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Acidic Properties of (Dimethyl sulfoxide)(1,5-diamino-3-azapentane)platinum(II) Perchlorate and Kinetics of the Displacement of Dimethyl Sulfoxide from the Conjugate Base

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$[Pt(dien)(Me_2SO)](ClO_4)_2$ (dien = 1,5-diamino-3-azapentane) is a weak acid; pK_a = 11.94 ± 0.02 at 25.0 °C and $I = 0.10$. ^1H and ^{13}C NMR evidence is presented to show that the proton is removed from the 3-nitrogen. The kinetics of the displacement of Me_2SO from the conjugate base by the nucleophiles X = Cl^-, Br^-, I^-, N_3^-, SCN^-, and $S_2O_3^{2-}$ have been studied by working in the presence of 0.50 mol dm^{-3} NaOH. The displacement of Me_2SO by X is followed by the displacement of X by OH^-, and in the case of the more weakly bound nucleophiles Cl^- and Br^-, the second stage is much faster than the first and the reaction appears to be a halide-catalyzed replacement of Me_2SO by OH^-. The reactions, studied under first-order conditions, follow the simple rate law $k_{obsd} = k_2[X]$, and values of k_2 for the corresponding reactions of the amine complex in the absence of OH^- but at $I = 1.0$ have also been obtained. Deprotonation leads to a relatively small decrease in reactivity (a factor of ~2 at $I = 1.0$, extrapolating to a factor of ~8 at $I = 0$). $[Pt(en)(Me_2SO)_2]^{2+}$ (en = 1,2-diaminoethane) undergoes a similar deprotonation in basic solution but, because of its solvolytic lability, the pK_a could not be determined. Its amido conjugate base, however, is some 10 times *more* labile than the amine species.

Introduction

Deprotonation of a suitably placed amine ligand in an octahedral cobalt(III) complex can enhance the substitutional lability of the other ligands by factors ranging from 10^5 to 10^{13}. A similar, but less dramatic, labilization can be observed in the analogous complexes of Ru(III), Cr(III), and Rh(III).[1] Although there is still some discussion as to whether these processes are D or I_d, there is no doubt that they are dissociatively activated.

There are only a few studies of the effect of amine deprotonation on the associatively activated substitution reactions of four-coordinate planar complexes of d^8 reaction centers, and the effects are small in comparison with those encountered in the octahedral systems. The high acidity of the amine complexes of gold(III) allowed Baddley and Basolo[2] to compare $[Au(dien)Cl]^{2+}$ with $[Au(dien\text{-}H)Cl]^+$ (dien-H = singly deprotonated 1,5-diamino-3-azapentane, presumably at the 3-position) although it was only possible to make a proper comparison with Br^- as the entering ligand. The reactivity was halved in the amido complex. Deprotonation at the 3-position was confirmed by a single-crystal X-ray diffraction study of $[Au(dien\text{-}H)Cl]ClO_4$.[3] The amide group was shown to exert a greater trans influence than the corresponding amine group, but the small reduction in reactivity was confirmed. Replacement of some, or all, of the terminal amine protons by methyl or ethyl groups increases the acidity of the secondary amine proton still further,[4,5] and while this serves to reduce the reactivity and the importance of the nucleophile-dependent pathway, there is, at the same time, a reversal of behavior with the conjugate base becoming some 40 times more labile than the amine species. Unfortunately, these substituted-amine complexes are more prone to the displacement of the amine ligand and it has been suggested that substitution may take place indirectly through ring opening.[4,5]

The acidity of the corresponding Pt(II) complexes is far less marked, and there is no evidence of any significant deprotonation in the reactions of $[Pt(dien)X]^+$ in basic solution. The $[OH^-]$-dependent solvolysis of $[Pd(Et_4dien)Cl]^+$ has been explained in terms of the greater lability of the deprotonated amine species, a conclusion compatible with the observation that no such catalysis is observed in the fully tertiary $[Pd(Et_4Medien)Cl]^+$ species.[6] A recent extension of such studies to other ethyl- and methyl-substituted dien complexes of palladium(II) has shown $[OH^-]$-dependent solvolysis even in the case of $[Pd(Me_4dien)Cl]^+$ and of $[Pd(1,4,7\text{-}Me_3dien)Cl]^+$.[7,8]

In the course of our studies of the displacement of Me_2SO from $[Pt(en)(Me_2SO)_2]^{2+}$ we observed anomalies that might be attributable to amine deprotonation[9] and, in order to study this effect more conveniently, we have examined the effect of base upon the substitution reactions of $[Pt(dien)(Me_2SO)]^{2+}$. The results of this work are reported in this paper.

