

Contribution from the Istituto di Chimica Generale ed Inorganica, University of Venice, Venice, Italy, and the Chemistry Department, University College, London, England

The Cis Effect of Dimethyl Sulfoxide in the Reactions of the Cationic Complex Chloro(dimethyl sulfoxide)(1,2-diaminoethane)platinum(II) Chloride

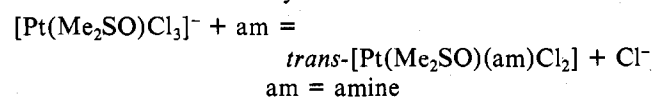
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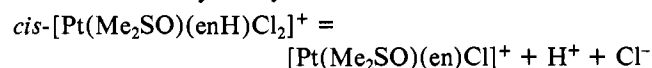
The kinetics of the replacement of the chloride in the $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})\text{Cl}]^+$ and $[\text{Pt}(\text{NH}_3)(\text{en})\text{Cl}]^+$ cations (Me_2SO = dimethyl sulfoxide, en = 1,2-diaminoethane) by NH_3 , N_3^- , NH_2OH , N_2H_4 , Br^- , I^- , SCN^- , SeCN^- , SO_3^{2-} , and $\text{SC}(\text{NH}_2)_2$ have been studied in aqueous solution at 25.0 °C. Apart from the solvolytic reaction, where both substrates have similar reactivity, the Me_2SO complex is at least 1 order of magnitude more labile than that of ammonia. The reactivity difference increases with the nucleophilicity of the entering group. The greater cis effect of Me_2SO arises from the greater nucleophilic discrimination factor of its complex.

Introduction

Attention has been paid in recent years to the role of dimethyl sulfoxide in platinum(II) chemistry. This nucleophile is known³ to react with $[\text{PtCl}_4]^{2-}$ to give the anion $[\text{Pt}(\text{Me}_2\text{SO})\text{Cl}_3]^-$ in which dimethyl sulfoxide is bound to the metal through sulfur and there are indications that the chloride trans to sulfur in the latter species is exchanged faster than the cis chloride,⁴ thus suggesting a relatively high trans effect and low cis effect. In a complete study of the platinum(II) system containing Me_2SO with chloro and aquo ligands, Elding and Gröning⁵ recently reported that Me_2SO has an intermediate kinetic trans effect and that, while the absolute magnitude of the cis effect was small in comparison, it was larger than that of other ligands. The trans effect of Me_2SO has also been explored in a kinetic study dealing with the forward and reverse reactions of the system^{6,7}



and more recently the system⁸



(en = 1,2-diaminoethane) and the analogous systems with (3-aminopropyl)ammonium and (4-aminobutyl)ammonium⁹ were investigated in order to study the effect of ring size on the kinetics of ring closing and ring opening. Making use of the high stability and inertness of chelated 1,2-diaminoethane, we have examined the reactions of nucleophiles with the complex $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})\text{Cl}]^+$ in the hope that these might lead to chloride substitution instead of trans ring opening. This indeed occurs, and we have therefore been able to investigate the kinetic cis effect of dimethyl sulfoxide on the lability of the leaving chloride and on the capacity of the substrate to discriminate between various nucleophiles.

In this paper we report the kinetics of the displacement of chloride from $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})\text{Cl}]^+$ in water at 25.0 °C by a range of neutral and charged nucleophiles, NH_3 , NH_2OH , H_2NNH_2 , N_3^- , Br^- , I^- , SCN^- , SeCN^- , SO_3^{2-} , and $\text{SC}(\text{NH}_2)_2$, and compare them with the kinetics of the analogous reactions

of the amine complex $[\text{Pt}(\text{NH}_3)(\text{en})\text{Cl}]^+$.

