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Synthesis and Characterization of Anionic Platinum(II) Complexes Containing the Tridentate Ligand Pyridine-2,6-dicarboxylato (O-N-O) and the Kinetics of Chloride Displacement from $[Pt(O\text{-}N\text{-}O)Cl]^-$

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Complexes of the type $K[Pt(O\text{-}N\text{-}O)X]$ (O-N-O = pyridine-2,6-dicarboxylato; X = Cl, Br, I, NO_2, SCN) have been prepared and characterized. The rate constants for the displacement of the coordinated chloride from the anionic substrate $[Pt(O\text{-}N\text{-}O)Cl]^-$ by H_2O, OH^-, Br^-, I^-, SCN^-, $SeCN^-$, CN^-, and SO_3^{2-} in water at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)] have been determined, and the deviations from a linear plot of log $k°_2$ vs $n°_{Pt}$ of points relating to neutral and dianionic nucleophiles are discussed in terms of the effect of the charge of the substrate.

Since the introduction of the $n°_{Pt}$ nucleophilicity scale for substitution reactions at platinum(II) complexes, based upon the rate of the replacement of chloride in the neutral standard substrate *trans*-$[Pt(py)_2Cl_2]$,[1] deviations from the expected reactivity patterns have been observed in several cases, due either to steric hindrance,[2] biphilicity of some ligand,[3] or charge effects[4] or to a combination of these factors.

As far as cationic platinum(II) complexes are concerned, the main deviations seem to be that the biphilic nucleophiles, i.e. thiourea and $SeCN^-$, are less reactive than predicted from their $n°_{Pt}$ values, while the same nucleophiles can be more reactive than predicted toward dianionic substrates.[3] This behavior is attributed to the effect of charge on the π-basicity of platinum and the extent of back-donation to these nucleophiles in the transition state.

Kinetic data for substitution reactions at monoanionic platinum(II) substrates have become available recently, mainly from the study of dichloro(pyridine-2-carboxylato)platinate(II), where minor deviations from the $n°_{Pt}$ scale were observed,[5] and of a number of anionic substrates of the type $[PtLCl_3]^-$, characterized by the presence of a ligand (L = Me_2SO, Me_2S, Et_2S, PR_3, $P(OMe)_3$, $AsEt_3$) of high trans effect.[6] In this case a charge effect was clearly observed, since anionic and neutral nucleophiles behave differently, the latter being more reactive than expected from their $n°_{Pt}$ values as compared to the former.

In this paper, we report the preparation and characterization of complexes of the type $[Pt(O\text{-}N\text{-}O)X]^-$ (O-N-O = pyridine-2,6-dicarboxylato; X = Cl, Br, I, NO_2, SCN) and the kinetics of the reactions

$$[Pt(O\text{-}N\text{-}O)Cl]^- + Y^{n-} = [Pt(O\text{-}N\text{-}O)Y]^{n-} + Cl^-$$

(Y^{n-} = H_2O, OH^-, NO_2^-, Br^-, I^-, SCN^-, $SeCN^-$, CN^-, SO_3^{2-}) in water at 25 °C and at constant ionic strength (I = 0.5 mol dm^{-3}).

Experimental Section

Potassium Chloro(pyridine-2,6-dicarboxylato)platinate(II) Hydrate. A solution of K_2PtCl_4 (0.415 g, 1 mmol) in water (15 cm^3) was slowly added, with stirring, to a solution of pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) in water (30 cm^3), brought to pH 6 with KOH. The mixture was allowed to react at 80 °C for 1 h, during which time the color of the solution gradually changed from reddish to yellow, and was then cooled in an ice bath. The red product, which precipitated within a few minutes, was filtered off, washed with cold water (2 cm^3), and dried under vacuum: yield 0.315 g (70%); mp >220 °C. Anal. Calcd for $C_7H_5ClKNO_5Pt$: C, 18.6; H, 1.11; Cl, 7.83; N, 3.09. Found: C, 18.7; H, 0.8; Cl, 7.88; N, 2.99. Characteristic infrared bands (KBr and polyethylene pellets): 1670 sb [ν(−COO)], 334 m cm^{-1} [ν(Pt−Cl)].

