carbon atoms that are directly bonded to the metal.

Registry No. I, 90968-72-2; II, 90968-73-3; III, 90968-74-4; IV, 90968-75-5; V, 90968-76-6; VI, 40901-27-7; VII, 53821-91-3; VIII, 53821-89-9; IX, 41121-63-5; X, 90990-45-7; XI, 90990-46-8; XII, 90968-77-7; XIII, 90968-78-8; $[BrCH_2CH_2NH_3]Br$, 2576-47-8; $Mn(CO)_5Br$, 14516-54-2; $Mn(CO)_5I$, 14879-42-6; $Re(CO)_5Cl$, 14099-01-5; $Re(CO)_5Br$, 14220-21-4; $[BrCH_2CH_2CH_2NH_3]Br$, 5003-71-4; $Re(CO)_5I$, 13821-00-6; $Mn(CO)_5Cl$, 14100-30-2; $BrCH_2CH_2OH$, 540-51-2; NaBr, 7647-15-6; NaCl, 7647-14-5; $Re_2(CO)_{10}$, 14285-68-8; $[Re(CO)_5(CH_3CN)]PF_6$, 55057-83-5; NaI, 7681-82-5; aziridine, 151-56-4; oxirane, 75-21-8.

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Reactivity of *cis*-Diamminebis(dimethyl sulfide)platinum(II) Perchlorate

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The reaction between *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ and a range of anionic nucleophiles has been studied in aqueous solution at 25.0 °C by using a combination of absorption spectrophotometry and ^{1}H NMR measurements. In all cases, the first leaving group is ammonia and the relative second-order constants are Cl^- (1) < NO_2^- (2.4) < N_3^- (3.7) < Br^- (5.6) < SCN^- (260) < I^- (480). In all cases a second anion enters in a subsequent step, displacing ammonia in the case of Cl^-, Br^-, and I^- and dimethyl sulfide in the case of NO_2^-, N_3^-, and SCN^-. It is suggested that the relatively high trans effect of dimethyl sulfide is the main factor that determines the leaving group in the first stage of the reaction.

Introduction

In our studies of the factors that determine the reactivities of four-coordinate complexes of platinum(II), we have found that, contrary to the early suggestions of Basolo and Pearson,[3] the charge of the substrate plays an important part in determining the reactivity of the complexes and the relative nucleophilicity of the entering groups. For example, whereas the original $n_{Pt}°$ nucleophilicity scale[4] can be applied quite well to substrates of the same charge type as the standard *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine), there are a number of nucleophiles whose reactivities are significantly greater or less than those predicted on the basis of their $n_{Pt}°$ values when they enter an ionic or cationic substrates, respectively. Such species were termed "biphilic"[5] in accordance with a hypothesis that they owed part of their reactivity to their ability to function additionally as π acids, and one might therefore expect that their reactivity relative to that of pure σ bases might change according to the π basicity of the reaction center. It has been shown that, by using a new standard substrate, $[Pt(en)(NH_3)Cl]^+$ (en = 1,2-diaminoethane), a nucleophilicity scale that applies very well to 1+ cationic substrates can be developed,[6] and more recently, Romeo[7] has extended this approach to assign a standard to 2+ cationic substrates. The number of dipositive Pt(II) substrates whose reactivity is sufficiently large to allow a detailed study of their reactions with a wide range of nucleophiles is quite restricted, and the first purpose of the work reported in this paper was to extend the number of dicationic species studied.

