyanopyridine	1.86[d]	2.23 ± 0.16	28.1 ± 0.9	1.12 ± 0.06[f]	17.7 ± 0.4[f]	1.59
3,5-dichloropyridine	0.67[d]	2.13 ± 0.21	37.1 ± 1.3	1.26 ± 0.04[f]	21.6 ± 0.3[f]	1.72

[a]In methanol, Temperature = 30.0 °C, μ = 0.5 ($LiClO_4$), [complex] = 1×10^{-4} *M*. [b]$[Cl^-]$ = 0.025 *M*. [c]Data from Ref. 8. [d]Data from Ref. 9. [e]Analysed from data at $[Cl^-]$ = 0.50 *M* and 0.015 *M* (see text). [f]Data from Ref. 2.

SP 874 constant temperature cell housing. The reaction temperature was monitored by a platinum resistance thermometer which could be placed in the cell, out of the light path, but which was generally located in an adjacent cell, the temperature difference being determined in a separate experiment.

Results

The preparation of the $[Et_4N][Pt(SEt_2)Cl_3]$ complex by the reaction of Et_4NCl with the chloro-bridged dimer, $Pt_2Cl_4(SEt_2)_2$ is straightforward and not complicated by the reversibility problems encountered in the preparation of the dimethylsulphide analogue [2]. The reactions between this complex and a variety of amines can be studied conveniently by repetitive scanning spectrophotometry. In general, the spectral changes closely resembled those observed in the corresponding reactions of $[Pt(SMe_2)Cl_3]^-$ and it was assumed that similar reactions were being followed, namely the displacement of the chloride *trans* to the thioether. The product of the reaction with pyridine was isolated and characterised in order to confirm that it was indeed the *trans* chloride that was being replaced.

The kinetics of the reaction were followed in the presence of a sufficient excess of amine to ensure that the reaction went to completion and that the kinetics were first-order. In preparing the solutions for kinetics, problems arose from the solvolysis of the substrate to give *trans*-$[Pt(SEt_2)(MeOH)Cl_2]$ and so it was necessary to prepare stock solutions containing 0.50 *M* LiCl to eliminate interference from this source. Subsequent dilution in preparing the reaction mixture reduced the chloride concentration from this source by a factor between 30 and 100, at which level mass-law retardation due to competition between Cl^- and the amine for the *trans*-$[Pt(SEt_2)(MeOH)Cl_2]$ intermediate was negligible. In order to maintain a constant concentration of chloride ions, LiCl was also added to the solution of the amine in methanol in the reaction cell such that $[Cl^-]$ = 0.025 *M*. At all but the lowest concentrations of amine used within the range 0.002 to 0.1 *M* interference was negligible and the plot of k_{obs} against [amine] was linear. The data were analysed by a linear least squares regression and the values of the slope (k_2^f) and intercept (k_1^f) are collected in Table I. As in the case of the SMe_2 complexes [2], the reverse reaction was very slow and could only be studied in the case of the least strongly bound amines. In the presence of 0.10 *M* $HClO_4$, the reverse reaction went to completion within the range of chloride ion concentrations used (0.1 to 0.5 *M*) and the simple two-term rate law was obeyed, *i.e.*, $k_{obs} = k_1^r + k_2^r[Cl^-]$. For the reaction, *trans*-$[Pt(SEt_2)(3\text{-Cl-py})Cl_2] + Cl^- + H^+ = [Pt(SEt_2)Cl_3]^- + 3\text{-Cl-py}H^+$, $k_1^r = (1.27 \pm 0.04) \times 10^{-4}\ s^{-1}$ and $k_2^r = (1.31 \pm 0.14) \times 10^{-4}\ M^{-1}\,s^{-1}$ at 30.0 °C.

Discussion

At first sight the kinetics of the replacement of chloride by amines under the experimental conditions used appear to follow the classical two-term rate law, $-d[complex]/dt = (k_1^f + k_2^f[am])[complex]$, where k_1^f is the first-order rate constant for the solvolysis of the substrate and k_2^f is the second-order rate constant for the direct attack by the amine on the substrate. This is a limiting form of the more general expression where, $k_{obs} = k_1^f k_{am}^i(k_{am}^i[am] +$