Potassium Bromo(pyridine-2,6-dicarboxylato)platinate(II). A solution of KBr (0.119 g, 1 mmol) in water (2 cm^3) was dropped, with stirring, into a warm solution (70 °C) of $K[Pt(O\text{-}N\text{-}O)Cl]\cdot H_2O$ (0.113 g, 0.25 mmol) in water (3 cm^3) and the mixture left to react for $^1/_2$ h. The resulting deep yellow solution was then cooled and the light yellow product that precipitated was filtered off, washed with cold water (1 cm^3), and dried under vacuum: yield 0.1 g (83%); mp >220 °C. Anal. Calcd for $C_7H_3BrKNO_4Pt$: C, 17.5; H, 0.60; Br 16.7; N, 2.92. Found: C, 17.5; H, 0.59; Br, 16.4; N, 2.76. Characteristic infrared bands: 1670 sb [ν(−COO)], 246 m cm^{-1} [ν(Pt−Br)].

Potassium Iodo(pyridine-2,6-dicarboxylato)platinate(II). A solution of KI (0.091 g, 0.55 mmol) in water (1 cm^3) was slowly added with stirring to a solution of $K[Pt(O\text{-}N\text{-}O)Cl]\cdot H_2O$ (0.226 g, 0.5 mmol) in water (3 cm^3), and the resulting mixture was left to react at 70 °C for 15 min. The color of the solution changed from yellow to orange. Then 20 cm^3 of ethanol were added and the solution cooled in an ice bath. A white microcrystalline precipitate (KCl) formed rapidly and was filtered off, and the clear solution was left to crystallize overnight at 0 °C. Orange needle crystals were obtained and were filtered off and dried under vacuum: yield 0.08 g (30%), mp 180 °C dec. Anal. Calcd for $C_7H_3IKO_4Pt$: C, 16.0; H, 0.57; N, 2.66. Found: C, 15.7; H, 0.70; N, 2.52. Characteristic infrared bands: 1670 sb [ν(−COO)], 172 mb cm^{-1} [ν(Pt−I)].

Potassium Nitro(pyridine-2,6-dicarboxylato)platinate(II) Dihydrate. A solution of KNO_2 (0.021 g, 0.25 mmol) in water (1 cm^3) was slowly added, with stirring, to a warm solution (70 °C) of $K[Pt(O\text{-}N\text{-}O)Cl]\cdot H_2O$ (0.113 g, 0.25 mmol) in water (3 cm^3). Within 15 min the color of the resulting solution changed from yellow to very pale yellow. After 1 h at 70 °C, solid $AgNO_3$ (0.042 g, 0.25 mmol) was added, and the mixture was left to react for 30 min, during which time a whitish precipitate of AgCl formed. This was filtered off and the solution slowly cooled to room temperature, and the dark red needles formed were filtered off and dried under vacuum: yield 0.11 g, (90%); mp >300 °C. Anal. Calcd for $C_7H_7KN_2O_8Pt$: C, 17.5; H, 1.46; N, 5.82. Found: C, 17.5; H, 1.16; N, 5.74. Characteristic infrared bands: 3550 and 3420 sb [ν(−OH)], 1670 sb [ν(−COO)], 1390 sb [$\nu_{as}(NO_2)$], 1338 m [$\nu_{sym}(NO_2)$], 362 m cm^{-1} [ν(Pt−NO_2)].[7]

Potassium (Thiocyanato)(pyridine-2,6-dicarboxylato)platinate(II). A solution of KSCN (0.025 g, 0.25 mmol) in dimethylformamide (2 cm^3) was slowly added, with stirring, to a solution of $K[Pt(O\text{-}N\text{-}O)Cl]\cdot H_2O$ (0.113 g, 0.25 mmol) in the same solvent (3 cm^3), and the resulting mixture was left to react at 70 °C. After 10 min, solid $AgNO_3$ (0.042 g, 0.25 mmol) was added, and the mixture was left to react for 30 min during which time a whitish precipitate of AgCl formed. This was filtered off, and to the resulting clear orange solution was added diethyl ether (30 cm^3). The orange precipitate that formed was filtered off and

