Kinetics and Mechanism of the Reaction between Dimethyl Sulphoxide and Dichloro(pyridine-2-carboxylato)platinate(II) Anion and the *cis-trans* Isomerization of the Products. *X*-Ray Crystal Structure of *trans*-(O,S)-Chloro(dimethyl sulphoxide)(pyridine-2-carboxylato)platinum(II)†

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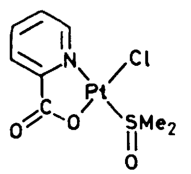
The reaction between $[Pt(pyca)Cl_2]^-$ (pyca = pyridine-2-carboxylate) and Me_2SO in methanol–water (95 : 5, v/v) at 40 °C gives a mixture of the two isomeric forms of $[Pt(pyca)(Me_2SO)Cl]$ which undergo a subsequent slow sulphoxide-catalysed isomerization to form an equilibrium mixture. The two isomers, *trans*-(N,S) and *trans*-(O,S) [(**1**) and (**2**) respectively], have been independently synthesized and the isomer (**2**) characterized by a single-crystal *X*-ray analysis. Crystals of (**2**) are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 9.748(4)$, $b = 13.870(6)$, $c = 8.154(4)$ Å and $\beta = 100.37(3)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.034$ for 1 700 observed reflections. The co-ordination of the platinum atom is square planar, by a chlorine atom, a sulphur atom from the Me_2SO, and by the nitrogen and one oxygen atom from pyridine-2-carboxylate acting as a chelating ligand. The kinetically controlled product ratio [**1**]/[**2**] = 3.8 relates to the greater *trans* effect of N and differs considerably from the thermodynamic ratio of 0.38. Chloride also catalyses the isomerization but eventually displaces the dimethyl sulphoxide. The relative reactivities show that the chloride-catalysed isomerization cannot proceed through a reversible replacement of Me_2SO by Cl^-.

As part of our studies of the ways in which nucleophilicity, substrate charge, and nucleophilic discrimination are interrelated in the substitution reactions of four-co-ordinate planar platinum(II) complexes,[1] we have been examining the kinetics of the displacement of chloride from the anionic substrate $[Pt(pyca)Cl_2]^-$ (pyca = pyridine-2-carboxylate). A study of the reactions with anionic reagents has been completed.[2] An extension of their study to neutral nucleophiles, designed to elucidate the effect of reagent charge on the reactivity patterns, led us to investigate the reaction with dimethyl sulphoxide. It has recently been shown in a very clear way[3] that Cl^- and Me_2SO catalyse the isomerization of complexes of the type $[Pt(N–O)(Me_2SO)Cl]$ where N–O is the anion of an α-amino acid, and it is of interest to compare the behaviour of aliphatic amines with that of a heterocyclic nitrogen base.

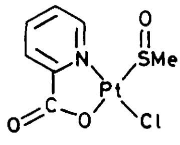
In this paper we report the kinetics of the reversible entry of Me_2SO into $[Pt(pyca)Cl_2]^-$ (**3**), the preparation of the two isomers (**1**) and (**2**), the structure of (**2**), and the reaction of (**1**) and (**2**) in the presence of Cl^-.

Experimental

Dipotassium tetrachloroplatinate(II) was obtained from Johnson Matthey and Co. Pyridine-2-carboxylic acid, dimethyl sulphoxide, the inorganic salts, and the solvents were reagent grade products.



(**1**) *trans*-(N,S)



(**2**) *trans*-(O,S)

Preparation of Complexes.—The salts $K[Pt(Me_2SO)Cl_3]$[4] and $K[Pt(pyca)Cl_2]$, (**3**),[2] were prepared according to published methods and characterized by elemental analysis and i.r. spectra.