Experimental Section

Materials. *cis*-Dichlorobis(dimethyl sulfoxide)platinum(II) was prepared from K_2PtCl_4 and dimethyl sulfoxide by the method of Wayland et al.¹⁰ Chloro(dimethyl sulfoxide)(1,2-diaminoethane)platinum(II) chloride was prepared by the action of 1,2-diaminoethane on a methanolic solution of $[\text{Pt}(\text{Me}_2\text{SO})_2\text{Cl}_2]$ by the method of Romeo et al.¹¹

Chloro(ammine)(1,2-diaminoethane)platinum(II) Chloride. *trans*- $[\text{Pt}(\text{NH}_3)(\text{enH})\text{Cl}_2]\text{Cl}$, prepared by the method of Drew,¹² was suspended in methanol and neutralized by the careful addition of dilute aqueous sodium hydroxide solution. The product was filtered from the small amount of solid material and the filtrate evaporated to small volume under vacuum. Addition of acetone and ether precipitated the required material as fluffy white crystals which were filtered off, washed with acetone and ether, and dried in vacuo for 2 h. Anal. Calcd for $\text{C}_2\text{H}_{11}\text{N}_3\text{Cl}_2\text{Pt}$: C, 7.00; H, 3.23; N, 12.25; Cl, 20.7. Found: C, 6.92; H, 3.20; N, 12.07; Cl, 20.9.

The complexes $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})\text{X}]\text{BPh}_4$ (X = I, N_3) and $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})(\text{tu})]\text{BPh}_4$ were prepared as follows. Stoichiometric amounts of solid NaI, NaN_3 , and thiourea, respectively, were added to concentrated (approximately 0.1 M) aqueous solutions of $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})\text{Cl}]\text{Cl}$, and the resultant mixtures were stirred at room temperature for several hours, the spectra of the solutions at this time corresponded closely with those observed at the end of the kinetic runs. On the addition of an excess of aqueous sodium tetraphenylborate solution, white to yellow products were precipitated. These were filtered off, washed with water, ethanol, and diethyl ether and dried under vacuum. Care must be taken with the washing and drying if good analytical results are to be obtained. Because of its solubility in organic solvents, the complex with thiourea was washed with water only. The analytical data are collected in Table I. The products of some of the reactions between $[\text{Pt}(\text{NH}_3)(\text{en})\text{Cl}]^+$ and the various nucleophiles, with the exception of $[\text{Pt}(\text{NH}_3)_2\text{en}]^{2+}$, were isolated and characterized in a similar way. The latter was characterized as $[\text{Pt}(\text{NH}_3)_2\text{en}]\text{Cl}_2$, an intermediate in the preparation of the starting material.¹² Analytical data for these complexes are also collected in Table I.

Reagent grade LiClO_4 , KNO_3 and the other inorganic salts GPR NaBr, NaN_3 , NaI, KSCN, and Na_2SO_3 were dried over P_2O_5 in a vacuum desiccator and used without further purification. GPR NaSeCN was recrystallized twice from warm AR acetone, washed with anhydrous ether, and dried over P_2O_5 in a vacuum desiccator. AR ammonia, hydrazine hydrate and hydroxylamine sulfate solutions were diluted with water and standardized potentiometrically against HCl.

Kinetics. All of the reactions were followed spectrophotometrically by using a variety of instruments depending upon the nature of the reaction and the laboratory at which they were studied. The reactions of $[\text{Pt}(\text{Me}_2\text{SO})(\text{en})\text{Cl}]\text{Cl}$ were initiated by mixing equal volumes of a solution of the complex and one of the other reagents, previously

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Table I. Analytical Data for the Isolated Reaction Products

compd	empirical formula	% C		% H		% N	
		calcd	found	calcd	found	calcd	found
[Pt(Me ₂ SO)(en)I]BPh ₄	C ₂₈ H ₃₄ N ₂ BiOPtS	43.1	43.7	4.40	4.59	3.59	3.68
[Pt(Me ₂ SO)(en)(N ₃)]BPh ₄	C ₂₆ H ₃₄ N ₂ BOPtS	48.4	48.4	4.93	4.95	10.10	9.87
[Pt(Me ₂ SO)(en)(tu)](BPh ₄) ₂	C ₅₃ H ₅₈ N ₄ B ₂ O ₂ PtS ₂	60.8	59.9	5.58	6.22	5.35	5.61
[Pt(NH ₃)(en)I]BPh ₄	C ₂₆ H ₃₁ N ₃ BiPt	43.5	43.8	4.35	4.45	5.85	5.90
[Pt(NH ₃)(en)(N ₃)]BPh ₄	C ₂₆ H ₃₁ N ₆ BiPt	49.3	48.8	4.93	4.96	13.2	13.2
[Pt(NH ₃)(en)(SCN)]BPh ₄	C ₂₇ H ₃₁ N ₄ PtS	49.9	49.5	4.81	5.14	8.63	8.05
[Pt(NH ₃) ₂ (en)]Cl ₂	C ₂ H ₁₄ N ₄ Cl ₂ Pt	6.67	6.74	3.92	3.86	15.6	15.4