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Table I. Experimental First-Order Rate Constants, k_{obs}, for the Reaction of Chloride Ion with an Aged 10^4 mol dm^{-3} Solution of $[Pt(O\text{–}N\text{–}O)Cl]^-$ in Water at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)]

$10^4[Cl^-]$, mol dm^{-3}	10^3k_{obs}, s^{-1}	$10^4[Cl^-]$, mol dm^{-3}	10^3k_{obs}, s^{-1}
8.14	6.7 ± 0.1	48.8	31.7 ± 0.3
16.3	11.8 ± 0.2	65.1	44.7 ± 0.6
32.6	22.5 ± 0.5	81.4	56 ± 2

dried under vacuum: yield 0.07 g (60%); mp >220 °C. Anal. Calcd for $C_8H_3KN_2O_4SPt$: C, 21.0; H, 0.66; N, 6.12. Found: C, 20.4; H, 0.85; N, 6.24. Characteristic infrared bands: 3500 sb [ν(–OH)], 2100 m [ν(CN)], 1670 sb cm^{-1} [ν(–COO)].

All the chemicals used were reagent grade products (Hoechst and Aldrich). K_2PtCl_4 was prepared from platinum metal as reported in the literature.[8] The microanalyses were performed by the Microanalytical Laboratory of the University of Padua.

Kinetics. The reactions were started by adding a small volume of a concentrated fresh solution of the substrate to a solution of the appropriate nucleophile previously brought to the reaction temperature (25 °C) in the thermostated cell of a Perkin-Elmer Lambda-5 spectrophotometer. The concentration of the entering group was always large enough to provide pseudo-first-order conditions. All the reactions were studied at constant ionic strength I = 0.5 mol dm^{-3} ($LiClO_4$). The kinetics were studied by periodically scanning the spectrum of the reaction mixture in the range 260–360 nm and/or measuring the changing absorbance at a fixed wavelength, as a function of time. The values of k_{obs} were obtained from a nonlinear regression of the function $D_t = D_\infty + (D_0 - D_\infty)\exp(-k_{obs}t)$ (where D_0, D_t, and D_∞, are the absorbances at time zero, time t, and time after 10 half-lives respectively) by using the Gauss-Newton algorithm.

Results

Reaction of [Pt(O-N-O)Cl]$^-$ with Water. When the chloro complex is dissolved in water in the spectrophotometric cell, a relatively small and slow spectral change is observed. The absorbance variation at any wavelength depends upon the presence of added chloride, becoming smaller on increasing chloride concentration and reducing to zero for $[Cl^-] > 5 \times 10^{-3}$ mol dm^{-3}. Experiments have been carried out by adding various amounts of chloride ion to an aged solution of the $[Pt(O\text{-}N\text{-}O)Cl]^-$ substrate; the spectrum of the reaction mixture evolves with time in a first-order fashion, finally becoming in any single case identical with that of the original chloro complex. The observed rate constants are summarized in Table I.

Reaction of [Pt(O-N-O)Cl]$^-$ with Hydroxide. A slow reaction takes place when the chloro complex K[Pt(O-N-O)Cl] is dissolved in water in the presence of hydroxide ion. The absorbance of the reaction mixture at any wavelength changes in a first-order fashion with time, and the final absorbance at all wavelengths studied is that of a solution of the same substrate after treatment with $AgNO_3$, separation of AgCl, and addition of NaOH. Acidification of the reaction mixture at the end of the process gives rise to the same spectrum observed for aged neutral or acidic solutions of K[Pt(O-N-O)Cl]. The values of the first-order rate constants, k_{obs}, are summarized in Table II.