Experimental Section

$[Pt(en)(Me_2SO)_2](PF_6)_2$[9] and $[Pt(dien)(Me_2SO)](ClO_4)_2$[10] were prepared by methods reported elsewhere.

Proton NMR spectra were recorded at 80 MHz on a Bruker WP 80 spectrometer in D_2O using TSP (3-(trimethylsilyl)propionic acid, sodium salt) as an internal standard. FT carbon-13 spectra were obtained at 20.15 MHz with broad-band proton decoupling on a Varian FT 80 spectrometer employing the D_2O deuterium signal as an internal lock and DSS as an internal reference.

Aqueous solutions of weighed samples of $[Pt(dien)(Me_2SO)](ClO_4)_2$ ((1-2) × 10^{-3} M) were titrated with standard, CO_2-free sodium hydroxide solution ($I = 0.1$ ($NaClO_4$), 30 °C). The titrations were carried out with a Radiometer automatic titration system calibrated with standard buffers, after replacing the saturated KCl solution in the standard calomel reference electrode with NaCl to avoid precipitation of $KClO_4$ in the perchlorate medium.

Reagent grade inorganic salts were dried over P_2O_5 in a vacuum desiccator and used without further purification.

The kinetics were carried out in a silica cell in the thermostated cell compartment of a double-beam Perkin-Elmer Lambda 5 or a Cary 219 spectrophotometer, with a temperature constant of ±0.05 °C.

Results

(A) Base Hydrolysis of $[Pt(en)(Me_2SO)_2](PF_6)_2$. Addition of excess sodium hydroxide to a freshly prepared aqueous solution of $[Pt(en)(Me_2SO)_2](PF_6)_2$ leads to an immediate change in the spectrum. The new spectrum depends, to some extent, on $[OH^-]$, but with a sufficient concentration (>0.2 mol dm^{-3}) it is independent of $[OH^-]$ with a peak at 302 nm. Immediate reacidification leads to a spectrum that is identical with that of the starting material once correction has been made for the fairly rapid

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Table I. Proton and Carbon-13 NMR Chemical Shifts[a,b] and Coupling Constants (^{195}Pt–^{1}H and ^{195}Pt–^{13}C)[c] for [Pt(dien)(Me_2SO)](ClO_4)$_2$ and Their Changes upon Deuteration and Deprotonation

		^{1}H			^{13}C		
complex	solvent	CH_3	–CH_2–NH–	–CH_2–NH_2–	CH_3	–CH_2–NH–	–CH_2–NH_2
[Pt(dien)(Me_2SO)]$^{2+}$	D_2O	3.53 (23)	3.20	3.03	47.7 (49)	55.8 (26)	53.0 (10)
[Pt(dien-H)(Me_2SO)]$^+$	NaOD		2.40[d]	3.06[d]		59.2 (40)	53.7 (5)
[Pt(dien)(Me_2SO)]$^{2+}$	H_2O				47.8 (49)	56.0 (26)	53.2 (11)
[Pt(dien-H)(Me_2SO)]$^+$	NaOH				47.8 (38)	58.7 (41)	53.9 (5)

[a] Hydrogen-1 shifts in ppm vs. internal TSP. [b] Carbon-13 shifts in ppm vs. internal TSP. [c] Coupling constants (in Hz, Pt–H and Pt–C) are given in parentheses. [d] See text for ^{1}H–^{1}H coupling constants.

spectral changes due to solvolysis. The spectrum of the basic solution changes in a simple first-order manner to one that is identical with that of an authentic sample of [Pt(en)(Me_2SO)-OH]$^+$. The behavior on acidification with $HClO_4$ and with subsequent addition of Cl^- and I^- is quantitatively identical with that of [Pt(en)(Me_2SO)(H_2O)]$^{2+}$.

The rate constant for the solvolysis in the presence of NaOH ((2.36 ± 0.01) × 10^{-3} s^{-1}, [OH^-] = 0.1 mol dm^{-3}; (2.53 ± 0.03) × 10^{-3} s^{-1}, [OH^-] = 0.2 mol dm^{-3}; 30 °C) is essentially independent of [OH^-] once sufficient hydroxide is present. In the absence of added hydroxide the displacement of Me_2SO is some 10 times slower (rate constant 2.55 × 10^{-4} s^{-1}, I = 0.1 ($NaClO_4$); 2.51 × 10^{-4} s^{-1}, I = 0.2; 30.0 °C).