brought to the reaction temperature, in the cell of a Perkin-Elmer 575 spectrophotometer. Preliminary studies of the reactions of [Pt(NH₃)(en)Cl]Cl were made with a Unicam SP 800 spectrophotometer, but once the best experimental conditions were determined, the kinetic runs were carried out by using a Unicam SP 1750 spectrophotometer in the single wavelength mode. In this case the reactions were initiated by adding either 10 or 20 μ L of a 0.15 M aqueous solution of the complex to 3.0 cm³ of the thermostated solution of all the other reagents. In all cases the nucleophile was present in concentrations at least 10 times greater than that of the complex in order to ensure pseudo-first-order conditions. At the very low nucleophile concentrations used to establish the value of the k_1 rate constant, the concentration of the complex was reduced accordingly and special scale expansion facilities were used to record the small absorbances. Generally, interference from subsequent stages was not serious or could be minimized by a suitable choice of wavelength, and the experimental value for A_∞ , taken after 10 half-lives of the reaction, could be used. Where this was not possible the standard Guggenheim treatment, taking ΔT between 2.5 and 3 half-lives, was used. Reactions with NH₃, NH₂OH, and N₂H₄ were carried out in the presence of sufficient hydroxide to prevent protonation of the nucleophile, it previously being demonstrated that hydroxide had no effect upon the reaction. In the case of the [Pt(NH₃)(en)Cl]⁺ cation the reaction with hydrazine was complicated by the appearance of platinum metal at late stages, and the reaction with hydroxylamine was accompanied by the evolution of gas which, while only slight, prevented a reliable spectrophotometric study. Reactions with SO₃²⁻ were also carried out in the presence of sufficient hydroxide to prevent significant protonation of the nucleophile. Some reactions with N₃⁻ were carried out in the presence of hydroxide to avoid significant concentrations of HN₃ which is known to act as a catalyst in other systems. In these reactions however, addition of hydroxide did not change the observed rate constants significantly.

Results and Discussions

In all of the reactions examined, the first change, often characterized by well-defined isosbestic points, could be studied without interference from any subsequent steps which, when observed, were very much slower. The subsequent changes were most pronounced when the entering nucleophiles were also relatively strong trans effect ligands, e.g., SeCN⁻, SO₃²⁻, and thiourea. The initial spectrum always corresponded very closely to that of the substrate, and the spectrum of the reaction mixture at the end of the first stage of reaction agreed closely with that of the isolated and characterized reaction product [Pt(en)LX]ⁿ⁺ ($n = 2$ or 1 ; L = NH₃ or Me₂SO; X = entering nucleophile). It is clear that the observed kinetics relate to the displacement of the chloride, but it is necessary to consider the possibility that the rate-determining step is the displacement of one end of the coordinated 1,2-diaminoethane. The opening of the ring trans to Me₂SO has been reported elsewhere⁸ and an upper limit of $1.3 \times 10^{-5} \text{ s}^{-1}$ placed on k_1 at 30 °C. k_2 , for the entry of chloride, is $1.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C. Such a ring-opening mechanism cannot account for more than a very small part of the observed rates of reaction and, in any case, it is difficult to see how it can lead to the observed product. Opening of the ring cis to dimethyl sulfoxide could account for the observed product if it was followed by rapid ring closing involving the displacement of chloride, but this would be expected to be very much slower than opening under the trans effect of Me₂SO and is therefore