Reaction of [Pt(O-N-O)Cl]$^-$ with Sulfite. The reaction, followed in the range 260–360 nm, proceeds in two detectable stages, the second of which shows a well-defined isosbestic point at 282 nm. The first step was conveniently studied at this wavelength, and the first-order rate constants, k_{obs}, are reported in Table II.

Reaction of [Pt(O-N-O)Cl]$^-$ with Bromide or Iodide. When the chloro complex is allowed to react with bromide or iodide ion in water, the spectral changes of the mixtures in the range 260–380 nm clearly show that only one process is taking place since isosbestic points develop at 280 and 301 nm, respectively, for the bromide and iodide substrate. The kinetics were measured by repetitive scanning of the whole spectrum, and the pseudo-first order rate constants were calculated at 340 and 352 nm, respectively, where the absorbance changes are at a maximum (Table II). The final spectra correspond exactly to those of independently prepared and characterized samples of the bromo and the iodo species, respectively, at the same concentrations.

Table II. Experimental First-Order Rate Constants, k_{obs}, for the Substitution Reactions at the Substrate $[Pt(O\text{–}N\text{–}O)Cl]^-$ with Nucleophiles in Water at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)]

nucleophile	$10^3[Y^{n-}]$, mol dm^{-3}	10^3k_{obs}, s^{-1}	nucleophile	$10^3[Y^{n-}]$, mol dm^{-3}	10^3k_{obs}, s^{-1}
OH^-	1	4.2 ± 0.2	SCN^-	1.04	5.6 ± 0.3
	2	4.50 ± 0.03		1.56	7.8 ± 0.4
	10	4.1 ± 0.1		2.08	10.1 ± 0.2
	20	4.9 ± 0.2		2.6	13.0 ± 0.1
NO_2^-	10	3.90 ± 0.1		2.97	14.5 ± 0.3
	25	4.09 ± 0.05		4.16	20.5 ± 0.4
	50	4.75 ± 0.08	$SeCN^-$	0.2	14.2 ± 0.7
	75	5.50 ± 0.07		0.4	24.3 ± 0.4
	100	5.95 ± 0.2		0.6	34.0 ± 1.2
	125	6.77 ± 0.15		0.8	42.7 ± 1.2
Br^-	49.2	6.79 ± 0.01		1.0	54.7 ± 0.9
	98.3	9.8 ± 0.1		12	64.1 ± 7.6
	147.5	12.8 ± 0.4	CN^-	0.1	34.5 ± 2
	196.7	15.1 ± 0.4		0.15	41.5 ± 1
	245.9	19.75 ± 0.5		0.2	54 ± 1
	295.1	21.5 ± 0.3		0.25	68 ± 2
I^-	1	4.35 ± 0.08		0.3	82 ± 3
	2	6.2 ± 0.1		0.35	89 ± 2
	3	8.1 ± 0.3	SO_3^{2-}	1	2.8 ± 0.2
	4	9.55 ± 0.2		1.5	3.2 ± 0.1
	5	11.2 ± 0.2		2.5	4.1 ± 0.1
	6	13.2 ± 0.2		3.5	4.9 ± 0.4
				5.0	6.05 ± 0.08

Table III. Experimental First-Order Rate Constants, k_{obs}, for the Substitution Reactions at the Substrate $[Pt(O\text{–}N\text{–}O)Cl]^-$ (10^{-4} mol dm^{-3}) with Nitrite Ion, in the Presence of Chloride, in Water at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)]

$10^3[NO_2^-]$, mol dm^{-3}	$10^3[Cl^-]$, mol dm^{-3}	10^5k_{obs}, s^{-1}	$10^3[NO_2^-]$, mol dm^{-3}	$10^3[Cl^-]$, mol dm^{-3}	10^5k_{obs}, s^{-1}
2.5	20	27.6 ± 0.2	2.5	40	16.9 ± 0.3
2.5	25	22.3 ± 0.3	2.5	60	12.85 ± 0.02
2.5	30	19.9 ± 0.1	2.5	160	8.75 ± 0.12