trans-(*N,S*)-*Chloro(dimethyl sulphoxide)(pyridine-2-carboxylato)platinum*(II), (**1**). A neutralized solution of pyridine-2-carboxylic acid (0.3 g, 2.4 mmol) in water (2 cm^3) was added slowly, with stirring, to a solution of $K[Pt(Me_2SO)Cl_3]$ (1.00 g, 2.4 mmol) in water (20 cm^3). A yellow precipitate formed immediately and was filtered off, washed twice with water, ethanol, and diethyl ether, and dried *in vacuo*. Yield about 90%. I.r. absorptions in the 500—25 cm^{-1} range: 482s, 449s, 367s, and 330w cm^{-1} (Found: C, 22.1; H, 2.35; Cl, 8.25; N, 3.25. $C_8H_{10}ClNO_3PtS$ requires C, 22.3; H, 2.35; Cl, 8.25; N, 3.25%).

trans-(*O,S*)-*Chloro(dimethyl sulphoxide)(pyridine-2-carboxylato)platinum*(II), (**2**). This was prepared by a method analogous to that of Kong *et al.*[5] The *trans*-(N,S) isomer (0.5 g, 1.2 mmol) was dissolved in warm (70 °C) dimethyl sulphoxide (5 cm^3) and the solution left to cool slowly at room temperature. The pale yellow crystals formed were filtered off, washed with

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† *Supplementary data available* (No. SUP 56437, 12 pp.): H-atom co-ordinates, thermal parameters, non-bonded contacts, torsion angles, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

Table 1. Crystallographic data for complex (**2**)

Crystal system	Monoclinic
M	430.77
Space group	$P2_1/n$
a/Å	9.748(4)
b/Å	13.870(6)
c/Å	8.154(4)
β/°	100.37(3)
U/Å^3	1 084.5(8)
Z	4
D_c/g cm^{-3}	2.638
$F(000) = 800$	
Crystal dimensions/mm	0.19 × 0.26 × 0.38
μ/cm^{-1}	134.92
Diffractometer	Siemens AED
Scan	
type	θ—2θ
speed/° min^{-1}	3—12
width	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$*
Radiation	Nb-filtered Mo-K_α ($\lambda = 0.7107$ Å)
2θ Range/°	6—54
Reflections measured	$\pm h, k\ l$
Standard reflections	1 every 50
Total unique data	2 490
Observed data [$I > 2\sigma(I)$]	1 700
No. of variables	136

* $\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda]\tan\theta$.

dimethyl sulphoxide (1 cm^3), water, ethanol, and diethyl ether, and dried *in vacuo*. Yield 65%. More of the compound could be precipitated from the filtrate by adding water (20 cm^3). The total yield was nearly quantitative. Elemental analysis and i.r. spectra of the crystalline product and powder were identical (Found: C, 22.2; H, 2.30; Cl, 8.25; N, 3.20%). I.r. absorptions in the 500—250 cm^{-1} range: 480s, 451s, 385m, 335m, 330s, and 292 cm^{-1}.

Infrared spectra of Nujol mulls between KBr or polyethylene (below 500 cm^{-1}) plates were recorded with a Perkin-Elmer 683 spectrophotometer. Proton n.m.r. spectra of CD_3NO_2 solutions, using $SiMe_4$ as internal standard, were recorded with a Varian EM390 spectrometer. Electronic spectra were obtained with a Cary 219 spectrophotometer.

Kinetics.—The reactions examined were all slow enough to be followed spectrophotometrically by repeatedly scanning the spectrum over the range 250—400 nm at suitable times. Pseudo-first-order rate constants ($k_{obs.}$) were calculated, at a suitable wavelength, either from the slopes of the linear plots of $\ln(A_t - A_\infty)$ against time, where A_t and A_∞ 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 using $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$ with A_0, A_∞, and $k_{obs.}$ as the parameters to be optimized (A_0 being the absorbance immediately after mixing the reagents). The rate constants were independent of the method used for their calculation.

X-Ray Crystallography.—Crystals of complex (**2**), suitable for *X*-ray analysis, were obtained by slow cooling of a solution of (**1**) in warm dimethyl sulphoxide. An irregularly shaped pale yellow crystal was selected and mounted on the diffractometer. Crystal data and data-collection parameters are given in Table 1. Unit-cell parameters were obtained by least-squares refinement of the θ values of 29 carefully centred reflections (with θ in the range 10—15°), chosen from diverse regions of the reciprocal space.

