# Kinetics of Displacement of Dimethyl Sulphoxide (dmso) from $[Pt(N–N)(dmso)X]^+$ by $X^-$ [N–N = 1,10-phenanthroline, 2,2′-bipyridyl, or 2,2-bis(2′-pyridyl)-1,3-dioxolane; X = Cl or Br]

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On reaction with $Cl^-$ or $Br^-$ in methanol, dimethyl sulphoxide (dmso) is displaced from $[Pt(N–N)(dmso)X]^+$. When N–N is 1,10-phenanthroline or 2,2′-bipyridyl the reactions are relatively rapid and the reaction with $Cl^-$ obeys the rate law $-d[\text{complex}]/dt = (k_1 + k_2[Cl^-] + k_3[Cl^-]^2)[\text{complex}]$. The reaction with bromide can only be studied under conditions where the second-order dependence on $[Br^-]$ is not expected. The reactions with N–N = 2,2-bis(2′-pyridyl)-1,3-dioxolane (bipyoxo) are much slower and, even at the highest chloride concentrations used, the dependence on $[Cl^-]$ is strictly first order. The kinetics are explained in terms of addition of a chloride to form an intermediate that can undergo an associative displacement of dmso by a second chloride in addition to the normal mode of reaction. It is suggested that this intermediate is truly five-co-ordinate. The absence of the second-order dependence in the reactions of the bipyoxo complex is ascribed to a blocking of an axial position on the platinum by the oxygen. An alternative mechanism in which the intermediate remains four-co-ordinate and has the di-imine acting as monodentate is considered and rejected. Comparisons are made with the behaviour of $[Pt(N–N)(C_2H_4)Cl]^+$.

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Although the displacement of one dimethyl sulphoxide (dmso) from square-planar platinum(II) complexes containing two or more such ligands is frequently rapid,[1,2] the displacement of a single sulphoxide can be very slow indeed. For example, heating with concentrated hydrochloric acid is required to remove dmso from $[Pt(en)(dmso)Cl]^+$ (en = ethylenediamine) and the products are $Me_2S$ and the platinum(IV) species $[Pt(Hen)Cl_5]$.[3] Recently we examined the mode of bonding of dimethyl sulphoxide in complexes of the type $[M(N–N)(dmso)Cl]^+$ [M = Pd, N–N = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), or en; M = Pt, N–N = bipy or phen] and showed that the donor atom of dimethyl sulphoxide depended upon the nature of M and N–N. While all the platinum(II) complexes were S-bonded the palladium complexes with bipy and phen had the sulphoxide bound through oxygen in the crystal and there was an equilibrium between the two modes of bonding in solution.[4] In addition, it was found that the sulphoxide was readily displaced from the platinum by anionic nucleophiles such as $Cl^-$ and $Br^-$.

In this paper we report the kinetics of displacement of dimethyl sulphoxide from the previously described cations, $[Pt(N–N)(dmso)X]^+$ (N–N = bipy or phen; X = Cl or Br), as well as from the newly prepared $[Pt(bipyoxo)(dmso)Cl]^+$ [bipyoxo = 2,2-bis(2′-pyridyl)-1,3-dioxolane]. The reactivity of the corresponding palladium(II) species is too high to allow kinetic studies.

## Experimental

*Compounds.*—2,2-Bis(2′-pyridyl)-1,3-dioxolane(bipyoxo)was prepared by the method of Newkome *et al.*[5] from bis(2-pyridyl) ketone and ethylene glycol in toluene containing a catalytic amount of sulphuric acid (Found: C, 68.4; H, 5.35; N, 12.25. $C_{13}H_{12}N_2O_2$ requires C, 68.4; H, 5.30; N, 12.25%).

$[Pt(bipyoxo)Cl_2]$. A solution of bipyoxo (0.55 g, 2.4 mmol) in water (10 cm$^3$) was added slowly to a stirred solution of $K_2[PtCl_4]$ (1.0 g, 2.4 mmol) in water (50 cm$^3$). After standing for 1 week the yellow precipitate which formed was filtered off, washed twice with cold water, and air-dried. Yield 75% (Found: C, 31.6; H, 2.45; Cl, 14.35; N, 5.65. $C_{13}H_{12}ClN_2O_{22}Pt$ requires C, 31.6; H, 2.45; Cl, 14.35; N, 5.65%).