Reaction of [Pt(O-N-O)Cl]$^-$ with Thiocyanate. Examination of the changing spectrum of a mixture of the chloro substrate and thiocyanate ion in water, in the range 260–360 nm, shows that two consecutive stages take place, the first of which is characterized by an isosbestic point at 309 nm. Since this first stage is much faster than the second and is associated with a much greater absorbance change, the latter does not interfere in the calculation of the pseudo-first-order rate constants of the former, which were determined at 336 nm, during the time in which the isosbestic point is maintained (Table II). The spectrum of the mixture at the end of the first stage is quite similar to that of a sample of the thiocyanate complex prepared independently.

Reaction of [Pt(O-N-O)Cl]$^-$ with Selenocyanate or Cyanide. When selenocyanate or cyanide ions are added to diluted solutions ($<10^{-4}$ mol dm^{-3}) of K[Pt(O-N-O)Cl] in water, rapid reactions occur that develop in a single stage, characterized by an isosbestic point at 305 or 282 nm, respectively. The kinetics were followed by measuring the absorbance changes with time at fixed wavelengths, 340 or 330 nm, respectively. The pseudo first order rate constants are summarized in Table II.

Reaction of [Pt(O-N-O)Cl]$^-$ with Nitrite. The reaction, followed in the range 260–360 nm, proceeds in three detectable stages, the third of which does not interfere with the other two as it is much slower and displays a very small spectral change. The second stage has been followed separately on measuring the kinetics of the entering of the nitrite ion on the nitro species $[Pt(O\text{-}N\text{-}O)NO_2]^-$, independently prepared. It shows a strong dependence of the first-order rate constant k_{obs} from the concentration of nitrite ion, and a well-defined isosbestic point is developed at 274 nm. Thus the first step was studied at this wavelength. For a very low concentration of entering nitrito ion under pseudo-first-order conditions, the spectrum at the end of the first stage corresponds exactly to that of $[Pt(O\text{-}N\text{-}O)NO_2]^-$.

Experiments have been also carried out in the presence of chloride ion, which clearly affects the rates of substitution in this case (Table III).

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Table IV. First- and Second-Order Rate Constants for the Reactions of the Nucleophiles Displacing Chloride from the Substrate $[Pt(O-N-O)Cl]^-$ in Water at 25 °C [I = 0.5 mol dm^{-3} ($LiClO_4$)]

nucleophile	k_1, s^{-1}	$n°_{Pt}$	k_2, mol^{-1} dm^3 s^{-1}	$k°_2$, mol^{-1} dm^3 s^{-1}
NO_2^-	$(3.53 \pm 0.08) \times 10^{-3}$	3.22	0.025 ± 0.001	0.0096
Br^-	$(3.6 \pm 0.4) \times 10^{-3}$	4.18	0.0625 ± 0.002	0.024
SO_3^{2-}	$(2.00 \pm 0.03) \times 10^{-3}$	5.79	0.81 ± 0.01	0.116
I^-	$(2.6 \pm 0.1) \times 10^{-3}$	5.46	1.74 ± 0.02	0.67
SCN^-	$(4 \pm 2) \times 10^{-4}$	5.75	4.81 ± 0.09	1.82
$SeCN^-$	$(4 \pm 0.7) \times 10^{-3}$	7.11	49.9 ± 0.9	18.9
CN^-	$(9 \pm 4) \times 10^{-3}$	7.14	230 ± 10	86

Discussion

The process that takes place when the chloro substrate is allowed to react in water in the absence of chloride ion is indicative of an aquation equilibrium of the type

$$[Pt(O-N-O)Cl]^- + H_2O \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} [Pt(O-N-O)(H_2O)] + Cl^-$$

The presence in neutral solution of significant amounts of the conjugate base $[Pt(O-N-O)OH]^-$ can be reasonably ruled out by the fact that the observations are fully reproducible also in acid solutions, with $[H^+]$ up to 10^{-3} mol dm^{-3}. We avoided a further increase in acidity in order to prevent the possible opening of the carboxylato chelating groups, but they seem to be very inert, at least under the present experimental conditions.