Data were collected at room temperature, the individual reflection profiles having been analysed according to Lehmann and Larsen.[6] The structure amplitudes were obtained after usual Lorentz and polarization reduction. A correction for absorption effects was applied[7] using the program ASSORB[8] (maximum and minimum transmission factors 1.2047 and 0.7628 respectively). Only the observed reflections were used in the structure solution and refinement.

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c
Pt	1 570(1)	856(1)	1 215(1)
Cl	2 531(3)	445(2)	−1 051(3)
S	3 411(2)	320(2)	2 872(3)
N	395(7)	1 291(5)	2 900(8)
O(1)	3 341(7)	249(6)	4 639(8)
O(2)	−5(7)	1 496(6)	−332(8)
O(3)	−1 920(8)	2 315(6)	−430(10)
C(1)	4 015(13)	−813(8)	2 285(16)
C(2)	4 789(10)	1 098(8)	2 616(14)
C(3)	−929(11)	1 872(7)	381(12)
C(4)	−767(9)	1 753(7)	2 189(11)
C(5)	−1 718(11)	2 105(8)	3 078(14)
C(6)	−1 472(12)	1 952(8)	4 802(15)
C(7)	−313(10)	1 466(8)	5 508(12)
C(8)	617(10)	1 146(7)	4 542(13)

Structure solution and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least squares, first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. In the final Fourier difference map it was not possible to locate clearly the positions of all the hydrogen atoms, so they were placed at their geometrically calculated positions and included in the final structure-factor calculation with fixed isotropic thermal parameters ($B = 7.0$ Å^2). The function minimized during the refinement was $\Sigma w|\Delta F|^2$. The weighting scheme used in the last cycles was $w = K/[\sigma^2(F_o) + gF_o^2]$; at convergence the values of K and g were 0.7358 and 0.0043 respectively. The final R and R' values were 0.034 and 0.046 $\{R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. A final difference map was featureless. The scattering factors used were taken from ref. 9, with the exceptions of those for the hydrogen atoms which were taken from ref. 10. Corrections for the real and imaginary components of anomalous dispersion were made for Pt, Cl, and S atoms.[9] Calculations were carried out with the SHELX 76 system of programs[11] on a Cyber 7600 computer at the Centro di Calcolo dell' Italia Nord-Orientale, Bologna. Final atomic co-ordinates for the non-hydrogen atoms are listed in Table 2.

Results and Discussion

Preparation of Complexes.—The reaction of K[Pt(Me_2SO)Cl_3] with the pyridine-2-carboxylate anion in aqueous solution gives the yellow complex (**1**) which is transformed into the pale yellow isomer (**2**) in Me_2SO. Both isomers contain S-bonded Me_2SO [ν(S=O) 1 140 cm^{-1}] and a co-ordinated carboxylic group [ν(COO) 1 690 and 1 680 cm^{-1} for (**1**) and (**2**) respectively]. The ^1H n.m.r. spectra (90 MHz, solvent CD_3NO_2, standard $SiMe_4$) of their solutions show 1:4:1 triplets (central peak and ^{195}Pt satellites) due to co-ordinated Me_2SO at δ 3.46 [^3J(Pt–S–Me) = 20 Hz] and 3.63 p.p.m. [^3J(Pt–S–Me) = 24 Hz] for (**1**) and (**2**) respectively.