(B) Acid–Base Properties of [Pt(dien)(Me_2SO)](ClO_4)$_2$. When NaOH is added to an aqueous solution of [Pt(dien)(Me_2SO)]-(ClO_4)$_2$, there is an immediate change in spectrum. This process is reversible on acidification, but unlike the case for the [Pt-(en)(Me_2SO)$_2$]$^{2+}$ cation, there is no subsequent reversible change in the absence of added nucleophiles. With use of a weak base, cyclohexylamine, similar reversible spectral changes can be obtained in methanol and in water, but the initial rapid reversible change was followed by a slow irreversible change in absorbance, presumably due to the entry of the amine. This was not studied further. It is of interest to note that the monocationic species [Pt(dien)I]$^+$ undergoes no immediate reversible spectral change on the addition of sodium hydroxide or cyclohexylamine, but the subsequent slow change, corresponding to the displacement of iodide, has been well studied.[11]

A combined spectrophotometric and pH titration indicated that a single proton was involved. The treatment of this change as an acid dissociation (rather than the addition of a hydroxide ion) is justified by the NMR studies reported below. At any suitable wavelength in the range 240–350 nm, addition of NaOH leads to a considerable increase in absorbance, the plot of absorbance vs. pH having the typical sigmoid form of a titration curve. With use of data at 255 nm, at 25.0 °C and I = 0.10 ($NaClO_4$), the maximum rate of change of absorbance with pH occurs at pH 12.25.

A more quantitative and controlled evaluation of the data was carried out by plotting pH against log $(A - A_0)/(A - A_\infty)$, where A is the absorbance, at 255 nm, of the solution at the measured pH and A_0 and A_∞ are the absorbances, at the same wavelength, in the absence of added base and in the presence of sufficient base to convert all the substrate to the base form, respectively. Values were corrected for any dilution caused by adding the reagents. In keeping with the relationship pH = pK_a + log $[(A - A_0)/(A_\infty - A)]$, the plot was a straight line with intercept = pK_a = 11.94 ± 0.02 at 25.0 °C and I = 0.10 ($NaClO_4$).

A direct titrimetric determination using a nonlinear least-squares ACBA computer program to fit the pH/titer curve[12] gave pK_a = 12.1 ± 0.1 at 25.0 °C and I = 0.10 ($NaClO_4$).

These values can be compared with values reported for the pK_a's of other +2 Pt(II) cations with strong trans-effect ligands, e.g., [Pt(NH_3)$_3$(Me_2SO)]$^{2+}$ (8.18)[13] and [Pt(NH_3)$_3$(C_2H_4)]$^{2+}$ (8.67).[13] Whether the trans NH_3 remains bound in these determinations was not established.

The ^{1}H NMR spectrum of [Pt(dien)(Me_2SO)]$^{2+}$ in D_2O has a sharp signal at δ 3.53 (6 H), with ^{195}Pt satellites, typical of coordinated Me_2SO, with two broad unresolved bands at δ 3.03 (4 H) and δ 3.20 (4 H) assigned to the methine protons of dien. Chemical shifts and coupling constants are summarized in Table I. The amine proton signals are absent because proton exchange is facile under the conditions of study and they have been replaced by D. In NaOD solution, the ^{1}H NMR spectrum is further simplified. The Me_2SO signal disappears because of exchange of H with D. This has already been shown for [Pt(en)-(Me_2SO)Cl]$^+$ [14] even though the monocationic complex shows no obvious acidic properties. The spectrum of the methine protons consists of two sets of triplets, showing some second-order character consistent with an AA′BB′ spin system with $^1/_2(J_{1,3} + J_{1,4})$ = 5.8 Hz. In Me_2SO-d_6, the ^{1}H NMR spectrum shows the NH signal at δ 7.6 (intensity 1, broad) and the NH_2 signal at δ 6.14 (J_{PtH} = 50 Hz, intensity 4). The relative chemical shifts are consistent with the acidity of the two types of protons. Magnetization transfer shows exchange between the water impurity in the solution and *only* the NH proton. If the excess line width of the NH proton is attributed to exchange, then the NH proton is leaving at ca. 90 s^{-1}. This exchange is also consistent with the marked acidity of this proton.