The salt $[Pt(bipyoxo)(dmso)Cl][ClO_4]$ was prepared from the dichloro complex by the method of Annibale *et al.*[4] Yield 90% (Found: C, 28.4; H, 2.75; Cl, 11.1; N, 4.40. $C_{15}H_{18}Cl_2N_2O_7PtS$ requires C, 28.3; H, 2.85; Cl, 11.1; N, 4.40%).

*Kinetics.*—The reactions were followed spectrophotometrically either by repetitively scanning the spectrum over the range 230—400 nm at suitable times if the reactions were slow enough or by following the change of absorbance with time at a chosen wavelength. Pseudo-first-order rate constants ($k_{obs.}$) were calculated either from the slopes of the linear plots of $\ln(A_t - A_\infty)$ against time, where $A_t$ and $A_\infty$ are the absorbances at time $t$ and after at least six half-lives respectively, or from a non-linear least-squares fit of the experimental data to the expression $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$ with $A_0$, $A_\infty$, and $k_{obs.}$ as the parameters to be optimised ($A_0$ being the absorbance immediately after mixing the reagents). The values of the rate constants were independent of the method used to calculate them.

*Apparatus.*—Electronic spectra were obtained with Cary 219 and Coleman 575 spectrophotometers. Proton n.m.r. spectra of $CD_3NO_2$ solutions, using $SiMe_4$ as internal standard, were recorded with a Varian EM390 spectrometer. Infra-red spectra of Nujol mulls between sodium chloride or polyethylene (below 600 cm$^{-1}$) plates were recorded with a Perkin-Elmer 683 spectrophotometer.

## Results and Discussion

The cations $[Pt(N–N)(dmso)Cl]^+$ (N–N = bipy or phen) have

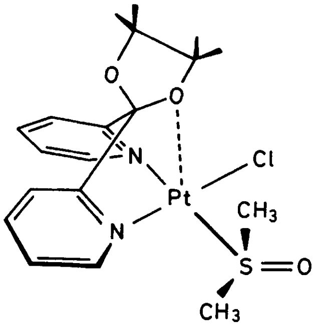


**Figure 1.** Suggested structure for the $[Pt(bipyoxo)(dmso)Cl]^+$ cation in nitromethane to account for the presence of two methyl proton resonances in the $^1H$ n.m.r. spectrum

been described previously.[4] The corresponding bromo complexes, prepared in a similar way from the $[Pt(L\text{–}L)Br_2]$ adducts, also contain S-bonded dimethyl sulphoxide both in the solid and in solution, having identical S=O stretching frequencies in the i.r. spectrum and methyl proton chemical shifts as well as Pt–H coupling constants as the characterised chloro analogues.[3] The i.r. spectrum of $[Pt(bipyoxo)(dmso)Cl][ClO_4]$ is also consistent with the presence of S-bonded dimethyl sulphoxide, with ν(S=O) 1 150 $cm^{-1}$. The $^1H$ n.m.r. spectrum of this complex in $CD_3NO_2$ solution is of interest in that two methyl resonances are observed, each with $^{195}Pt$ satellites, at δ 3.62 and 3.69 ($SiMe_4$ as internal standard) with $J$(Pt–H) = 22.8 and 24.3 Hz respectively. We propose that, in nitromethane, the ligand adopts the same conformation as is found in the $[Pd(bipyoxo)Cl_2]$ complex in the solid state,[6] in which the six-membered ring formed by co-ordination of the bipyoxo ligand to the metal through its nitrogens assumes a boat conformation with one acetal oxygen in close intramolecular contact with the metal. The ligand is thus prochiral and the two methyl groups of the dimethyl sulphoxide are diastereotopic, Figure 1. The solubility of the complex in methanol is too low to allow its n.m.r. spectrum to be recorded in this solvent. A referee has pointed out that the prochirality does not prove that there is a bond with the metal but only shows that the oxygen does not move rapidly from one side of the co-ordination plane to the other. Such a rearrangement is unlikely without Pt–N bond fission.