Although it is well established that amines (am) react with the [Pt(Me_2SO)Cl_3]$^-$ anion to give the *trans*-[Pt(Me_2SO)(am)Cl_2] isomer,[12] presumably due to the high *trans* effect of Me_2SO, and the reactions with amino acids (N–O) are predicted to give,

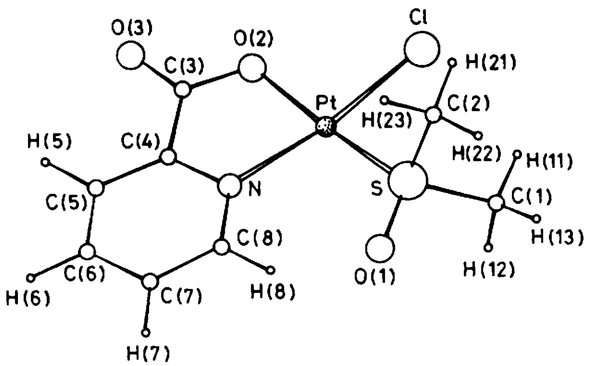


Figure. View of complex (2) with the atomic numbering system

preferentially, the *trans*-(N,S) isomer of [Pt(N-O)(Me_2SO)Cl] on the basis of the greater nucleophilicity of N than O, it was thought prudent to establish the configurations of the two isomers by single-crystal *X*-ray diffraction.

Description of the Structure of Complex (**2**).—The structure of isomer (**2**) is presented in the Figure together with the atomic numbering system. Bond distances and angles are given in Table 3. It is clearly the *trans*-(O,S) isomer and the Me_2SO molecule is bonded to the platinum atom through the sulphur atom. The co-ordination around the platinum atom is square planar, the deviations of the five atoms Pt, S, Cl, N, and O(2) from the mean plane passing through them being 0.007(1), −0.017(3), 0.006(3), 0.040(7), and −0.172(8) Å respectively. The chelating ligand has a narrow 'bite angle [80.6(3)°]. The Pt–Cl bond length [2.289(3) Å] is quite normal, but the Pt–S bond [2.174(2) Å] is the shortest reported for platinum complexes with R_2SO: 2.186(4) in *cis*-[Pt(Me_2SO)(NH_3)Cl_2],[13] 2.193(5) in K[Pt(Me_2SO)Cl_3],[14] 2.200(3) in *cis*-[Pt(Me_2SO)(2Me-py)Cl_2],[15] 2.212(3) in *trans*-[Pt(Me_2SO)(2Me-py)Cl_2][16] (2Me-py = 2-methylpyridine), 2.220(4) in *trans*-[Pt(Me_2SO)(cyd)Cl_2] (cyd = cytidine),[17] 2.225(2) in *trans*-[Pt(Me_2SO)(py)Cl_2],[18] 2.237(2) in *trans*-[Pt(Pr^i_2SO)(mcyt)Cl_2] (mcyt = 1-methylcytosine),[19] 2.229(2) and 2.244(2) Å in *cis*-[Pt(Me_2SO)$_2$$Cl_2$].[20] There does not seem to be any systematic effect here and the differences are not large enough to relate these numbers to the changing *trans* influence on the opposite donor. The distances and angles found in the Me_2SO ligand are in good agreement with those found in free Me_2SO[21,22] and in the platinum sulphoxide complexes cited above.

The Pt–N distance [2.032(7) Å] is slightly shorter than that [2.062(10) Å] reported for *cis*-[Pt(Me_2SO)(2Me-py)Cl_2];[15] in both complexes the nitrogen atom is *cis* to sulphur. Dimethyl sulphoxide does not seem to have a marked influence on *trans* Pt–N bond lengths as values of 2.034(13), 2.046(10), and 2.058(7) Å have been reported for *trans*-[Pt(Me_2SO)(cyd)Cl_2],[17] *trans*-[Pt(Me_2SO)(2Me-py)Cl_2],[16] and *trans*-[Pt(Pr^i_2SO)(mcyt)Cl_2],[19] respectively; in all these complexes the nitrogen atom is *trans* to sulphur.

The Pt–O distance [1.994(7) Å] has the expected value, although until now no structure of a platinum sulphoxide complex containing an oxygen atom co-ordinated to the metal had been reported.