Apart from H_2O and alcohols, neutral ligands are generally poor nucleofuges in polar solvents. This situation does not apply in nonpolar solvents such as dimethoxyethane, where complexes such as *cis*-$[Pt(Me_2S)_2Cl_2]$ react with neutral nucleophiles such as amines and lose the neutral ligand Me_2S[8] in spite of the fact that chloride is normally a good leaving group, especially under the moderate trans effect of Me_2S.[9] This is a consequence of the inability of the nonpolar solvents to facilitate ionogenic reactions, but the relatively high reactivity of this system is worth noting. The substrate reverts to normal behavior, i.e. loss of chloride, in polar solvents.[10] The complex *cis*-$[Pt(Me_2SO)_2Cl_2]$ also undergoes displacement of the neutral sulfoxide in 1,2-dimethoxyethane,[11] but in this case, the neutral ligand is also often displaced in aqueous and methanolic solutions as well.[12] Considerable attention is now being paid to this mutual labilization of a pair of cis sulfoxides, and it is of considerable interest to compare the behavior of sulfoxides and thioethers in this context. The two threads of interest, namely the nucleophilicity scales appropiate to dicationic complexes and the mutual labilization of a pair of cis sulfur donor ligands, come together in this work. We have synthesized the species *cis*-$[Pt(Me_2SO)_2(NH_3)_2]^{2+}$ and *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ in order to make this comparison with anionic nucleophiles in aqueous solution. The first undergoes reaction with the loss of dimethyl sulfoxide at a rate that requires a stopped-flow technique to follow it. The much slower reactions of the latter complex can be followed by classical methods and are reported in this paper.

Experimental Section

Preparations. ***cis*-$[Pt(Me_2S)_2(NH_3)_2](ClO_4)_2$.** *cis*-$[Pt(NH_3)_2Cl_2]$ (256.5 mg, 0.855 mmol), prepared by the method of Kauffman,[13] was suspended in methanol (65 cm^3); silver perchlorate (354.5 mg, 1.71 mmol) was added and the mixture stirred at room temperature for 24 h. The precipitated AgCl was filtered off and the filtrate treated with excess dimethyl sulfide (0.25 cm^3). After 1 h the solution was concentrated in a rotatory evaporator, and the required product was precipitated by addition of diethyl ether and dried under vacuum; yield 375 mg (79%). Anal. Calcd for $C_4Cl_2H_{18}N_2O_8S_2Pt$: C, 8.70; H,

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[1] Università di Venezia.

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3.29; N, 5.07; Cl, 12.84; S, 11.61. Found: C, 8.81; H, 3.38; N, 5.07; Cl, 12.61; S, 11.59.

***trans*-[Pt(Me$_2$S)$_2$(NH$_3$)$_2$](ClO$_4$)$_2$** was prepared in a similar way from *trans*-[Pt(NH$_3$)$_2$Cl$_2$] (250 mg, 0.833 mmol), prepared by the standard method.[13] This was suspended in methanol (25 cm^3) and stirred with AgClO$_4$ (340 mg, 1.64 mmol) for 36 h. The rest of the procedure was the same as for the cis isomer; yield 320 mg (70%). Anal. Calcd for $C_4Cl_2H_{18}N_2O_8S_2Pt$: C, 8.70; H, 3.29; N, 5.07. Found: C, 8.62; H, 3.35; N, 5.20.

Other reagents were analytical grade and used without further purification. ^{1}H NMR spectra were spectra were measured with an EM 390 Varian spectrometer.

Kinetics. The reactions were started by mixing known prethermostated volumes of freshly prepared solutions of the complex and nucleophile at a predetermined ionic strength, in the thermostated cell of a Varian Cary 219 and/or Perkin-Elmer Coleman 575 spectrophotometer. The optical density variations were followed by periodically scanning the spectrum over the range 240–350 nm and/or measuring the changing absorbance at a suitable predetermined wavelength as a function of time. All the kinetics were carried out in the presence of a sufficient excess of nucleophile to ensure pseudo-first-order kinetics in the separable stages of the reactions.

Numerical Treatment of the Data. The kinetic data for substitution by iodide, thiocyanate, nitrite, and water were calculated by a nonlinear regression program, following the Gauss–Newton algorithm, with three optimized parameters, D_0, D_∞, and k_{obsd}, where D_0 is the optical density at time zero, D_∞ is the optical density at the end of the reaction, and k_{obsd} is the observed first-order rate constant. The kinetic data of the consecutive reactions with chloride, bromide, and azide were calculated by a nonlinear regression program, following the Gauss–Newton algorithm, with five optimized parameters, namely D_0, D_1, D_2, k_{obsd}(I), k_{obsd}(II), where D_0 is the optical density at time zero, D_1 is the calculated optical density at the end of the first stage of substitution, D_2 is the optical density at the end of the reactions, and k_{obsd}(I) and k_{obsd}(II) are the first-order rate constants of the first and second stages of substitution, respectively.