The reactions of the three complexes of the type $[Pt(N\text{–}N)(dmso)X]^+$ with excess of halide $X^-$ were followed spectrophotometrically in methanol–water (95:5, v/v) at 25 °C, where, because of the low solubility of the reaction product, $[Pt(N\text{–}N)X_2]$, the concentration of complex was kept at $10^{-5}$ mol $dm^{-3}$. In all the cases examined, the spectra showed well defined isosbestic points throughout the reaction and the final spectra corresponded exactly with those of authentic samples of $[Pt(N\text{–}N)X_2]$ measured under the same experimental conditions. The spectrophotometric changes therefore relate to the displacement of dimethyl sulphoxide [equation (1)]. The

$$[Pt(N\text{–}N)(dmso)X]^+ + X^- \longrightarrow [Pt(N\text{–}N)X_2] + \text{dmso} \quad (1)$$

linearity of the semi-logarithmic plots and the regularity of the fit in the regression analysis (see Experimental section) show that the process follows a first-order rate law. The rate constants, determined over a range of halide-ion concentrations, are collected in Table 1. In all cases pseudo-first-order conditions ($[X^-] \gg$ [complex]) were maintained and the ionic strength was held constant by adding $LiClO_4$.

*Displacement of Dimethyl Sulphoxide from* $[Pt(bipyoxo)(dmso)Cl]^+$ *by Chloride.*—This was the least reactive of the complexes studied. The ionic strength was held constant at $I$ = 1.0 mol $dm^{-3}$ in order to be able to examine the reaction at high halide concentration. The plot of $k_{obs.}$ against $[Cl^-]$ is linear and passes through the origin [intercept = $(2.2 \pm 4.7) \times 10^{-7}$ $s^{-1}$]. The slope, $k_2 = (1.59 \pm 0.04) \times 10^{-4}$ $dm^3$ $mol^{-1}$ $s^{-1}$.

*Displacement of Dimethyl Sulphoxide from* $[Pt(N\text{–}N)(dmso)X]^+$ *by* $X^-$ (N–N = *bipy or phen;* X = Cl *or* Br).—In the reaction with $Cl^-$, the dependence of $k_{obs.}$ on $[Cl^-]$ follows a rate law that is more complicated than the usual first-order dependence. Plots of $k_{obs.}$ against $[Cl^-]$ are linear only at low halide concentration but plots of $(k_{obs.} - k_1)/[Cl^-]$ against $[Cl^-]$ are linear throughout, indicating the relationship $k_{obs.} = k_1 + k_2[Cl^-] + k_3[Cl^-]^2$ is obeyed. Values of the rate constants, obtained from a non-linear regression analysis of the $k_{obs.}$ *vs.* $[Cl^-]$ data to the above expression, are collected in Table 3 and values of the pseudo-first-order constants, calculated from these, $k_{calc.}$, are compared with $k_{obs.}$ in Table 1. The $[Cl^-]$-independent contribution to the rate is too small to be seen in the direct analysis of the $[Cl^-]$ dependence of $k_{obs.}$ and is obtained from a study of the reaction in the absence of $Cl^-$ but in the presence of a small excess of $OH^-$. It may possibly be the rate constant for the solvolytic displacement of $Cl^-$ from the complex rather than dmso and therefore represents an upper limit to the first-order rate constant for the displacement of the latter ligand. In the presence of $Cl^-$, of course, the replacement of chloride by chloride does not lead to any net chemical change and the overestimation of $k_{calc.}$ at low $[Cl^-]$ (Table 1) might be due to this.