The ^{13}C NMR spectrum of [Pt(dien)(Me_2SO)]$^{2+}$ in D_2O contains three peaks with ^{195}Pt satellites; the chemical shifts and coupling constants are summarized in Table I. In NaOD/D_2O the peak at δ 47.7 seems to vanish, but this is a consequence of the replacement of the dimethyl sulfoxide protons by deuterium. The consequent increase in the relaxation time of the ^{13}C nucleus greatly reduces the intensity of the signal, and on close examination, a very small unshifted resonance is seen among the noise. The peak at δ 59.2 has been much more shifted than that at δ 53.7. In H_2O, where deuteration of Me_2SO obviously does not occur, all three peaks are seen in the ^{13}C NMR spectrum. The assignment of the methine carbons is that of Hartley,[15] who reports the spectrum of [Pd(dien)(Me_2SO)]$^{2+}$ (assignment of the C adjacent to NH_2 is based on the similarity of δ to that in diaminoethane). There is a considerable difference between this spectrum and the one we report here. No evidence is presented to demonstrate that Me_2SO remains bound to the palladium at the time of measuring. Since the chemical shift of the carbons adjacent to –NH– is much more affected than the others on basification, it is concluded that the reaction involved is indeed a deprotonation and, as in the case of the [Au(dien)Cl]$^{2+}$ complex,[3] the proton is removed from the secondary nitrogen.

(C) Kinetics of the Displacement of Me_2SO from [Pt(dien)-(Me_2SO)]$^{2+}$ and [Pt(dien-H)(Me_2SO)]$^+$. The kinetics of the reaction [Pt(dien)(Me_2SO)]$^{2+}$ + $Y^{n-} \rightarrow$ [Pt(dien)Y]$^{(2-n)+}$ + Me_2SO have already been studied.[10] The ionic strength used, 0.10, was too low, however, to allow the amounts of hydroxide needed to deprotonate the substrate to be added, and so the reactions were reexamined at the higher ionic strength of 1.0 to facilitate the comparison. The data are collected in Table II.

In the presence of sodium hydroxide, 0.50 mol dm^{-3}, the substrate is completely converted to the deprotonated form. In the

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Table II. Pseudo-First-Order Rate Constants for the Reaction $[Pt(dien)(Me_2SO)]^{2+} + X^{n-} \rightarrow [Pt(dien)X]^{(2-n)+} + Me_2SO$[a]

X	[X]/ mol dm^{-3}	10^4k_{obsd}/ s^{-1}	X	[X]/ mol dm^{-3}	10^4k_{obsd}/ s^{-1}
Cl^-	0.20	0.204	SCN^-	0.050	6.65
	0.40	0.370		0.10	13.4
	0.60	0.607		0.15	19.9
	1.00	1.10			
			I^-	0.050	35.4
N_3^-	0.10	0.213		0.10	61.2
	0.125	0.277		0.15	88.9
	0.15	0.309			
	0.175	0.365	$S_2O_3^{2-}$	0.0025	65.1
	0.20	0.428		0.0050	122
				0.010	232
Br^-	0.050	0.680		0.015	380
	0.10	1.32		0.020	473
	0.15	2.01			

[a] At 30 °C and $I = 1.0$ ($LiClO_4$) in water.

absence of added nucleophile there is no slow subsequent absorbance change over a period of hours at 30 °C, but addition of NaCl or NaBr causes the spectrum to change to that of $[Pt(dien)OH]^+$ at a rate that is proportional to the concentration of the anion. The product of the reaction with NaI is a mixture of $[Pt(dien)OH]^+$ and $[Pt(dien)I]^+$, the latter changing slowly to the former at longer reaction times. Reactions with N_3^-, $S_2O_3^{2-}$, and SCN^- lead to the formation of $[Pt(dien)(N_3)]^+$, $[Pt(dien)(S_2O_3)]$, and $[Pt(dien)(SCN)]^+$, respectively, and subsequent hydroxide substitution is very much slower than the rate of formation of the complex. The deprotonation of the 2+ substrate, which causes a very large increase in absorbance in the region 280–340 nm, is not observed in any of the products, and all the reactions, therefore, are characterized by large reductions in absorbance.