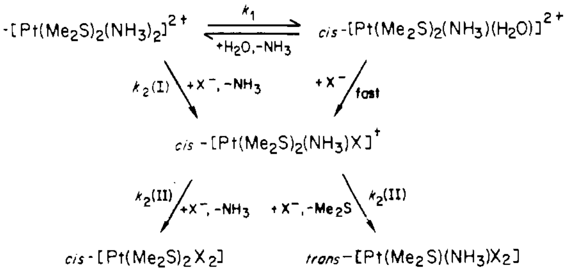
The second-order k_2 values were obtained by a weighted linear regression program, the weighting being $1/\sigma^2$, where σ is the standard deviation of the values of k_{obsd} obtained by the above treatment. The deviation was $[A_{ii}\theta^2/(n-3)]^{1/2}$ in the case of the kinetics calculated by the three-parameter nonlinear regression and $[A_{ii}\theta^2/(n-5)]^{1/2}$ in the case of the kinetics calculated by the five-parameter nonlinear regression, where A_{ii} is the diagonal element of the inverse matrix obtained from the linear equation system, following the Gauss–Newton algorithm, for the treated parameters, θ is the standard deviation, and n is the number of points used in the regression. The k_2 deviations were standard deviations on the slope of the regression straight line. In both cases no confidence limits are imposed.

Results and Discussion

Aqueous solutions of *cis*- and *trans*-[Pt(Me$_2$S)$_2$(NH$_3$)$_2$](ClO$_4$)$_2$ closely obey Beer's law at room temperature. The changes in absorption spectra consequent upon adding nucleophiles can be readily followed and analyzed kinetically, but in order to establish the nature of the intermediates and products, it was necessary to carry out parallel experiments in which the changing ^{1}H NMR spectra of D$_2$O solutions are examined. In general, the reactivity of the trans complex is considerably (at least 2 orders of magnitude) less than that of the cis isomer, and it is only the reactions of the latter that are considered in this paper.

When *cis*-[Pt(Me$_2$S)$_2$(NH)$_2$](ClO$_4$)$_2$ reacts with Cl$^-$ or Br$^-$ in aqueous solution, the absorbance changes can be analyzed in terms of two consecutive first-order processes; but with I$^-$ only a single first-order change is observed. The ^{1}H NMR spectrum of the starting material in D$_2$O consists of a single peak (δ 2.56) with two satellites ($J_{^{195}Pt-^1H} = 46.5$ Hz). The ammonia protons exchange readily with the solvent and are not observed. Addition of a twofold excess of I$^-$ or Br$^-$ did not lead to the appearance of an uncoupled peak that could be assigned to free dimethyl sulfide even after the spectrophotometric change was complete. The two-stage change in the absorption spectrum is therefore due to the displacement of the two ammonias, and in these reactions, the thioethers remain bound to the platinum throughout. Under the higher concentration conditions of the NMR experiments, some product crystallized out toward the end of the reaction and was shown to be [Pt(Me$_2$S)$_2$X$_2$] by analysis.

Scheme I



X = Cl, Br: $k_2(\mathrm{II}) < k_2(\mathrm{I})$ X = NO$_2$, SCN: $k_2(\mathrm{II}) > k_2(\mathrm{I})$
X = I: $k_2(\mathrm{II}) > k_2(\mathrm{I})$ X = N$_3$: $k_2(\mathrm{II}) < k_2(\mathrm{I})$

In the presence of excess NO$_2^-$ or SCN$^-$, the spectrophotometric changes followed a simple first-order rate law. The ^{1}H NMR spectrum of a 1:2 mole ratio mixture of the substrate and NO$_2^-$ or SCN$^-$ changed from that of the substrate to one in which two peaks of equal area, attributable to the Me$_2$S protons, are present, one at δ 2.47 or 2.50, respectively, with ^{195}Pt satellites and the other at δ 2.11 assigned to free Me$_2$S. In this case, therefore, one of the coordinated dimethyl sulfides has been displaced, but the experimental evidence does not allow us to say whether the displacement of the Me$_2$S precedes or follows the displacement of ammonia, or indeed whether any ammonia displaced at all.