The chelating ring is planar, the Pt, O(2), C(3), C(4), and N atoms deviating from the mean plane passing through them by −0.001(1), 0.024(8), −0.036(10), 0.007(10), and 0.006(7) Å respectively. This plane makes a dihedral angle of 6.1(2)° with the co-ordination plane. The pyridine ring is perfectly planar and practically lies in the same plane as the chelating ring [the dihedral angle being only 1.9(3)°]. It is noteworthy that all the atoms of the complex (except those of the methyl groups) are approximately coplanar. As the O(1) atom of Me_2SO is out of the pyridine plane by only 0.20 Å, a short C(8) • • • O(1) contact is present [2.920(12) Å]. Although the hydrogen atom H(8) is in its calculated position, the very short O(1)–H(8) distance (2.00 Å) and the C(8)–H(8)–O(1) angle (141°) suggest a weak interaction between the atom O(1) and the CH group of the pyridine.

Table 3. Bond distances (Å) and angles (°)

Pt–Cl	2.289(3)	C(3)–O(3)	1.232(12)
Pt–S	2.174(2)	C(3)–C(4)	1.464(13)
Pt–N	2.032(7)	C(4)–N	1.339(11)
Pt–O(2)	1.994(7)	C(4)–C(5)	1.366(15)
S–O(1)	1.458(7)	C(5)–C(6)	1.399(16)
S–C(1)	1.774(12)	C(6)–C(7)	1.352(15)
S–C(2)	1.765(11)	C(7)–C(8)	1.377(15)
C(3)–O(2)	1.285(13)	N–C(8)	1.333(12)

Cl–Pt–S	90.3(1)	O(2)–C(3)–C(4)	116.7(9)
S–Pt–N	100.6(2)	O(3)–C(3)–C(4)	121.9(9)
N–Pt–O(2)	80.6(3)	C(3)–C(4)–N	114.8(8)
Cl–Pt–O(2)	88.6(2)	C(3)–C(4)–C(5)	122.3(9)
Pt–S–O(1)	117.2(3)	N–C(4)–C(5)	122.9(9)
Pt–S–C(1)	114.3(4)	C(4)–C(5)–C(6)	118.0(10)
Pt–S–C(2)	106.2(4)	C(5)–C(6)–C(7)	118.8(11)
O(1)–S–C(1)	106.5(5)	C(6)–C(7)–C(8)	120.2(10)
O(1)–S–C(2)	109.3(5)	C(7)–C(8)–N	121.4(9)
C(1)–S–C(2)	102.3(5)	C(8)–N–C(4)	118.6(8)
C(3)–O(2)–Pt	115.0(6)	C(8)–N–Pt	128.7(6)
O(2)–C(3)–O(3)	121.3(9)	C(4)–N–Pt	112.7(5)

Kinetics.—(*a*) *The reaction of complex* (**3**) *with dimethyl sulphoxide*. When dimethyl sulphoxide is added to a dilute solution of K[Pt(pyca)Cl_2] in methanol–water (95:5, v/v) at 40 °C there is a single step reaction, characterized by isosbestic points at 283 and 259 nm, in which the dichloro complex is converted into a mixture of the two isomers (**1**) and (**2**) in the ratio [**1**]/[**2**] = 3.8 ± 0.2. This ratio is independent of the concentration of Me_2SO used. A second and much slower stage, which corresponds to the isomerization of the product to a mixture in which [**1**]/[**2**] = 0.39 does not interfere with the kinetics of the first stage and, apart from observing that the rate was dependent on [Me_2SO], it was not studied further.

The entry of Me_2SO, studied in the presence of a sufficient excess to ensure that the concentration remained constant during any reaction, was monitored by the change in absorbance at 326 nm and followed a first-order rate law. The rate constants $k_{obs.}$ reported in Table 4 obey the relationship $k_{obs.} = k_s + (k_{-2} + k_{-3})[Me_2SO]$ where $k_s = (3.4 \pm 0.5) \times 10^{-5}$ s^{-1} and $(k_{-2} + k_{-3}) = (1.12 \pm 0.02) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. The individual values of k_{-2} and k_{-3} can be evaluated using the composition of the kinetically controlled product (k_{-2}/k_{-3} = [**1**]/[**2**]) and are collected in Table 5.