The reactions between $[Pt(dien)X]^{n+}$ and OH^- to give $[Pt(dien)OH]^+ + X^{(2-n)-}$ were also studied briefly in order (a) to ascertain the positions of the isosbestic points and (b) to investigate the feasibility of the explanation that the hydroxo product is formed by a relatively rapid displacement of $X^{(2-n)-}$ from the first product of the reaction. The reactions follow first-order rate laws with rate constants that are independent of $[OH^-]$. These are reported in Table III. The reactions of $[Pt(dien-H)(Me_2SO)]^+$ with Cl^- and Br^- were studied at the isosbestic points of the halide displacement reaction (260 and 264 nm, respectively), but I^- absorbs too strongly at the appropriate isosbestic point (265 nm). Consequently, the reaction with NaI was studied at 275 nm, where the difference in the absorbances of the iodo and hydroxo complexes is not large.

All the spectrophotometric changes under these conditions of study followed first-order rate laws, and the rate constants, k_{obsd}, evaluated from the slopes of the plots of $\ln (A_t - A_\infty)$ vs. time (A_t and A_∞ being the absorbances at time t and after 8 half-lives, respectively) are collected in Table III.

Discussion

The large increase in the absorbance that accompanies the addition of excess hydroxide to an aqueous solution of $[Pt(dien)(Me_2SO)]^{2+}$ is due to the formation of the amido species $[Pt(dien-H)(Me_2SO)]^+$. The dien complex has a pK_a of 11.94 at 25.0 °C and $I = 1.0$ ($NaClO_4$), and the ^1H and ^{13}C NMR spectra indicate clearly that the process involves the removal of a proton rather than the addition of OH^- (in contrast to the behavior of $[Pt(phen)_2]^{2+}$, which has been shown to give the five-coordinate $[Pt(phen)_2OH]^+$ [16]). This parallels the behavior of the Au(III) complex $[Au(dien)Cl]^{2+}$, which also loses a proton. There, single-crystal X-ray diffraction studies indicate that the proton on the secondary nitrogen trans to Cl is removed,[3] and here the NMR spectra indicate that the secondary proton trans to the sulfoxide is removed from the platinum(II) complex.

Table III. Pseudo-First-Order Rate Constants for the Reaction $[Pt(dien-H)(Me_2SO)]^+ + X^{n-} + H_2O \rightarrow [Pt(dien)X]^{(2-n)+} + Me_2SO + OH^-$[a]

X	[X]/ mol dm^{-3}	10^4k_{obsd}/ s^{-1}	X	[X]/ mol dm^{-3}	10^4k_{obsd}/ s^{-1}
Cl^- (1.5)[b]	0.10	0.0491	SCN^-	0.025	1.46
	0.15	0.0732		0.050	2.91
	0.20	0.0976		0.075	4.18
	0.25	0.121		0.10	5.52
				0.125	6.71
N_3^- (0.049)	0.050	0.0412		0.150	8.08
	0.10	0.072			
	0.125	0.109	I^- (0.77)	0.025	6.82
	0.15	0.132		0.050	15.1
	0.175	0.143		0.075	21.1
	0.20	0.158		0.10	30.7
				0.125	38.6
Br^- (2.2)	0.050	0.237		0.15	45.5
	0.075	0.379			
	0.10	0.476	$S_2O_3^{2-}$	0.0050	66.3
	0.125	0.636		0.0075	96.4
	0.150	0.763		0.010	131
	0.175	0.856		0.0125	165
				0.015	188
				0.0175	228

[a] At 30 °C in aqueous NaOH (0.50 mol dm^{-3}) and $I = 1.0$ ($LiClO_4$). [b] Values in parentheses are 10^4k_{obsd} values for displacement of X^{n-} by OH^- from $[Pt(dien)X]^{(2-n)+}$ under the same conditions.

The reactions of $[Pt(dien-H)(Me_2SO)]^+$ with nucleophiles, which have to be studied in the presence of excess hydroxide, take place in two consecutive stages:

$$\begin{tikzcd}
\mathrm{[Pt(dien{-}H)(Me_2SO)]^+ + X^-} \arrow[r, "(1)"] & \mathrm{[Pt(dien{-}H)X] + Me_2SO} \arrow[d, "\text{fast}"', "+H_2O"] \\
\mathrm{[Pt(dien)OH]^+ + X^-} \arrow[r, shift right] & \mathrm{[Pt(dien)X]^+ + OH^-} \arrow[l, shift right, "(2)"']
\end{tikzcd}$$

In all cases stage 1 obeys the rate law $-d[\text{substrate}]/dt = k_2[\text{substrate}][X^-]$, i.e., $k_{obsd} = k_2[X^-]$ and there is no significant nucleophile independent contribution.