Two separate consecutive first-order precesses are observed spectrophotometrically in the reaction with N$_3^-$, the second being about 10 times slower than the first. The ^{1}H NMR spectrum of a D$_2$O solution of the cis complex with a twofold molar excess of N$_3^-$ changes over the first 30 min to give two new peaks (δ 2.54 and 2.52) each with their ^{195}Pt satellites, while the peak at δ 2.56 decreases. As the reaction progresses further, the peak due to free Me$_2$S at δ 2.11 appears and the relationship between the area under this peak and the reaction time is sigmoid. It is concluded that the first reaction step is the displacement of ammonia while the second is the displacement of dimethyl sulfide, presumably trans to the attached azido group. The complete reaction process is represented in Scheme I.

In all cases, the first-order rate constants for the first stage (k_{obsd}(I)) could be determined reliably from the spectrophotometric data, but those for the second stage (k_{obsd}(II)) are far less precise because complications such as the precipitation of the product intervene before sufficient reaction has taken place. The values of k_{obsd}(I) and k_{obsd}(II) (where available) are collected in Table I. There is a good linear relationship between k_{obsd} and the concentration of the nucleophile, and the values of the slopes (k_2(I) and k_2(II), respectively) are collected in Table II. The scatter of the data and the relatively small contribution from any nucleophile-independent path did not permit a determination of these first-order constants (k_1(I) and k_1(II)) from the intercepts of these plots. The value of k_1(I), the first-order rate constant for the solvolysis of *cis*-[Pt(NH$_3$)$_2$(Me$_2$S)$_2$]$^{2+}$, was measured independently in acidic and basic solution. In acid, in the absence of added nucleophile, there is a two-stage reaction that is attributed to the successive displacement of the two ammonia ligands since the ^{1}H NMR spectrum of an acidified D$_2$O solution shows the absence of free dimethyl sulfide. The solvolytic rate constant, $k_1(\mathrm{I}) = 5.5 \times 10^{-5}$ s^{-1} (25 °C), shows that the nucleophile-independent pathway does not play a significant part in the reaction with the stronger nucleophiles. In basic solution (provided [OH$^-$] < 10^{-3} M), the solvolysis is irreversible and the first step again corresponds to the diplacement of ammonia

Table I. First-Order Rate Constants, k_{obsd}, for the Reactions[a]

cis-$[Pt(Me_2S)_2(NH_3)_2]^{2+} + Y^- \rightarrow$ *cis*-$[Pt(Me_2S)_2(NH_3)Y]^+ + NH_3$ (k_{obsd}(I))

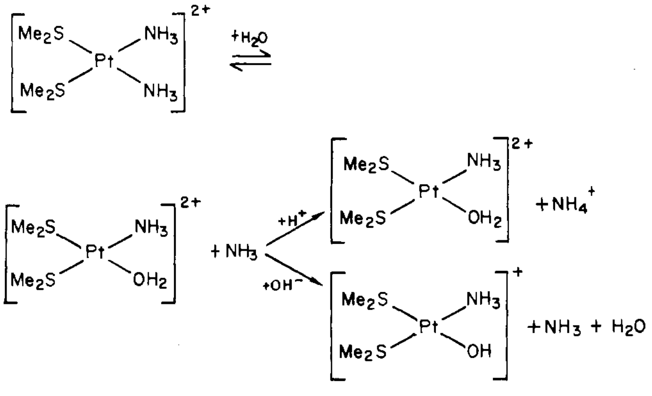
cis-$[Pt(Me_2S)_2(NH_3)Y]^+ + Y^-$ $\nearrow$ *cis*-$[Pt(Me_2S)_2Y_2] + NH_3$ (k_{obsd}(II)