(*b*) *Reactions of isomers* (**1**) *and* (**2**) *with chloride*. When a solution of complex (**1**) or (**2**) is treated with an excess of lithium chloride there are two separable spectrophotometric changes. The first leads to a spectrum that is identical to that of a mixture of (**1**) and (**2**) in the ratio [**1**]/[**2**] = 1/(2.6 ± 0.1) while the second, much slower step with isosbestic points at 308 and 260 nm leads to a final spectrum identical to that of an authentic sample of the dichloro complex. The kinetics of the first stage were followed at 308 nm where there is no interference from the second step and obey a first-order rate law. The rate constants $k'_{obs.}$ collected in Table 4 depend linearly on [Cl^-] with $k'_{obs.} = p[Cl^-]$, where $p = (1.10 \pm 0.07) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, the

Table 4. Pseudo-first-order rate constants for the reactions in methanol–water (95:5, v/v) at 40 °C, of complex (3) with Me_2SO ($k_{obs.}$) and of isomers (1) and (2) with chloride in the absence ($k'_{obs.}$ and $k''_{obs.}$) and presence ($k'_{obs.}$ and $k'''_{obs.}$) of dimethyl sulphoxide

$[Me_2SO]$	[LiCl]	$10^4k_{obs.}$	$10^4k'_{obs.}$	$10^5k''_{obs.}$	$10^5k'''_{obs.}$
mol dm^{-3}		s^{-1}			
0.032		0.68 ± 0.01			
0.052		0.86 ± 0.01			
0.075		1.22 ± 0.03			
0.101		1.54 ± 0.02			
0.205		2.62 ± 0.07			
0.302		3.68 ± 0.03			
0.400		4.92 ± 0.08			
	0.100		1.08 ± 0.01	*	
	0.276		3.02 ± 0.05	1.54 ± 0.02	
	0.410		4.53 ± 0.06	2.32 ± 0.03	
	0.553		5.7 ± 0.1	3.00 ± 0.02	
	0.820		9.63 ± 0.07	4.72 ± 0.07	
0.005	0.820		9.71 ± 0.08		5.10 ± 0.05
0.010	0.820		10.2 ± 0.3		5.77 ± 0.03
0.021	0.820		9.75 ± 0.1		6.85 ± 0.07
0.040	0.820		9.68 ± 0.08		9.1 ± 0.3
0.060	0.820		10.5 ± 0.3		11.4 ± 0.4
0.081	0.820		10.3 ± 0.1		13.7 ± 0.4
0.101	0.820		10.2 ± 0.4		15.4 ± 0.1
0.200	0.820		9.80 ± 0.08		25.3 ± 0.2
0.301	0.820		10.0 ± 0.4		35.0 ± 0.3

* Not determined.

intercept being smaller than the standard deviation. The second stage was followed at 326 nm once the two isosbestic points had developed and also obeyed a first-order rate law. The rate constants, $k''_{obs.}$ (collected in Table 4) are independent of the starting isomer and linearly dependent on $[Cl^-]$ with an intercept smaller than its standard deviation, *i.e.* $k_{obs.} = q[Cl^-]$, where $q = (5.7 \pm 0.3) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}.

(*c*) *Reactions of isomers* (**1**) *and* (**2**) *in the presence of chloride and dimethyl sulphoxide.* Whereas the reactions with chloride alone lead first to isomeric equilibration and then to loss of dimethyl sulphoxide, the presence of sufficient dimethyl sulphoxide ($[Me_2SO]/[Cl^-] \geqslant 3$) suppresses the loss of co-ordinated Me_2SO to the point where no complex (3) can be detected spectrophotometrically and only the isomerization is observed. At low enough Me_2SO concentrations the two stages of the reaction were again observed. The first (isomerization) process occurred at the same rate as that observed in the absence of Me_2SO, but the second process {conversion into the (3) + [Pt(pyca)(Me_2SO)Cl] equilibrium mixture} occurred at a rate that obeyed the equation $k'''_{obs.} = k_q[Cl^-] + k_r[Me_2SO]$. Since this made the rate constant for the second step approach the magnitude of that of the first, the separation of the two stages required more careful treatment. However, by working at the isosbestic point for the second step no difficulty arose in obtaining $k'_{obs.}$.