$k^i_{Cl}[Cl^-])^{-1} + k^f_2[am]$, where k^i_{Cl} and k^i_{am} are the second-order rate constants for the displacement of methanol from *trans*-$[Pt(SEt_2)(MeOH)Cl_2]$ by chloride and the amine respectively. With the exception of the data for the reaction between the substrate and piperidine or cyclohexylamine, where the value is low, and morpholine, where the value is high, k^f_1 is essentially independent of the nature of the entering nucleophile. Similar low values for k^f_1 when the most basic amines were reacting have been observed in the corresponding reactions of the SMe_2 and Me_2SO analogues but it is believed that all of these discrepancies are due to inadequate correction for the effects of the mass-law retardation of the k^f_1 step by chloride. Indeed, the 'constant' value for k^f_1 (2.1×10^{-3} s^{-1}) is probably underestimated by some 10–15% because of this: thus, the direct determination of k^f_1 by studying the replacement of the *trans* chloride in $[Pt(SEt_3)Cl_3]^-$ by hydroxide gives a value of $(2.4 \pm 0.1) \times 10^{-3}$ s^{-1} that is esssentially independent of the concentration of hydroxide concentration within the range 3.9×10^{-3} $M < [OH^-] < 7.7 \times 10^{-3}$ M. A similar observation was made in the case of the SMe_2 complex [2]. A series of runs were carried out for the reaction with pyridine in which $[Cl^-]$ was varied over the range $0.010\ M < [Cl^-] < 0.50\ M$ with [pyridine] held constant at 0.0015 M and the data analysed using the full expression for k_{obs} feeding in the value obtained for k^f_2 at much higher concentrations of pyridine (1.0×10^{-1} M^{-1} s^{-1}). This gives a value of $k^f_1 = (2.34 \pm 0.06) \times 10^{-3}$ s^{-1} and $k_{Cl}/k^i_{am} = (6.00 \pm 0.23) \times 10^{-3}$. The error introduced by ignoring mass-law retardation when $[Cl^-] = 0.025\ M$ is about 10% of k_{obs} at the lowest concentration of pyridine used (0.0020 M) but becomes insignificant (0.6%) at the highest pyridine concentration (0.060 M). If the data are treated as if the k_{obs} *versus* [pyridine] relationship was linear, with equal weighting to each point, k^f_1 will be underestimated by about 5% and k^f_2 by 2%. The plot should be curved but the amount of curvature is too small compared to the error in each of the data points to make the full analysis significant.

A re-examination of some reactions of $[Pt(SMe)Cl_3]^-$ with amines, combining the original data [2] with a set measured at $[Cl^-] = 0.50\ M$ and using the BDMP 3R non-linear regression program written by Steve Chasen of the Health Science Computing Facility of the University of California gives the data reported in the Table. This non-approximate treatment of the data does not change the results drastically but it is of interest to note that the ratio k^i_{Cl}/k^i_{am} increases from 6×10^{-3} for pyridine to 8×10^{-3} for 3,4-dimethylpyridine [2], 1.4×10^{-2} for cyclo-hexylamine and 2.6×10^{-2} for piperidine, indicating that the least basic heterocyclic amines are more able to compete with chloride for the solvents intermediate than the most basic primary and secondary amines. The effects of mass-law retardation will be most serious when the most basic amines are entering groups. The corresponding analysis was not made for the SEt_2 system but it is reasonable to believe that the low values obtained for k^f_1 in the simplified analysis of the data for the reactions with the most basic amines was caused by inadequate correction for mass-law retardation.

The change in *trans effect* on going from Me_2S to Et_2S is seen, in most of the cases studied, as an increase in reactivity. The most marked difference is found in the replacement of 3-chloropyridine *trans* to Cl by methanol or chloride. Using the data for the SMe_2 complex in Ref. 2, the ratio $k^r_1(SEt_2)/k^r_1(SMe_2)$, *i.e.*, entry of methanol, is 3.3 and the ratio $k^r_2(SEt_2)/k^r_2(SMe_2)$, *i.e.*, entry of chloride, is 3.2. The absence of data for the displacement of other amines precludes any consideration of the extent to which this ratio depends upon the nature of the leaving group. The effect is less, but still significant, when chloride *trans* to SR_2 is replaced by methanol. Using the values obtained directly from the solvolysis of the trichloro anions in basic methanol, the ratio $k^f_1(SEt_2)/k^f_1(SMe_2)$ becomes 1.7. This is similar to that found when chloride is replaced by the less basic heterocyclic amines (Table I) but the discrimination seems to decrease and finally disappears as the basicity of the entering group increases. It is even possible that the effect reverses itself when the entering groups are saturated primary and secondary amines but the errors introduced by the inadequate correction for mass-law retardation are of a similar magnitude to the observed differences in the rate constants.