The reactions of the bromo complexes with bromide are some twenty times faster and plots of $k_{obs.}$ against $[Br^-]$ are linear without significant intercepts (the solvolytic rate constants are smaller than the experimental error in determining the intercepts of the linear plot). No departures from linearity are observed but the reactions become too fast to follow by the techniques at our disposal before the concentration of $Br^-$ is high enough for the second-order term to make a significant contribution. It is unlikely that much of this increase of reactivity is due to the change in the substrate as *cis* effects are usually quite small, and the major part of the increase in $k_2$ is almost certainly due to the increase in nucleophilicity ($n^{\circ}_{Pt}$) of the entering group. Since the difference between the $n^{\circ}_{Pt}$ values of $Cl^-$ and $Br^-$ is 1.14,[7] the increased reactivity is consistent with the high nucleophilic discrimination shown by substrates containing dimethyl sulphoxide.[2]

In general, the rate constants for the bipyridyl and phenanthroline complexes do not differ greatly from one another, those for the bipy complex being somewhat less than an order of magnitude greater than those for the less basic phenanthroline.[8] This is a common observation and reflects the relationship between the electrophilicity of the reaction centre and the extent of the displacement of charge towards it by the spectator ligands.

The observation of a second-order dependence upon nucleophile concentration is unusual in platinum(II) chemistry. Many examples are being found of such dependences in the displacement of ligands from dicationic and, occasionally, monocationic species by hydroxide[9–11] but the acid/base relationship between hydroxide and water creates ambiguities in the general interpretation which have not yet been overcome. Second- and even third-order dependences of rate on $[X^-]$ are known, for example, in the displacement of bipyridine from $[Au(bipy)Br_2]^+$ by bromide in acid solution[12] but they are usually associated with the displacement of a multidentate ligand and can be related to the reversibility of ring opening.

Since the substrate and the nucleophile are both charged it is

**Table 1.** Pseudo-first-order rate constants for the reaction[a] $[Pt(N\text{-}N)(dmso)X]^+ + X^- \longrightarrow [Pt(N\text{-}N)X_2] + dmso$

| N-N | X | $I$ / mol dm$^{-3}$ | $10^2[X^-]$ / mol dm$^{-3}$ | $10^3k_{obs.}$/s$^{-1}$ | $10^3k_{calc.}{}^b$/ s$^{-1}$ |
|---|---|---|---|---|---|
| bipyoxo | Cl | 1.0 | 9.10 | 0.0135 ± 0.0001 | 0.0130 |
| | | | 18.2 | 0.0278 ± 0.0004 | 0.0285 |
| | | | 45.5 | 0.0685 ± 0.0012 | 0.0713 |
| | | | 63.7 | 0.106 ± 0.001 | 0.100 |
| | | | 90.9 | 0.139 ± 0.002 | 0.143 |
| bipy | Cl | 0.1 | 0.523 | 0.913 ± 0.012 | 0.945 |
| | | | 1.05 | 1.89 ± 0.01 | 1.89 |
| | | | 2.09 | 3.94 ± 0.01 | 3.86 |
| | | | 3.14 | 6.08 ± 0.02 | 6.01 |
| | | | 5.23 | 11.1 ± 0.1 | 10.7 |
| | | | 6.28 | 12.9 ± 0.1 | 13.4 |
| | | | 7.32 | 16.4 ± 0.1 | 16.1 |
| | | | 8.02 | 17.5 ± 0.1 | 18.0 |
| | | | 9.07 | 20.6 ± 0.1 | 21.0 |
| | | | 10.5 | 25.7 ± 0.1 | 25.4 |
| | | 1.0 | 0.398 | 0.233 ± 0.001 | 0.239 |
| | | | 0.990 | 0.535 ± 0.002 | 0.529 |
| | | | 1.96 | 1.03 ± 0.01 | 1.01 |
| | | | 3.85 | 1.97 ± 0.01 | 1.97 |
| | | | 5.60 | 2.83 ± 0.02 | 2.88 |
| | | | 7.20 | 3.69 ± 0.01 | 3.74 |
| | | | 8.00 | 4.15 ± 0.03 | 4.17 |
| | | | 10.0 | 5.29 ± 0.02 | 5.29 |
| | | | 20.0 | 11.2 ± 0.1 | 11.4 |
| | | | 28.0 | 16.8 ± 0.1 | 16.8 |
| | | | 40.0 | 26.1 ± 0.2 | 26.0 |
| bipy | Br | 1.0 | 0.400 | 3.95 ± 0.03 | 3.94 |
| | | | 0.800 | 8.52 ± 0.05 | 7.88 |
| | | | 1.20 | 11.8 ± 0.1 | 11.8 |
| | | | 1.60 | 15.2 ± 0.1 | 15.8 |
| | | | 2.00 | 19.6 ± 0.2 | 19.7 |
| | | | 2.40 | 24.2 ± 0.2 | 23.6 |
| phen | Cl | 1.0 | 0.990 | 0.148 ± 0.001 | 0.146 |
| | | | 2.00 | 0.306 ± 0.001 | 0.283 |
| | | | 4.00 | 0.595 ± 0.004 | 0.567 |
| | | | 5.60 | 0.786 ± 0.005 | 0.804 |
| | | | 6.80 | 1.03 ± 0.01 | 0.99 |
| | | | 8.00 | 1.25 ± 0.01 | 1.18 |
| | | | 10.0 | 1.45 ± 0.01 | 1.50 |
| | | | 15.0 | 2.36 ± 0.01 | 2.38 |
| | | | 20.0 | 3.39 ± 0.06 | 3.35 |
| | | | 30.0 | 5.33 ± 0.04 | 5.56 |
| | | | 40.0 | 7.88 ± 0.06 | 8.13 |
| | | | 50.0 | 10.7 ± 0.1 | 11.1 |
| | | | 66.0 | 17.0 ± 0.1 | 16.5 |
| | | | 80.0 | 23.9 ± 0.2 | 22.0 |
| | Br | 1.0 | 0.320 | 1.16 ± 0.01 | 1.15 |
| | | | 0.960 | 3.48 ± 0.02 | 3.46 |
| | | | 1.28 | 4.40 ± 0.01 | 4.61 |
| | | | 1.60 | 5.79 ± 0.02 | 5.76 |
| | | | 1.92 | 6.80 ± 0.02 | 6.91 |
| | | | 2.56 | 9.02 ± 0.02 | 9.22 |
| | | | 3.84 | 13.8 ± 0.1 | 13.8 |
| | | | 6.40 | 23.0 ± 0.2 | 23.0 |