The solvolytic rate constant, k_1, can be better estimated from the experiments carried out in basic solutions, when the chloro substrate is allowed to undergo solvolysis in the presence of hydroxide ion. In this case (Table II) the observed rate constant is independent of the hydroxide concentration, as expected for substitutions at square-planar substrates, hydroxide being unable to compete with water.[9] The mean value (4.4×10^{-3} s^{-1}) is in agreement with those obtained, with less accuracy, as intercepts in the plots of k_{obs} vs $[Y^{n-}]$ for the reactions of the other nucleophiles (Table IV). The rate constant for the reverse reaction, k_{-1}, i.e. the displacement by chloride of the water molecule coordinated in $[Pt(O-N-O)H_2O]$, has been measured by reacting an aged solution of the chloro substrate with different amounts of chloride ion and monitoring the changing absorbance at different times. The rate of the reaction increases linearly with chloride concentration (Table I), and as expected, there is not any significant intercept in the plot of k_{obs} vs $[Cl^-]$. The value of k_{-1} is 6.6 ± 0.2 s^{-1} mol^{-1} dm^3.

The equilibrium constant for the aquation can be calculated from the ratio of the values of the forward and reverse rate constants, $K = k_1/k_{-1} = 6.7 \times 10^{-4}$ mol^{-1} dm^3.

The reactions of the various nucleophiles (Table II) obey the two-term rate law $k_{obs} = k_1 + k_2[Y^{n-}]$, which is usual for nucleophilic substitution at platinum(II) complexes. The k_1 term refers to the solvolytic pathway, involving the entry of water as nucleophiles,[9] and k_2 is the second-order rate constant for the direct attack by the nucleophile on the substrate. The values of k_1 and k_2 are summarized in Table IV, where we also report the values of $k°_2$, i.e. the second-order specific rate constants calculated at $I = 0$, with the usual expression $\log k° = \log k - 2\alpha z_A z_B (I)^{1/2}(1 + I^{1/2})$, ($\alpha = 0.51$), in order to facilitate any later comparison with reactions with nucleophiles or substrates of other charges.

The second-order rate constants (Table IV) show an order of nucleophilicity $NO_2^- < Br^- < I^- < SCN^- < SeCN^- < CN^-$, which is qualitatively the same as that found for neutral platinum(II) complexes[10] and also for the anionic substrate $[Pt(N-O)Cl_2]^-$ (N-O = pyridine-2-carboxylato).[5] In Figure 1 the values of $\log k°_2$ are plotted against the corresponding $n°_{Pt}$ values.

Since it is already known that neutral and anionic nucleophiles can respond differently to the charge of the substrate and that SCN^-, $SeCN^-$, NO_2^-, and CN^- can behave as biphilic reagents,[11] the best way to draw a linear plot that allows one to evaluate the ability of this substrate to discriminate between the entering nucleophiles is probably to take into account the purely monoanionic σ donors Br^- and I^- only, for which deviations from the $n°_{Pt}$ relationship, due to the charge of the substrate, have never been observed. If the second-order rate constants $k°_2$ for the entry of Br^- and I^- (Table IV) are compared with the corresponding $n°_{Pt}$ values, the increase of the reaction rate from 0.024 to 0.67 mol^{-1} dm^3 s^{-1} corresponds to a nucleophile discrimination factor $[\log (k°_2(I^-)/k°_2(Br^-))]/[n°_{Pt}(I^-) - n°_{Pt}(Br^-)] = 1.129 \pm 0.005$, larger than that (1.000) of the standard substrate *trans*-$[Pt(py)_2Cl_2]$. No significant deviations are observed, within the limit of experimental errors, for the nucleophiles SCN^-, $SeCN^-$, and CN^-, while NO_2^- presents a positive deviation.