Any attempt to account for these observed differences in the *trans effect* should carry the caveat that it is rarely valuable in mechanistic studies to build an hypothesis on relatively small differences in rate constants. Steric effects are clearly not dominant since the more bulky Et_2S should produce the less reactive complexes. Nevertheless we cannot rule them out as making a minor compensating contribution. In any case, steric hindrance from the ligand *trans* to the leaving group, even in very crowded molecules, is rarely important in the substitution reactions of platinum(II) complexes [10], since the congestion, which is mainly involving the ligand and its *cis* neighbours, is not greatly increased by the addition of the fifth ligand in the transition state. On the other hand, it has been suggested that steric hindrance is the reason why SEt_2 in a poorer nucleophile than SMe_2 in their reaction with $[Pt(dien)OH_2]^{2+}$ [11] (dien = 1,6-diamino-3-aza-penatne).

Electronically, the replacement of methyl by ethyl displaces more charge towards the sulphur ($\Sigma\sigma^* = 0.020$ [12]) and should increase its σ donor strength, while, at the same time, decreasing any π-acceptor

properties that might be present. This would be expected to increase the *trans* influence of the sulphur but the effect upon the rate constants would depend upon the relative contributions to the ground state and the transition state. The fact that the $k(SEt_2)/k(SMe_2)$ ratios depend upon the nature of the entering group shows clearly that discrimination in the transition state cannot be ignored. The change in the equilibrium constant for the reaction, $[Pt(R_2S)Cl_3]^-$ + 3-Cl-py = *trans*-$[Pt(R_2S)(3\text{-Cl-py})Cl_2]$ + Cl^- on going from R = CH_3, K = 3.2×10^3 [2] to R = C_2H_5, K = $k_2^f/k_2^r = 1.63 \times 10^3$, indicates that there is a substituent effect upon the *trans* influence of SR_2 and, in order that this be observed as a change in the equilibrium constant, this must depend upon the nature of the ligand *trans* to the thioether. The ligand dependence may only be upon the charge type, *i.e.*, the *trans* influence may depend upon the total charge of the complex. A similar, but much more marked effect is seen in the comparison of the *trans*-influences of Me_2S and Me_2SO [2].

The kinetic probe is much more sensitive than the properties used to monitor the *trans* influence, *e.g.*, bond lengths and bond stretching frequencies. In so far as any information is available, the *trans* influence of thioethers, when measured in this way, is no different from that of NH_3 and Cl and therefore considered to be small. An examination of substituent effects on the *trans* influence of thioethers is unlikely to yield a significant effect. The slight decrease in the frequency assigned to ν_{Pt-Cl} for the bond *trans* to S in $[Pt(SR_2)Cl_3]^-$ on going from R = Me (310 cm^{-1} to R = Et (307 cm^{-1}) [13] may be cited as evidence for a slight increase in the *trans* influence but it should be noted that, in the analogous Pd(II) complexes, the shift is in the opposite direction and the authors caution against giving significance to small differences that might arise from interaction with other vibrational modes in the molecule.

Although the *trans* influence of the thioether is not significantly different from that of ammonia, there is no doubt that the *trans*-effect is considerably greater. The analogous reaction of $[Pt(NH_3)Cl_3]^-$ has not been studied in methanol but, in aqueous solution, the solvolysis of the *trans* chloride (which is only a minor reaction pathway) has been assigned a rate constant of 6.3×10^{-6} s^{-1} at 25.0 °C [14], indicating that the corresponding SR_2 complexes are at least two orders of magnitude more labile. Since the change of solvent from methanol to water can increase the values of k_1 by between 1 and 2 orders of magnitude, for example in the reactions of *cis*-$[Pt(dmso)(chx)Cl_2]$ (chx = cyclo-hexylamine) k_1(in H_2O)/k_1(in MeOH) = 50 [15] and for $[Pt(dmso)Cl_3]^-$ this ratio is 20 [1, 18], the difference in the *trans* effects of NH_3 and SR_2 as assessed by the solvolytic rate constants, may be as great as 10^4. Compared to this the substituent effects are negligible. It is therefore of interest to examine the behaviour of analogous complexes with phosphine ligands, where the *trans* influence can be considerable, in order to determine whether the lack of a measurable *trans* influence for sulfur donors which exert a moderate *trans* effect is due to the low sensitivity of the methods used to determine *trans* influence or whether there is no simple relationship between the *trans* influence and *trans* effect of ligands that function as pure σ-donors. This work has been done and will be reported elsewhere.

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