[a] In methanol–water (95:5 v/v) at 25 °C. Ionic strength maintained with $LiClO_4$. [b] Using the appropriate rate constants from Table 3.

**Table 2.** Rate constants for the reaction $[Pt(bipy)(dmso)Cl]^+ + Cl^- \longrightarrow [Pt(bipy)Cl_2] + dmso$ at low ionic strengths[a]

| $10^3[Cl^-]$/ mol dm$^{-3}$ | $10^3k_{obs.}$/s$^{-1}$: $I$ = 0.01 mol dm$^{-3}$, $LiClO_4$ | $10^3k_{obs.}$/s$^{-1}$: $I = [Cl^-]$ | $10^3k_{calc.}{}^b$/s$^{-1}$ $I$ = 0.01 mol dm$^{-3}$ | $k_2{}^0$/dm$^3$ mol$^{-1}$ s$^{-1}$ ($I$ = 0.0) |
|---|---|---|---|---|
| 0.412 | | 0.407 ± 0.002 | 0.256 | 1.01 |
| 0.824 | | 0.740 ± 0.004 | 0.475 | 1.05 |
| 1.65 | 0.849 ± 0.001 | 1.26 ± 0.02 | 0.86 | 1.00 |
| 3.30 | 1.70 ± 0.01 | 2.29 ± 0.01 | 1.76 | 1.04 |
| 6.59 | 3.44 ± 0.01 | 3.94 ± 0.02 | 3.47 | 1.05 |
| 8.24 | 4.22 ± 0.03 | | | |
| 10.3 | 5.45 ± 0.02 | 5.45 ± 0.02 | 5.45 | 1.06 |

[a] In methanol–water (95:5 v/v) at 25.0 °C. [b] Using the relationship $\log k_2(I = I) = \log k_2(I = 0) - 3.44\sqrt{I}/(1 + 1.43\sqrt{I})$, with $k_2 = (k_{obs.} - k_1)/[Cl^-]$, where $k_1$ is taken from Table 3.