The first product of the reaction is more basic than the substrate and takes a proton from the solvent. The $[Pt(dien)X]^+$ species then undergoes reaction with OH^- at a rate that is strongly dependent upon the nature of X, may be reversible for the more tightly bound ligands, and is essentially independent of $[OH^-]$. Thus the most weakly bound nucleophiles Cl^- and Br^- appear to catalyze the base hydrolysis of the substrate.

The values of k_2, determined from the slope of the plot of k_{obsd} vs. $[X^-]$, are collected in Table IV, where they are compared with the values of k_2 for the corresponding reactions of $[Pt(dien)(Me_2SO)]^{2+}$, also determined at $I = 1.0$. A comparison of these data indicates that the removal of a proton has had remarkably little effect upon the reactivity of the substrate, the rate constants for the deprotonated species being approximately half the magnitude of those for the corresponding dicationic substrate. When such a comparison is made, it should be realized that these reactions exhibit very strong primary salt effects, and since we are dealing with substrates of different charge reacting with charged nucleophiles, the proper comparison ought to be made between the rate constants extrapolated to zero ionic strength. Because of the need to work in the presence of 0.5 mol dm^{-3} NaOH to ensure complete deprotonation, it was necessary to make the study at the high ionic strength of 1.0. This enters the region where the concept of the equivalence of electrolytes breaks down[17] and where the expressions used to estimate the activity coefficients lose their validity. It is of interest to note that, for the reaction of $[Pt(dien)(Me_2SO)]^{2+}$, for which data exist at two ionic strengths (0.10 and 1.0) with use of the expression $\log k_2 = \log k_2^0 + 2Az_Az_BI^{1/2}/(1 + I^{1/2})$[18] (where $A = 0.496$ at 30.0 °C), the values

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Table IV. Second-Order Rate Constants (10^3k_2/mol^{-1} dm^3 s^{-1}) at Various Ionic Strengths ($LiClO_4$) and $10^3k_2{}^0$/mol^{-1} dm^3 s^{-1}, Extrapolated to $I = 0$[a] for the Displacement of Me_2SO from $[Pt(dien)(Me_2SO)]^{2+}$ and $[Pt(dien\text{-}H)(Me_2SO)]^+$ by Various Nucleophiles, X[b]

	$[Pt(dien)(Me_2SO)]^{2+}$			$[Pt(dien\text{-}H)(Me_2SO)]^+$	
X	$I = 0.10$[c]	$I = 1.0$	$I = 0.0$[d]	$I = 1.0$	$I = 0.0$
Cl^-	0.380 ± 0.009	0.115 ± 0.008	1.14 (1.10)	0.0483 ± 0.0001	0.15
N_3^-	0.756 ± 0.03	0.207 ± 0.01	2.27 (2.04)	0.0824 ± 0.008	0.26
Br^-	3.72 ± 0.05	1.33 ± 0.03	11.2 (13.1)	0.504 ± 0.02	1.58
SCN^-	40.4 ± 0.2	13.2 ± 0.2	121 (130)	5.24 ± 0.07	16.3
I^-	226 ± 0.7	53.5 ± 1	678 (526)	31.2 ± 0.8	97.8
$S_2O_3^{2-}$	10180 ± 133	2380 ± 90	91600 (23500)	1280 ± 36	12570

[a] Using the expression $\log k_2 = \log k_2{}^0 + 2Az_Az_BI^{1/2}/(1 + I^{1/2})$ (where $A = 0.496$). [b] At 30 °C in water and 0.50 mol dm^{-3} NaOH, respectively. [c] Data from ref 10. [d] The values extrapolated from $I = 1.0$ are in parentheses.

of $k_2{}^0$ for the reactions with singly charged anionic nucleophiles determined from data at $I = 0.10$ are in reasonably good agreement with those determined from data obtained at $I = 1.0$. Unfortunately, there is a very wide discrepancy in the case of the data for the reaction with the dianionic $S_2O_3^{2-}$. When I is changed from 0.10 to 1.0, k_2 for this reagent is reduced by roughly the same fraction as those for the monoanionic reagents. Indeed, if we treated $S_2O_3^{2-}$ as a -1 reagent, the agreement between the two $k_2{}^0$ values would be good. There is no evidence in the literature that $S_2O_3^{2-}$ is sufficiently protonated under the experimental conditions. The extrapolation from $I = 1.0$ to $I = 0$ is probably too far for the simplified expression to work satifactorily, and the agreement for the -1 nucleophiles is probably fortuitous. This problem is worthy of much closer examination.