The kinetics of the reactions are fully consistent with the mechanism depicted in the Scheme. Analysis of the formation of [Pt(pyca)(Me_2SO)Cl] in the absence of added chloride gave k_{-2} and k_{-3} (Table 5) and suggests that the *trans* effects of the pyridine N and the carboxylate O are fairly similar (that of N being greater by a factor of 3.8).

Comparison with the values of Erickson *et al.*[3] for the corresponding complexes with glycinate (1.1), *N*-methylglycinate (1.2), *N,N*-dimethylglycinate (2.5), and prolinate (>95) shows that the relative *trans* effects of N + O are extremely dependent upon the nature of N. In fact, using their data for chloride exchange and dimethyl sulphoxide exchange it would appear that the *trans* effect of O can be up to three orders of magnitude greater than that of N in the glycinate complex. It would be of great interest to follow up and extend these studies to a much wider range of nucleophiles because a much greater sensitivity to minor variations is suggested than hitherto suspected. It therefore remains to be seen whether this phenomenon arises from the presence of dimethyl sulphoxide somewhere in the system.

Table 5. Second-order rate constants (dm^3 mol^{-1} s^{-1}) at 40 °C as defined in the Scheme

$k_1 = (8 \pm 1) \times 10^{-4}$

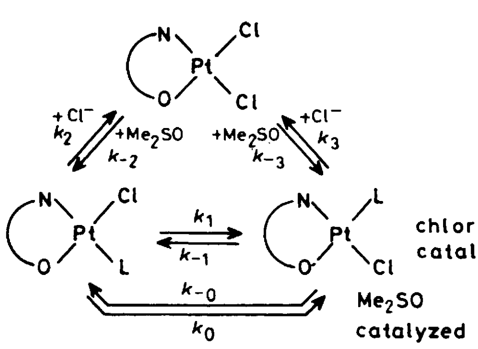
$k_{-1} = (3.1 \pm 0.4) \times 10^{-4}$

$k_2 = (1.7 \pm 0.3) \times 10^{-4}$

$k_{-2} = (9 \pm 1) \times 10^{-4}$

$k_3 = (1.7 \pm 0.3) \times 10^{-5}$

$k_{-3} = (2.4 \pm 0.3) \times 10^{-4}$



Scheme. N–O = pyca, L = Me_2SO

The rate constant for the reaction of substrate (3) with Me_2SO can be compared only indirectly with those with anionic reagents because the latter were carried out in aqueous solution at 25 °C. A proper analysis in terms of the alternative pathways was not possible, but the absence of disturbance in the second stage of the substitution suggested that either one pathway dominated or both produced species of identical reactivity. Taking $k_{-2} + k_{-3} = 1.15 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} as the total contribution of Me_2SO entry at 40 °C, this is still smaller than the rate constant for the weakest anionic nucleophile studied (NO_2^-, $k = 1.6 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}; at $I = 0$, 25 °C, in aqueous solution) in spite of the higher temperature. (The change in solvent may cause a small compensating change since reactions in methanol–water are somewhat slower than in methanol.) This can be compared to the reactivity with respect to dianionic species, *e.g.* $[PtCl_4]^{2-}$, where Me_2SO enters with a rate constant comparable to that for SCN^-, once corrections for ionic strength have been applied (3×10^{-3} and 10^{-3} dm^3 mol^{-1} s^{-1} respectively).[23]