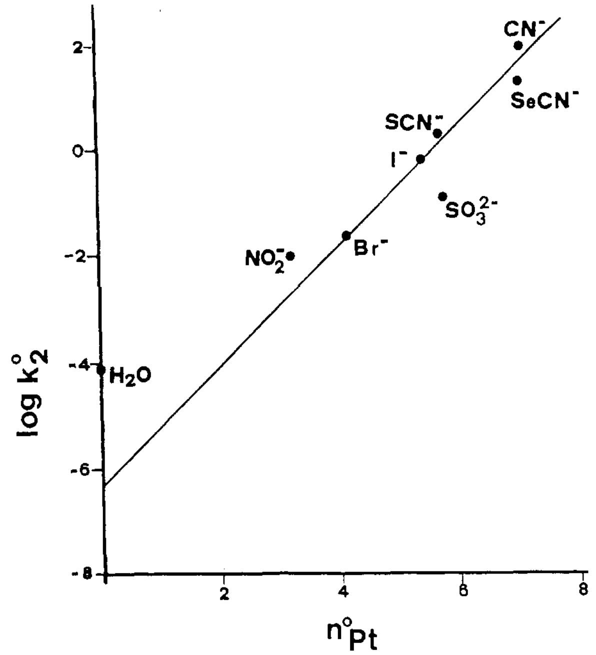

Figure 1. log $k°_2$ for the reactions of $[Pt(O-N-O)Cl]^-$ plotted against the $n°_{Pt}$ values of the entering nucleophiles.

Water, being a neutral nucleophile, is more reactive than expected from the comparison with neutral substrates. Unfortunately no other neutral reagents have been studied, due to the formation of precipitates. Probably for the same reason, i.e. charge effect, the dianionic nucleophile SO_3^{2-}, is less reactive than expected on the $n°_{Pt}$ scale, appearing less reactive than thiocyanate and iodide anions. However, it is to be pointed out that the extrapolation at $I = 0$ for SO_3^{2-}, according to the expression reported above, has been a matter of discussion regarding substitution reactions at Pt(II) substrates.[12]

The ability of the substrate to discriminate among the various nucleophiles usually decreases on going from neutral to anionic complexes. The nucleophilic discrimination factor for $[PtCl_4]^{2-}$ has been reported to be 0.31,[13] and in our previous work with the substrate $[Pt(N-O)Cl_2]^-$, it was evaluated to be in the region 0.4–0.5.[5] The relative increase of discrimination on going from the $[Pt(N-O)Cl_2]^-$ to the $[Pt(O-N-O)Cl]^-$ substrate (1.12) could be due to the fact that chloride ion is a better donor than oxygen toward platinum(II), and there is more negative charge localized at the reaction center in the first than in the second case. In other words, the Pt–O bond is relatively more ionic than the Pt–Cl bond.

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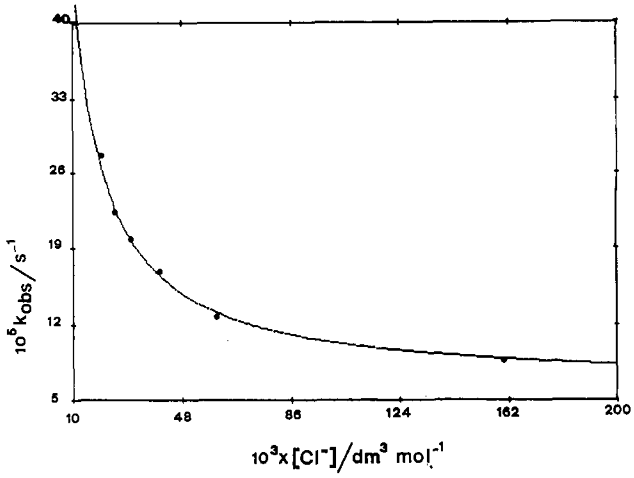
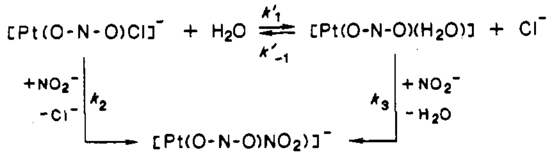