$\searrow$ *trans*-$[Pt(Me_2S)(NH_3)Y_2] + Me_2S$ (k_{obsd}(II))

Y	$[Y^-]$, mol dm^{-3}	μ[b]	10^3k_{obsd}(I), s^{-1}	10^3k_{obsd}(II), s^{-1}
Cl^-	0.1	1.0	1.18 ± 0.07	0.4 ± 0.2
	0.2	1.0	1.58 ± 0.01	0.130 ± 0.004
	0.35	1.0	2.35 ± 0.02	0.086 ± 0.002
	0.5	1.0	4.54 ± 0.03	0.41 ± 0.04
	0.6	1.0	5.20 ± 0.02	0.319 ± 0.008
	0.8	1.0	6.89 ± 0.05	0.277 ± 0.004
	1.0	1.0	8.1 ± 0.1	0.176 ± 0.003
Br^-	0.04	1.0	4.8 ± 0.1	0.191 ± 0.004
	0.15	1.0	8.8 ± 0.1	0.762 ± 0.008
	0.2	1.0	11.9 ± 0.3	0.80 ± 0.03
	0.2	1.0	12.0 ± 0.1	1.14 ± 0.02
	0.2	1.0	11.3 ± 0.4	1.16 ± 0.05
	0.4	1.0	24.2 ± 0.9	2.2 ± 0.1
	0.4	1.0	21.3 ± 0.3	1.71 ± 0.03
N_3^-	0.02	1.0	1.73 ± 0.04	0.339 ± 0.008
	0.05	1.0	3.68 ± 0.05	0.599 ± 0.006
	0.1	1.0	5.1 ± 0.1	0.576 ± 0.008
	0.1	1.0	5.94 ± 0.08	0.884 ± 0.008
	0.15	1.0	6.54 ± 0.07	0.903 ± 0.007
	0.2	1.0	11.8 ± 0.1	1.98 ± 0.07
I^-	0.002	1.0	12.2 ± 0.4	
	0.003	1.0	13.6 ± 0.7	
	0.004	1.0	16.2 ± 0.5	
	0.005	1.0	21.6 ± 0.7	
	0.006	1.0	24.4 ± 0.7	
	0.008	1.0	34.6 ± 0.7	
	0.01	1.0	42.3 ± 0.9	
SCN^-	0.0005	0.01	7.6 ± 0.1	
	0.001	0.01	14.3 ± 0.2	
	0.002	0.01	23.5 ± 0.1	
	0.003	0.01	28.6 ± 0.2	
	0.003	0.01	29.7 ± 0.1	
	0.004	0.01	47.3 ± 0.4	
	0.005	0.01	54.1 ± 0.4	
	0.006	0.01	70.4 ± 0.2	
	0.008	0.01	94.6 ± 0.4	
	0.01	0.01	112.7 ± 0.5	
NO_2^-	0.03	1.0	0.608 ± 0.002	
	0.05	1.0	0.957 ± 0.003	
	0.1	1.0	2.08 ± 0.02	
	0.2	1.0	4.23 ± 0.03	
	0.3	1.0	6.05 ± 0.07	

[a] In water at 25 °C. [b] Ionic strength maintained constant with $LiClO_4$.

by water, the latter being rapidly deprotonated to give the thermodynamically stable hydroxo species. A second stage follows and is probably the solvolytic displacement of the second ammonia, but this has only been studied superficially so far.



At higher base concentration ($[OH^-] > 10^{-3}$ M), the reaction becomes faster as $[OH^-]$ increases and a different mechanism appears to be operating. This is the subject of a separate study and will be reported eventually elsewhere.

The second-order rate constants in Table II have been extrapolated to $\mu = 0$ by using the standard relationship $\log k_2 = \log k_2° + 1.02z_1z_2\, \mu^{1/2}/(1 + \mu^{1/2})$ (in all cases z_1z_2, the product of the charges of the reagents, equals 2−).