The analysis of the reactions involving chloride is relatively simple. In the absence of the added Me_2SO it can be assumed to a first approximation that $k_{obs.} = (k_1 + k_{-1})[Cl^-]$ and $k_1/k_{-1} = K_e = [2]/[1]$ at the end of the first step, *i.e.* = 2.6 ± 0.1. The rate constants k_1 and k_{-1} can be therefore separated and are collected in Table 5. The second-stage displacement of Me_2SO from the complexes at their equilibrium concentrations would obey the equation $k''_{obs.} = (k_2 + K_ek_3)/(1 + k_e)[Cl^-]$. Using the requirement that in these cyclic processes $k_1/k_{-1} = (k_2/k_{-2})(k_{-3}/k_3)$, substitution of the values of k_1/k_{-1} and k_{-3}/k_{-2} obtained above gives the value of k_2/k_3 and allows the constants to be separated. The $[Me_2SO]$ dependence observed in the approach to the final equilibrium gives $k'''_{obs.} = [(k_2 + Kk_3)(1 + K)][Cl^-] + (k_{-2} + k_{-3})[Me_2SO]$. The slope of a plot of $k'''_{obs.}$ against $[Me_2SO]$ at constant $[Cl^-]$,

$(1.10 \pm 0.02) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} is in close agreement with the value of $(1.12 \pm 0.02) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} determined directly.

A final check was made by using the absorbance of a solution at the end of the reaction. At equilibrium, the concentrations of the three species are $[\mathbf{1}]_e$, $[\mathbf{2}]_e$ and $[\mathbf{3}]_e$ with the relationship $K_e = ([\mathbf{1}]_e + [\mathbf{2}]_e)[\mathrm{Cl}^-]/[\mathbf{3}]_e[\mathrm{Me_2SO}]$ so that $(A_0 - A_x)[\mathrm{Cl}^-]/(A_x - A_\infty)[\mathrm{Me_2SO}] = K_e$, where A_0 and A_∞ are the absorbances of a solution of complex (**3**) and of the equilibrium mixture of (**1**) + (**2**), and A_x is the absorbance of the finally equilibrated mixture of (**1**) + (**2**) + (**3**) at a constant concentration of complex. Consequently a plot of $(A_0 - A_x)/(A_x - A_\infty)$ against $[\mathrm{Me_2SO}]/[\mathrm{Cl}^-]$ should give a straight line of slope $K_e = k_2(1 + K)/k_{-2}$. The plot is linear with slope 21 ± 2 compared with 20 ± 1 from the data collected in Table 5. Examination of the derived rate constants in Table 5 shows that the assumption that we could treat the chloride-catalysed isomerization and subsequent displacement of $\mathrm{Me_2SO}$ as two successive processes is justified.

The comparison shows that the behaviour of the pyridine-2-carboxylato complexes is similar in many respects to that of the analogous *N*,*N*-dimethylglycine complexes of Erickson *et al.*[3] bearing in mind the different solvent and 5 K difference in temperature. The chloride-catalysed isomerization that does not require passage through the dichloro species is confirmed; the *trans*-(O,S) complex would require a considerable induction period if this were not so.

Although the exchange of chloride in $[\mathrm{Pt(pyca)(Me_2SO)Cl}]$ with radio labelled chloride was not studied as it was in the case of the aliphatic amino acids, it is certainly fast compared with the isomerization since the reactions $[\mathrm{Pt(pyca)(Me_2SO)Cl}] + \mathrm{X}^- \longrightarrow [\mathrm{Pt(pyca)(Me_2SO)X}] + \mathrm{Cl}^-$ are fast and take place without isomerization. Processes involving classical substitution pathways, *i.e.* those in which the ligands *cis* to the leaving group remain in the axial positions in the trigonal-bipyramidal transition state (intermediate) and in which the chelate ring is temporarily open, will not lead to isomerization and, as suggested by Erickson, a rearrangement of some five-co-ordinated species is required in order to exchange axial and equatorial sites before it dissociates. It is still not clear just what is the involvement of the sulphoxide in this process, although it has been suggested that $\mathrm{Me_2SO}$, like $\mathrm{C_2H_4}$, has the ability to increase the stability of the five-co-ordinated system.[24]

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