Table II. Slopes and Intercepts from the Linear Least-Squares Analysis of k_{obsd} vs. $[X^{n-}]$ for the Reaction^a [Pt(en)LCI]⁺ + Xⁿ⁻ \rightarrow [Pt(en)LX]⁽²⁻ⁿ⁾⁺ + Cl⁻

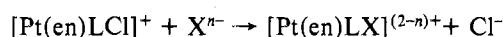
L	X	10 ³ (slope)/M ⁻¹ s ⁻¹	10 ⁵ (intercept)/ s ⁻¹	
NH ₃	NH ₃	0.95 \pm 0.07	2.3 \pm 2.4	
	N ₂ H ₄	3.32 \pm 0.24	8.3 \pm 12.6	
	N ₃ ⁻	1.52 \pm 0.08	4.2 \pm 0.6	
	Br ⁻	1.32 \pm 0.04	5.0 \pm 0.3	
	I ⁻	43.7 \pm 0.84	-4.8 \pm 3.8	
	SCN ⁻	73.9 \pm 1.7	9.1 \pm 12.3	
	SO ₃ ²⁻	99.6 \pm 8.7	-3.1 \pm 13.2	
	SC(NH ₂) ₂	184 \pm 3	1.5 \pm 9.3	
	SeCN ⁻	480 \pm 16	-8.8 \pm 53	
	(CH ₃) ₂ SO	NH ₃	8.7 \pm 0.5	6.9 \pm 8.7
		NH ₂ OH	6.8 \pm 0.3	-0.5 \pm 6.0
		N ₂ H ₄	11.7 \pm 0.3	0.5 \pm 6.2
N ₃ ⁻		18.8 \pm 1.1	6.2 \pm 6.4	
		23.7 \pm 0.1 ^b	5.6 \pm 0.04 ^b	
Br ⁻		53.4 \pm 1.1 ^c	4.5 \pm 8.5 ^c	
I ⁻		1544 \pm 80	34 \pm 24	
SCN ⁻		1336 \pm 25	-0.3 \pm 8.6	
SC(NH ₂) ₂		4476 \pm 284 ^d	-116 \pm 86 ^d	
SO ₃ ²⁻		9241 \pm 331 ^c	91 \pm 135 ^c	
SeCN ⁻	26130 \pm 2520	-490 \pm 226		

^a In water at 25.0 °C, $\mu = 0.10$ except where otherwise indicated.

^b Using data at low $[N_3^-]$, $\mu = 0.015$. ^c μ known but not held constant. Individual k_{obsd} corrected to $\mu = 0$, analysis of k_{obsd} .

^d No added electrolyte, $\mu \sim 10^{-4}$.

far too slow to be important. By the same token ring-opening processes in the ammine complex are not involved either. The observed reaction is, therefore



The plots of $\ln(A_t - A_\infty)$ against time (A_t and A_∞ being the absorbances at the wavelength of measurement at time t and at the end of the first stage of the reaction) were linear and the first-order rate constants, k_{obsd} , were obtained in the usual way. Plots of k_{obsd} against $[X]$ are linear, and the values of the slopes and intercepts obtained from a linear least-squares fit of the data are collected in Table II. Because of the slowness of the solvolytic reaction, the bulk of the data were collected under conditions where the solvolytic (k_1) pathway made an insignificant contribution to the reaction and so the errors in the analysis are greater than the magnitude of k_1 . In the reactions of both substrates with N₃⁻ and in the reaction of [Pt(en)(NH₃)Cl]⁺ with Br⁻, studies were made at low enough nucleophile concentration to allow a reasonable value to be assigned to the intercept k_1 . Since the substrate is charged, it is necessary to take account of the primary salt effect when comparing the reactivities of nucleophiles of different charge type and so the second-order rate constants have been extrapolated to zero ionic strength by using the standard relationship $\log k_2 = \log k_2^\circ + 1.02z_a z_b \mu^{1/2} / (1 + \mu^{1/2})^{-1}$, where z_a and z_b are the charges on the substrate and nucleophile, respectively. In some of the runs the ionic strength was controlled entirely by the concentration of the nucleophile salt, and in these cases k_{obsd} was corrected to zero ionic strength. Since the contribution from the k_1 path was neg-