The comparison of the rate constants extrapolated to $I = 0$ shows that, apart from $S_2O_3^{2-}$, the ratio does not vary much with the nature of the nucleophile but is now further decreased so that the amido species has about one-eighth of the reactivity of the amine species. The departure of the $S_2O_3^{2-}$ rate constant, once again, seems to be the result of treating it as a 2– reagent. Because of the problem of correcting for primary salt effects, it is not possible to discuss the reactivity differences between the amino and amide species in any detail; but the remarkable feature is that the rate constants are so little affected by the deprotonation and the behavior is probably consistent with a model in which the charges on the reagents make some contribution to the second-order rate constant. In this sense, the dicationic $[Pt(dien)(Me_2SO)]^{2+}$ and its amido conjugate base bear a remarkable similarity to the dicationic $[Au(dien)Cl]^{2+}$ and its amido conjugate base insofar as a comparison has been made with the Au(III) acid–base pair.

A great deal has yet to be done before the ways in which hydroxide can affect the rates of substitution reactions of d^8 square-planar complexes can be fully understood. The labilizing effect of the amido group that dominates the base-catalyzed reactions of octahedral complexes, especially those of Co(III), is absent; indeed, the nonsolvolytic substitutions are slightly slower in the deprotonated amido species. The first-order dependence on OH^- that is observed in the solvolytically controlled reactions of $[Pd(Et_4dien)X]^+$ and that is ascribed to the strong labilizing effect of the amido group because of its absence from the fully tertiary $[Pd(Et_4Medien)X]^+$[6] complexes suggests that it might only be the solvolytic reaction that is faster in the conjugate base. This is consistent with the 10-fold increase in solvolytic reactivity when $[Pt(en)(Me_2SO)_2]^{2+}$ is deprotonated, but that system does not lend itself to a more detailed treatment. The absence of a contribution from a solvolytic pathway, even when $[OH^-] = 0.50$ mol dm^{-3}, prevents us from applying this test to the $[Pt(dien)(Me_2SO)]^{2+}$ complex. The mixed first- and second-order dependence of the rate of solvolytic displacement of amine from *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$[19] cannot be assigned to amine deprotonation because the same effect is observed in the analogous reactions of *cis*-$[Pt(Me_2S)_2(py)_2]^{2+}$,[20] which contains no acidic hydrogens.

The question remains as to why these sulfoxide complexes, $[Pt(dien)(Me_2SO)]^{2+}$, $[Pt(en)(Me_2SO)_2]^{2+}$, and $[Pt(NH_3)_3(Me_2SO)]^{2+}$,[13] possess acidic amino groups. Although the dicationic nature of the complex seems to be important (sulfoxide complexes with lower charge do not seem to behave in this way), charge alone is not enough since $[Pt(NH_3)_4]^{2+}$ cannot be significantly deprotonated in aqueous solution and there is no evidence for acidic properties is *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$. It is necessary, therefore, to look for some specific contribution from coordinated dimethyl sulfoxide. Although the acidity enhancement appears to be a trans-specific phenomenon, it must not be confused with the classic trans influence of a strong σ donor,[21] which would weaken the Pt–N bond and thereby decrease the acidity of the N–H group. It is known that, although sulfoxides exert a moderately strong trans effect (rate enhancement) they do not exhibit any significant trans influence (ground-state bond weakening)[22] and it has been suggested that they function as π acceptors, facilitating the formation of the five-coordinate transition state. Although there is no evidence for significant π involvement in the ground state when the usual complexes are studied, we wish to suggest that such a function may stabilize the amido base sufficiently through the interaction of the π-donor nitrogen and the π-acceptor sulfoxide. However, this should serve to strengthen the Pt–S bond and may even make the platinum less electrophilic with respect to the entering nucleophiles and ought to have a greater effect upon the reactivity than is observed. This potential paradox deserves further investigation.

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Registry No. $[Pt(dien)(Me_2SO)]^{2+}$, 77863-16-2; $[Pt(dien\text{-}H)(Me_2SO)]^+$, 101247-91-0; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; N_3^-, 14343-69-2; SCN^-, 302-04-5; $S_2O_3^{2-}$, 14383-50-7.

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