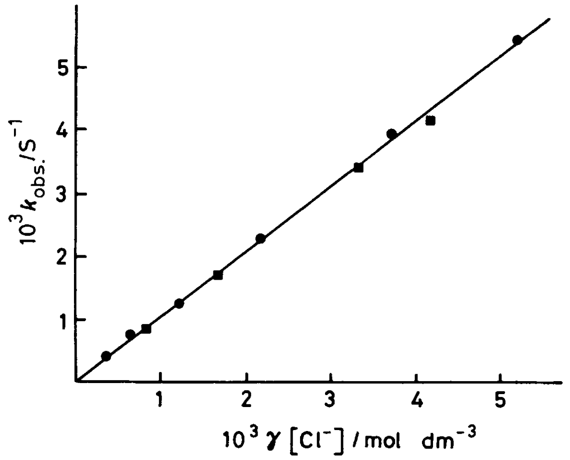
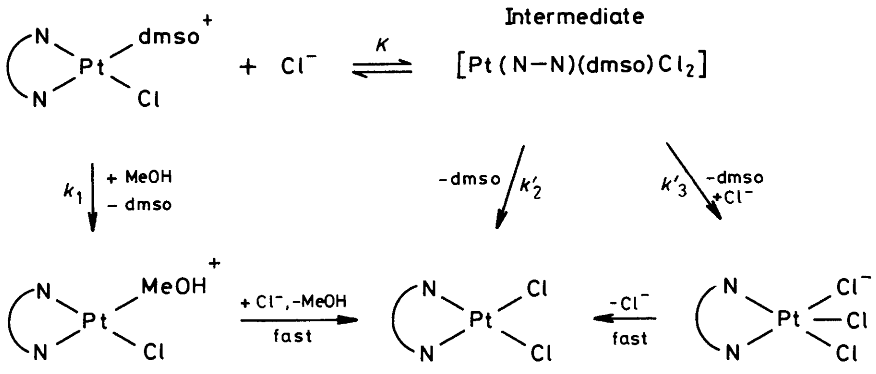


**Figure 2.** Plot of $k_{obs.}$ *versus* $\gamma[Cl^-]$ for the reaction $[Pt(bipy)(dmso)Cl]^+ + Cl^- \longrightarrow [Pt(bipy)Cl_2] + dmso$; $\gamma = \exp[-3.44\sqrt{I}/(1 + 1.48\sqrt{I})]$. (●) No $LiClO_4$ added, $I$ variable; (■) $I$ = 0.01 mol dm$^{-3}$ ($LiClO_4$)

necessary to be sure that the second-order chloride dependence is not simply due to the breaking down of the assumption that salt effects depend only upon ionic strength and are independent of the nature of the electrolyte. The reaction between $[Pt(bipy)Cl(dmso)]^+$ and $Cl^-$ has been studied at $I$ = 1.0, 0.1, and 0.01 mol dm$^{-3}$, with $LiClO_4$ being used to maintain constant ionic strength, and also at low $[Cl^-]$ in the absence of $LiClO_4$, the ionic strength changing with $[Cl^-]$, Table 2. At these low nucleophile concentrations the contribution from the $[Cl^-]^2$ pathway is negligible and the salt effects were treated in terms of a reaction between +1 and −1 reagents. Using the expression $\log k_2 = \log k_2{}^0 + 2z_Az_BA\sqrt{I}/(1 + B\sqrt{I})$, with $z_A = 1$, $z_B = -1$, $A = 1.72$, and $B = 1.48$ [estimated from the dielectric constant of methanol–water (95:5 v/v) at 25 °C],[13,14] the values of $k_{obs.}$ measured in the absence of $LiClO_4$ have been converted into those expected for $I$ = 0.01 mol dm$^{-3}$ and these values agree closely with those obtained when the ionic strength was held constant at 0.01 mol dm$^{-3}$ using $LiClO_4$. The plot of $k_{obs.}$ *versus* $\gamma[Cl^-]$, where $\gamma = \exp[-3.44\sqrt{I}/(1 + 1.48\sqrt{I})]$, is linear, Figure 2. It is clear, therefore, that in the region where the second-order chloride dependence does not make a significant contribution to $k_{obs.}$ the primary salt effect is the same whether or not $LiClO_4$ contributes to the ionic strength and is precisely that predicted by the Debye–Hückel theory.[14] The possibility