Table III. Second-Order Rate Constants (k_2°), Corrected to $\mu = 0$, for the Reaction^a $[\text{PtL}_3\text{Cl}]^+ + \text{X}^{n-} \rightarrow [\text{PtL}_3\text{X}]^{(2-n)+} + \text{Cl}^-$

X	$10^3 k_2^\circ \text{ M}^{-1} \text{ s}^{-1}$			ratio	
	$\text{L}_3 = \text{en, NH}_3$	$\text{L}_3 = \text{dien}^c$	$\text{L}_3 = \text{en, Me}_2\text{SO}$	en, Me ₂ SO/ en, NH ₃	en, Me ₂ SO/ dien
H ₂ O ^b	0.00090	0.0011	0.0010	1.2	0.9
NH ₃	0.95		8.7	9.2	
NH ₂ OH			6.8		
N ₂ H ₄	3.3		11.7	3.5	
N ₃ ⁻	2.7	3.3	33.1		10.0
Br ⁻	2.3	4.8	54	23	11
I ⁻	77	123	2710	35	22
SCN ⁻	130	201	2350	18	12
SC(NH ₂) ₂	184	432	4480	24	10
SO ₃ ²⁻	308		9240	30	
SeCN ⁻	844	1860	45900	54	25

^a In water at 25.0 °C. ^b $k_1/55.5$. ^c Data from ref 14 using activation parameters reported therein.

ligible in these cases, the slope of the plot of k_{obsd}° against $[\text{X}]$ was equal to the value of k_2° . Values of k_2° are collected in Table III. A comparison of the reactivities of the dimethyl sulfoxide complex with those of the corresponding ammine complex shows that, apart from the solvolytic, k_1 , reaction, where the two substrates have similar reactivity, the dimethyl sulfoxide complex is more labile by an order of magnitude or so, but the actual ratio depends upon the nature of the entering nucleophile. To some extent this is in keeping with the large cis effect assigned to dimethyl sulfoxide by Elding⁵ (the term "large" in this context being in relation to other cis effects; the ratio of the trans effects of Me₂SO and ammonia is in the region of 10⁴). Because of the dependence of the magnitude of the cis effect upon the nature of the entering nucleophile it is not possible to discuss the phenomenon in terms of intrinsic reactivity alone. This problem is well-known, as for example in the reactivity of complexes of the type *trans*-[PtL₂Cl₂], where L = NH₃, PR₃, AsR₃, SR₂, SeR₂, where one is able to examine the cis effect of L upon the displacement of Cl.¹³ Here the reactivity sequences depended upon the nature of the entering nucleophile and the effect of L upon the intrinsic reactivity was in the opposite direction to its effect upon nucleophilic discrimination. However, any attempt to discuss these effects in terms of nucleophilic discrimination and intrinsic reactivity depends upon the validity of the linear free energy relationship between $\log k_2^\circ$ and n_{Pt}° (Figure 1). The absence of a value for the n_{Pt}° of water precludes the inclusion of the solvolytic rate constants (converted to second-order rate constants by dividing by 55.5) in such a plot and yet these points would exert a dominant influence upon determining the lines that best fit the data. Although it has been done occasionally, there is no justification for assuming that the n_{Pt}° value for the solvent is always zero. Apart from excluding the points for the obviously biphilic reagents, SeCN⁻ and thiourea, we are faced with other data points that depart from the LFER. There are some significant inversions of reactivity of pairs of reagents, notably thiocyanate and iodide and, more surprisingly, azide and bromide, and the nucleophilic discrimination factor, as expressed by the slope of the plot of $\log k_2^\circ$ against n_{Pt}° , is very sensitive to the weighing given to the individual points in this plot. Within the errors imposed by these problems it would appear that the dimethyl sulfoxide complex has a greater nucleophilic discrimination factor than the ammine complex. This is demonstrated more clearly by the slope of the plot of $\log k_2^\circ$ for a particular nucleophile reacting with [Pt(en)(Me₂SO)Cl]⁺ against $\log k_2^\circ$ for the same nucleophile reacting with [Pt(en)(NH₃)Cl]⁺, Figure 2,