The sequence of reactivity Cl^- (1.0) < NO_2^- (2.4) < N_3^- (3.7) < Br^- (5.6) < SCN^- (260) < I^- (480) is the same as that observed for other dicationic species (note that SCN^- is always less reactive than I^- toward such substrates, whereas for neutral reagents the reactivity is reversed: $n_{Pt}°$ for SCN^- is greater than $n_{Pt}°$ for I^-). If we take the ratio of the second-order rate constants for the strongest (I^-) and weakest (Cl^-) of the nucleophiles studied as a measure of the nucleophilic discrimination of the substrate, we find that *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ ($k_2(I^-)/k_2(Cl^-)$ = 480) is nearly as discriminating as $[Pt(dien)(Me_2SO)]^{2+}$[7] (ratio 600) and both are much more discriminating than $[Pt(dien)(H_2O)]^{2+}$[7] (130) and $[Pt(Me\text{-}dien)(H_2O)]^{2+}$[14] (170), where water is displaced. This observation is consistent with the tighter binding in the rate-determining transition state in the first two cases.

The evidence that the first ligand to be displaced from *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ is the ammonia is unambiguous in the case of reaction with Cl^-, Br^-, I^-, and N_3^-, but because the reactions with NO_2^- and SCN^- occur in a single detectable stage with the displacement of one Me_2S and (probably) one NH_3, it is not possible to say which is displaced first. The fact that position of SCN^- and NO_2^- in the general nucleophilicity sequence is the same in this system as in the other dicationic substrates where is no ambiguity about the identity of the leaving group suggests that, in all cases, the first group to be displaced from *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ is ammonia.

At present it is not possible to discuss the relative nucleofugicities of Me_2S and NH_3 in their displacement from otherwise identical substrates because insufficient information is available. Attempts to study the displacement of Me_2S from $[Pt(dien)(Me_2S)]^{2+}$ in order to make comparison with the displacement of Me_2SO from $[Pt(dien)(Me_2SO)]^{2+}$ failed because of the slowness of the reaction (at least 2 orders of magnitude less than that for the displacement of the sulfoxide), and under forcing conditions there were complications that suggested that dimehtyl sulfide was not necessarily the first leaving group. The reaction of $[Pt(NH_3)_4]^{2+}$ with nucleophiles is very slow indeed. We have detected no significant change after many days at 30 °C in the spectrum of a solution in 0.1 M hydrochloric acid. The preparation of *trans*-$[Pt(NH_3)_2Cl_2]$ requires much more forcing conditions. No information is available about the analogous reaction of $[Pt(Me_2S)_4]^{2+}$. It would appear that ammonia, under the moderate trans effect of Me_2S, is more easily displaced than Me_2S under the poor trans effect of NH_3. It has been estimated that the displacement of a weak leaving group (e.g., Cl^- from $[Pt(L)Cl_3]^-$) is about 2.5×10^3 times faster when L = Me_2S than when it is NH_3[9] and that, for more tightly bound leaving groups, the magnitude of the difference might be considerably greater. The cis effect of Me_2S is somewhat greater than that of NH_3 in the reactions of complexes of the type $[Pt(en)(L)Cl]^+$, and the difference increases as the nucleophilicity of the entering group increases. However, since in *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ the cis effect will work equally on NH_3 and Me_2S, it is not expected that this will contribute to the choice of the leaving group. It is significant that the mutual labilization of S-bonded sulfoxides that leads to the very rapid displacement of the first sulfoxide from $[Pt(en)(Me_2SO)_2]^{2+}$ or *cis*-$[Pt(NH_3)_2(Me_2SO)_2]^{2+}$[15] either is absent in thioethers or else is too small

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Table II. Specific Rate Constants for the Entry of Nucleophiles on *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ [a]