**Scheme.** $k_{obs.} = k_1 + k'_2K[Cl^-] + k'_3K[Cl^-]^2$, $k_2 = k'_2K$, and $k_3 = k'_3K$

that the second-order dependence upon $[Cl^-]$ is an artefact arising from the invalidity of the assumptions used in the above expression at the higher chloride concentrations used can be ruled out because it is not observed in the reactions of the similarly charged $[Pt(bipyoxo)(dmso)Cl]^+$ cation where the first-order dependence on $[Cl^-]$ is maintained up to 1.0 mol $dm^{-3}$.

We propose, therefore, that the rate law is genuine and that there is an equilibrium between the substrate and a species that is uncharged and contains two chlorides and one dmso (Scheme). This intermediate, always present in concentrations that are small compared to those of the substrate, has two reaction pathways available and either loses dmso dissociatively or else undergoes associative displacement of dmso by an extra chloride ion, the product immediately losing the third $Cl^-$ ligand to give the dichloro species.

The absence of the second-order $[Cl^-]$ dependence, and the much lower reactivity of the analogous bipyoxo complex, is consistent with the blocking of an axial site by the oxygen of the six-membered ring in the boat conformation and it is likely that the substitution is much more like a classical A process. Much of the reduction of the reactivity is due to the fact that the bidentate ligand is no longer an α-di-imine. Di-imines, such as bipyridyl and phenanthroline, exert a considerable labilising effect when compared to saturated nitrogen donors such as ethylenediamine, or even *cis* monodentate primary amines, so that the displacement of the neutral ligand from $[Pt(bipy)(L)Cl]^+$ or $[Pt(phen)(L)Cl]^+$ is generally much easier than from $[Pt(en)(L)Cl]^+$. Surprisingly, little has yet been done to obtain quantitative data for the displacement of neutral ligands to determine whether the position of sulphoxides in the order of leaving-group effects changes on changing the other ligands in the substrate.

The possibility that the intermediate species is still four-co-ordinate with the N–N ligand acting as monodentate has not been ignored. Although bipyridine can adopt the *trans* conformation and act unambiguously as monodentate, phenanthroline cannot and the 'free' nitrogen must remain close to an axial position. Such complexes are reasonably common and all are distorted square pyramids in the solid state with a long M–N axial interaction compared to the bond in the plane. Whether or not this can be looked upon as a bond has been discussed at length[15,16] but, in solution, site exchange between the axial and equatorial nitrogens is fast on the n.m.r. time-scale at 300 K. The fact that the bipyridyl and phenanthroline complexes have much the same ratio for $k_3/k_2$ and differ in reactivity by an amount that is found when there is no suggestion of ring opening leads us to disregard this possibility.

Some inconsistencies remain in the salt effects. Since the intermediate species is uncharged, the salt effect must be associated with its formation only [*i.e.* $\log K = \log K_o - 2\log f_\pm$, where $f_\pm$ is the mean ion activity coefficient for the species involved in the equilibrium $= -A\sqrt{I}/(1 + B\sqrt{I})$, with $A$ and $B$ taking the values appropriate to methanol–water (95:5 v/v) at 25.0 °C as used in Table 2]. The ratio $k_3/k_2$ should therefore be independent of ionic strength but, in the reactions of the bipyridine complex where the rate constants have been determined over a range of ionic strengths, it changes from $4.17 \pm 0.37$ at $I = 0.1$ to $0.87 \pm 0.05$ at $I = 1.0$ mol $dm^{-3}$. Since $k_2$ has been shown to follow the classic expression very well, it follows that the $k_3$ term is anomalous. It should be pointed out that the same will apply to any process in which the transition states have the same composition as those proposed above. It is interesting that, while the analogous second-order rate constant for the reaction between $[Pt(Me_2S)_4]^{2+}$ and $OH^-$ in water obeys the Debye–Hückel relationship for primary salt effects closely, the analogous third-order rate constant does not[11] and that, while such salt effect corrections work with singly charged reagents reacting with $[Pt(dien)(dmso)]^{2+}$ (dien = diethylenetriamine), the effect of ionic strength on $S_2O_3^{2-}$ is best explained if the latter functions as a uninegative anion.[17]