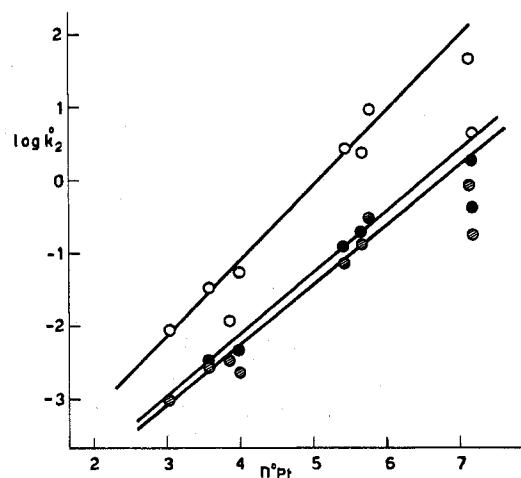


Figure 1. $\log k_2^\circ$ against n_{Pt}° for the reactions of (O) [Pt(Me₂SO)(en)Cl]⁺, (◐) [Pt(NH₃)(en)Cl]⁺, and (●) [Pt(dien)Cl]⁺.

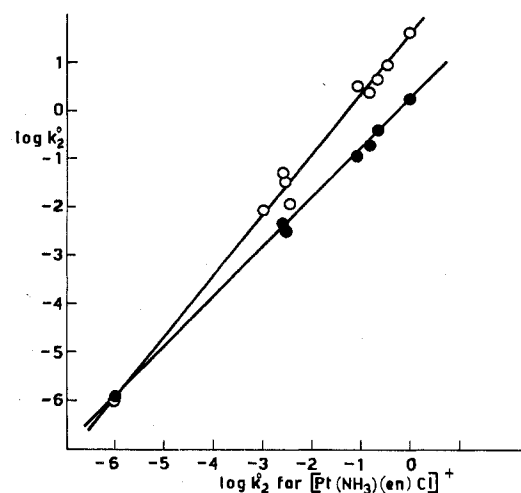


Figure 2. $\log k_2^\circ$ for the reactions of (O) [Pt(Me₂SO)(en)Cl]⁺ and (●) [Pt(dien)Cl]⁺ plotted against $\log k_2^\circ$ for the reactions of [Pt(NH₃)(en)Cl]⁺.

which allows the inclusion of the solvolytic rate constants, expressed as second-order rate constants, $k_1/55.5$. This treatment is essentially equivalent to choosing [Pt(en)(NH₃)Cl]⁺ as a new standard substrate, reacting in water at 25 °C, in order to define a nucleophilicity scale that is relevant to the +1 charged substrate in aqueous solution. This allows correction for electrostatic effects arising from the charge difference between these substrates and the original standard, *trans*-[Pt(py)₂Cl₂], for changes in the biphilic contribution arising from the charge difference and for solvation effects.

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The slope of this plot, 1.26 ± 0.05 , indicates that the nucleophilic discrimination power of the dimethyl sulfoxide complex is some 26% greater than that of the ammonia complex. A relationship between cis effect and the nucleophilic discrimination factor of the substrate indicates that we must look to the bond-forming transition state for the main site of the effect. The greater nucleophilic discrimination of the dimethyl sulfoxide complex suggests that it is better able to counteract the effects of the extra electron density brought in by the entering nucleophile than the ammonia complex.