Figure 2. Theoretical and experimentally observed dependence of k_{obs} from $[Cl]^-$ for the reaction $[Pt(O\text{-}N\text{-}O)Cl]^- + NO_2^- \rightleftharpoons [Pt(O\text{-}N\text{-}O)NO_2]^- + Cl^-$ in the presence of added chloride in the range $0.22 < [Cl^-] < 0.16$ mol dm^{-3}.

The data reported in Table II show that in the absence of added chloride the rate of substitution of chloride increases linearly with nitrite ion concentration. However both nitrite ion and chloride are poor nucleophiles toward platinum(II) complexes ($n^\circ_{Pt} = 3.04$ and 3.22, respectively)[14] and the entry of NO_2^- can be influenced by the presence of Cl^- in the reaction mixture. Experiments carried out in the presence of excess chloride are reported in Table III, and the data can be treated in terms of competition for the solvato intermediate, according to the scheme



By application of the stationary-state treatment to the concentration of the aquo intermediate complex, the following expression can be calculated:

$$k'_{obs} = \frac{k'_1 k'_3[NO_2^-]}{k'_{-1}[Cl^-] + k'_3[NO_2^-]} + k'_2[NO_2^-] \qquad (1)$$

From the independently determined values of k_2 [$(2.5 \pm 0.1) \times 10^{-2}$, the second-order rate constant for the entry of NO_2^- in the absence of added chloride], k_1, k_{-1}, and experimental k_{obs}, as well as the known $[NO_2^-]$ and $[Cl^-]$, a k_3 value of 2.53 $mol^{-1}\ dm^3\ s^{-1}$ can be evaluated, which is the rate of entry of nitrite ion on the aquo intermediate complex. The agreement between the theoretical curve k_{obs} vs $[Cl^-]$, calculated according to eq 1 by a nonlinear best fitting of the function using a modified Marquardt algorithm, and experimental k_{obs} values is shown in Figure 2.

A comparison of the second-order rate constants for the substitution of water in the neutral aquo complex by Cl^- (6.6) and NO_2^- (2.53) is then possible. The difference of nucleophilicity is not large, the nitrite appearing less nucleophile than chloride by a factor of about 2. In the case of the anionic chloro complex $[Pt(O\text{-}N\text{-}O)Cl]^-$, the rate of chloride exchange can be calculated from the nucleophilic discrimination factor 1.129 and the n°_{Pt} of Cl^- to be $k^\circ_2(Cl^-) = 1.25 \times 10^{-3}$ $mol^{-1}\ dm^3\ s^{-1}$, smaller than that measured for the entry of NO_2^- (9.6×10^{-3} $mol^{-1}\ dm^3\ s^{-1}$). In spite of the amount of error involved in the interpolation, and of the large difference in reactivity of the two systems (3 orders of magnitude), we are tempted to attribute the inversion of reactivity between Cl^- and NO_2^- on going from the neutral $[Pt(O\text{-}N\text{-}O)(H_2O)]$ complex to the anionic $[Pt(O\text{-}N\text{-}O)Cl]^-$ complex to the biphilicity of nitrite ion.

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Registry No. K[Pt(O-N-O)Cl], 117581-24-5; K[Pt(O-N-O)Br], 119695-29-3; K[Pt(O-N-O)I], 119695-30-6; $K[Pt(O\text{-}N\text{-}O)NO_2]$, 119695-31-7; K[Pt(O-N-O)SCN], 119695-32-8; K_2PtCl_4, 10025-99-7; OH^-, 14280-30-9; NO_2^-, 14797-65-0; Br^-, 24959-67-9; I^-, 20461-54-5; SCN^-, 302-04-5; $SeCN^-$, 5749-48-4; CN^-, 57-12-5; SO_3^{2-}, 14265-45-3.

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