Y	μ	k_2(I),[b] M^{-1} s^{-1}	k_2(II),[c] M^{-1} s^{-1}	μ	$10^3k_2{}^{\circ}$(I),[b] M^{-1} s^{-1}	$10^3k_2{}^{\circ}$(II),[c] M^{-1} s^{-1}
Cl^-	1.0	0.0083 ± 0.0006	−0.02 ± 0.25	0	0.087 ± 0.25	
Br^-	1.0	0.047 ± 0.003	4.5 ± 0.5	0	0.49 ± 0.03	15 ± 2
N_3^-	1.0	0.031 ± 0.005	4 ± 1	0	0.32 ± 0.05	13 ± 3
I^-	1.0	4.0 ± 0.2		0	42 ± 2	
SCN^-	0.01	11.7 ± 0.3		0	17.9 ± 0.5	
NO_2^-	1.0	0.0203 ± 0.0003		0	0.212 ± 0.003	

[a] At 25 °C in water; μ maintained constant with $LiClO_4$. [b] Specific rate constants for the first substitution on the substrate by the nucleophiles Y. [c] Specific rate constants for the second substitution by the nucleophiles Y.

to counter the trans effect labilization. Since the trans effect of Me_2SO is greater than that of Me_2S, the former explanation is most likely. It is of interest to note that the reactivity of *trans*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ is at least 2 orders of magnitude less than that of its cis isomer and that the product of its reaction with iodide is *trans*-$[Pt(NH_3)_2I_2]$. This is also consistent with the dominant role of the trans effect of Me_2S in this system.

The second stage of the substitution reaction is of particular interest in that the product and the rate constant relative to the first stage depend very much on the nature of the entering nucleophile. The intermediate is a 1+ cation, and there is evidence that the rate constant for the displacement of amines by anions decreases with the positive charge of the substrate. This would account for the approximate 10-fold decrease in rate constant for the displacement of NH_3 from $[Pt(Me_2S)_2(NH_3)X]^+$ by X^- when X = Cl or Br. However, when X = I, although ammonia is still the leaving group, the second rate constant is considerably greater than the first, suggesting a very strong cis effect by iodide in the intermediate complex.[16]

The reaction of SCN^- and NO_2^- leading to the formation of *trans*-$[Pt(Me_2S)(NH_3)X_2]$, with the rate constant for the second step being considerably greater than that for the first, is consistent with the moderately high trans effect of these ligands, but the similar behavior of N_3^- without the enhanced reactivity of the intermediate presents a puzzle because it suggests that azide suppresses the displacement of the ligand cis to itself. We intend to examine this effect in more detail in other substrates.

The labilization of ammonia and, presumably, other amines by dimethyl sulfide may be of some importance in the factors that govern the antitumor activity of complexes of the type *cis*-$[Pt(am)_2Cl_2]$.[17] While it is generally believed that the reversible displacement of chloride by water allows transfer of these reagents from the blood to the cells and the subsequent displacement of H_2O or Cl^- by the appropriate donors on the DNA bases is the pathway for the binding of this material to DNA, it has generally been assumed that the amine remains bound throughout. The strong variation of the antitumor activity and toxicity on the nature of the amine was explained in terms of the variation in the solubility and hence the transport properties of the complex. However, attention should be paid to the possibility that *cis*-$[Pt(am)_2Cl_2]$ might react with the strongly nucleophilic $-S^-$ (as in cysteine) or −SMe (as in methionine) sites in protein material and generate thiolate and thioether amine complexes from which the amine could be displaced by chloride. This will offer a pathway for the deactivation of the reagent.

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Registry No. *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$, 90670-30-7; *trans*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$, 90760-61-5; Cl^-, 16887-00-6; NO_2^-, 14797-65-0; N_3^-, 14343-69-2; Br^-, 24959-67-9; SCN^-, 302-04-5; I^-, 20461-54-5.

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(16) The possibility that the observed single-stage first-order change in absorbance in the reaction *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+} + 2I^- \rightarrow$ *cis*-$[Pt(Me_2S)_2I_2] + 2NH_3$ is due to a fortuitous combination of absorbance difference and rate constant is ruled out by the experiment in which equimolar amounts of *cis*-$[Pt(Me_2S)_2(NH_3)_2](ClO_4)_2$ and NaI are allowed to react. The product on isolation and separation can be shown to consist of equimolar amounts of *cis*-$[Pt(Me_2S)_2I_2]$ and unreacted starting material. This observation invites further study.

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