Also included in Table III are rate constants for the replacement of Cl^- from $[\text{Pt}(\text{dien})\text{Cl}]^+$ (dien = 1,5-diamino-3-azapentane) which have been extrapolated to $\mu = 0$, by using the expression discussed above, and to 25 °C, by using published activation parameters. It is of interest to note that, while the solvolytic rate constant is similar in magnitude to those of the other two complexes, the values of k_2° are somewhat larger than the corresponding values for the $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$ cation. A log-log plot comparing these two sets of data is shown in Figure 2 and suggests that the difference in behavior is due to a small (slope = 1.038 ± 0.020) but significant difference in the nucleophilic discrimination factors of the two substrates. It has been shown that the cis effect of an amine is quite significant and depends upon its proton basicity, the least basic amine generating the most labile substrate.⁶ If one assumes that the ethylenediamine ring and one of the dien rings were equivalent and that ammonia had a stronger cis effect than the more basic $-\text{CH}_2\text{NH}_2$, then one would predict that $[\text{Pt}(\text{dien})\text{Cl}]^+$ should be less reactive than $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]^+$. The contrary observation indicates that the problem is more complicated. It might be argued that coordination of the other nitrogens in dien might greatly decrease the basicity of the third, but the relative importance of transmitting these effects through the aliphatic chains and through the platinum has been discussed elsewhere⁹ and it was concluded that the linking of the nitrogens by aliphatic chains was only of secondary importance.

The greater cis effect of the sulfur in dimethyl sulfoxide compared to that of nitrogen in ammonia cannot be ascribed to the weaker σ donation that was invoked to account for the

variation of the amine cis effect.⁶ There is strong evidence to suggest that, in the ground state at least, sulfur is the better donor. However, the greater polarizability of the sulfur may allow some transfer of charge away from the reaction center through the σ framework as the incoming group becomes bound. Although we cannot rule out the possibility of charge withdrawal through the π -acceptor properties of sulfur, it should be realized that in these cationic complexes, the nonbonding d electrons on the metal are not readily available for such interaction. The most important thing to realize is that the magnitude of the "electronic" cis effect is small and the meaningfulness of any naive attempt to characterize these electron displacements in terms of polarizations, polarizabilities, or σ or π effects is equally small.

Mention should be made in passing of the departures from the reactivity order predicted by the n_{Pt}° values assigned to the nucleophiles. The potentially biphilic reagents are less reactive than predicted because the substrate is cationic and the relevant nonbonding electrons on the metal are less available for bonding with the entering group. It is less clear why thiocyanate should be less reactive than expected toward Me_2SO complex, becoming less reactive than iodide, and why azide becomes more reactive than bromide toward the ammonia complex but not toward the dien or the Me_2SO complex. These effects are small but, nevertheless, significant. It is possible that they are a minor manifestation of the well-known "steric hindrance" cis effect but much remains to be done before this aspect of the problem can be adequately discussed.

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Supplementary Material Available: A listing of k_{obsd} as a function of $[\text{X}^-]$ and ionic strength (5 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Ammonium Dicobalto(II)-40-tungstotetraarsenate(III). Allosteric Effects in the Ligand

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Crystals of $(\text{NH}_4)_{23}(\text{NH}_4\text{As}_4\text{W}_{40}\text{O}_{140}\text{Co}_2(\text{H}_2\text{O})_2) \cdot n\text{H}_2\text{O}$ ($18 \leq n \leq 20$) are orthorhombic, of space group $Pm\bar{m}n$, with $a = 29.688$ (7) Å, $b = 23.327$ (6) Å, $c = 12.794$ (3) Å, and $Z = 2$. The structure was determined from 3989 reflections collected on an automatic diffractometer and refined by a full-matrix least-squares method to $R = 0.065$. The ligand shows two types of coordination sites: an NH_4^+ ion is in a central site (S1) and two NH_4^+ and two Co^{2+} are in external coordination sites (S2). Interactions between these sites, depending on their relative positions, are discussed. In this complex the ligand is a cyclic system consisting of four $\text{AsW}_9\text{O}_{33}$ subunits related through a pseudo $\bar{4}$ axis and joined up by four extra WO_6 octahedra.

The formation of polynuclear complexes between tungsten and arsenic or antimony at the oxidation state III has been previously reported.¹⁻³ We recently developed this study for

two reasons: (a) As^{III} and Sb^{III} have a stereochemically active lone pair of electrons which is involved in the formation of the polyanionic structures; (b) these complexes show antiviral and antitumoral activities at noncytotoxic doses "in vitro"⁴⁻⁶ and

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