The unusual behaviour of dimethyl sulphoxide in terms of its low nucleophilicity, relatively high *trans* effect, and the mutual labilisation of a pair of sulphoxides have all been ascribed to the ability of S-bonded sulphoxides to act as π acceptors and stabilise the intermediates of higher co-ordination number. In this sense it resembles ethene but functions less effectively and it is of interest to examine analogous ethene compounds in order to see whether there is a similar pattern of behaviour. The $[Pt(bipy)(C_2H_4)Cl]^+$ cation is actually formed from the stable and isolable five-co-ordinated complex $[Pt(bipy)(C_2H_4)Cl_2]$ when the latter is dissolved in a polar solvent such as methanol.[18] In non-polar 1,2-dichloroethane, on the other hand, the complex loses ethene to give the non-electrolyte dichloro complex. When excess of chloride is added, ethene is displaced from the cationic complex in methanol at a rate that is first order in $[Cl^-]$ and no higher-order dependence is observed. The reaction is much slower than that observed for the analogous dimethyl sulphoxide complex (see Table 3) and it is not clear whether the reaction paths followed by the two complexes are totally different or whether the stability of the five-co-ordinate ethene-containing species is large enough for all of the substrate to be rapidly converted into it on the addition of excess of chloride. The subsequent reaction, involving attack by chloride, would then only have a first-order dependence on $[Cl^-]$. There is an indication in ref. 17 that the reaction in methanol is more complex than suggested and a revisitation is called for.

**Table 3.** Derived rate constants for the reaction $[Pt(N{-}N)(L)X]^+ + X^- \longrightarrow [Pt(N{-}N)X_2] + L$

| N–N | L | X | $10^5k_1/s^{-1}$ | $10^2k_2/$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $10^2k_3$/dm$^6$ mol$^{-2}$ s$^{-1}$ |
|---|---|---|---|---|---|
| bipy | dmso | Cl | 4.7 ± 0.2 | 53 ± 1[a] | |
| bipy | dmso | Cl | 4.7 ± 0.2 | 16.8 ± 0.3 | 70 ± 5[b] |
| bipy | dmso | Cl | 4.7 ± 0.2 | 4.82 ± 0.05 | 4.2 ± 0.2[c] |
| bipy | $Me_2S$ | Cl | | 0.3 | *d* |
| bipy | $C_2H_4$ | Cl | | 0.05 | *e* |
| phen | dmso | Cl | 1.42 ± 0.06 | 1.31 ± 0.03 | 1.8 ± 0.1[c] |
| bipy | dmso | Br | | 100 ± 3 | *c* |
| phen | dmso | Br | | 36.1 ± 0.2 | *c* |
| bipyoxo | dmso | Cl | 0.022 ± 0.047 | 0.0159 ± 0.0004 | *c* |

[a] This work. Methanol–water (95:5 v/v), $I = 0.01$ mol dm$^{-3}$. [b] This work. Methanol–water (95:5 v/v), $I = 0.10$ mol dm$^{-3}$. [c] This work. Methanol–water (95:5 v/v), $I = 1.0$ mol dm$^{-3}$. [d] L. Cattalini, G. Marangoni, S. Degetto, and M. Brunelli, *Inorg. Chem.*, 1971, **10**, 1545. In methanol. Derived from a plot of log $k_2$ *versus* $\Sigma\sigma^*$ (sum of Taft $\sigma^*$ constants). [e] In methanol–water (95:5 v/v). Extrapolated to $I = 0.10$ mol dm$^{-3}$ from data in ref. 18 measured at $I = 0.20$ mol dm$^{-3}$ using $\log k_o = \log k + 3.44\sqrt{I}/(1 + 1.48\sqrt{I})$.

## Acknowledgements

We thank the Italian Ministry of Education for financial support.

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*Received* 11*th April* 1989; *Paper* 9/01479I