warm slowly until its temperature reached −78°, at which time the dewar vessel was filled with Dry Ice. After about 12 hr at −78°, the cylinder was cooled to −183° and excess fluorine was removed. The product was then codistilled[3] to permit isolation of $SeF_4(OF)_2$. In a typical run the product consisted of 0.2 mmol of SeF_6, 0.9 mmol of SeF_5OF, and 1.0 mmol of $SeF_4(OF)_2$. The reaction was efficient for preparing about 1 mmol of $SeF_4(OF)_2$. *Caution!* When larger amounts of reactants were used, the reaction sometimes was mildly explosive and produced a high yield of SeF_6.

The compound was analyzed by allowing a 0.2211-g sample to react with excess sodium hydroxide solution in a closed glass flask. After standing about 12 hr the oxygen produced in the flask was determined by measuring the loss in weight upon pumping away the noncondensable gas while the vessel was held at −183°. The amount of hydroxide ion consumed by the reaction was determined by titrating the remaining base with 0.1 *N* HCl using bromothymol blue as an indicator. Fluoride ion was then determined by titrating with 0.2 *N* $La(NO_3)_3$ at pH 5 using an Orion fluoride-sensitive electrode. Selenium was determined gravimetrically as the element after reduction by hydroxylamine hydrochloride. *Anal.* Calcd for $SeF_4(OF)_2$: Se, 35.2; F, 50.7; OH^- consumed, 8.0 equiv/mol; O_2 liberated, 1.00 mol/mol. Found: Se, 33.5; F, 52.2; OH^- consumed, 8.09 equiv/mol; O_2 liberated, 0.97 mol/mol.

The amounts of base consumed and of oxygen produced on hydrolysis were calculated assuming that the reaction proceeded according to the equation $SeF_4(OF)_2 + 8OH^- \rightarrow SeO_4^{2-} + 4H_2O + 6F^- + O_2(g)$.

Physical Properties

Molecular Weight.—The molecular weight of the compound was determined by its vapor density. Values found were 224 and 226 (theory, 225).

Vapor Pressure and Boiling Point.—The temperature dependence of the vapor pressure, as determined by the method described by Kellogg and Cady,[4] over the range 241–286°K is given by the equation $\log P_{mm} = -(1386/T) + 7.726$, where T is the temperature in degrees Kelvin. This equation corresponds to a boiling point of 12.9°. Assuming ideal gas behavior and using the Clausius–Clapeyron equation, the latent heat of vaporization was calculated to be 6340 cal/mol, which corresponds to a Trouton constant of 22.2 cal deg^{-1} mol^{-1}.

Infrared Spectrum.—The infrared spectrum was recorded by a Beckman IR-10 spectrophotometer using a glass cell with silver chloride windows. The spectrum shown in Figure 1 has absorptions at 917 (w), 743 (s), 664 (m), and 430 cm^{-1} (s). The absorption at 917 cm^{-1} may be due to O–F stretch.[5–7] Strong absorptions occur for SeF_6 at 780 and 430 cm^{-1} and for SeF_5OF at 750 and 422 cm^{-1}.

Nuclear Magnetic Resonance Spectrum.—The nmr spectrum was obtained using a Varian Associates Model V-4311 nuclear magnetic resonance spectrometer with a 56.4-Mc oscillator. The spectrum consisted of a triplet at −47.0 ppm relative to $CFCl_3$, which was due to the four fluorine atoms in a plane around the selenium atom, and a quintuplet at −179.0 ppm relative to $CFCl_3$, which was due to the two fluorine atoms bonded to the oxygen atoms *trans* to one another. On either side of the quintuplet was a satellite about equally spaced from the center of the absorption. The relative areas of the two resonances was 2.1:1, which is close to that expected for the compound $SeF_4(OF)_2$, so it is felt that these satellites were due to the splitting of the fluorine atoms bonded to oxygen by the ^{77}Se. This spectrum shows that the two fluorine atoms of the OF groups occupy *trans* positions in the molecule.

The spin–spin coupling constant between the two sets of nonequivalent fluorine atoms was 26.8 Hz. The spin–spin coupling constant between the ^{77}Se and the four fluorine atoms in the plane had a value of 1420 Hz. This is close to ^{77}Se–F coupling constants for other compounds.[1]

Acknowledgment.—Nuclear magnetic resonance spectra were obtained with the assistance of B. J. Nist. J. E. S. thanks NASA for financial support in the form of a traineeship from 1966 to 1969.

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Kinetics of the *cis*-Dichlorodiammineplatinum(II)–Diethylenetriamine Reaction

BY J. E. TEGGINS, J. A. MCCANN, AND E. D. SMITH

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The kinetics of reactions in which the tribasic amine diethylenetriamine (dien) displaces three halide ligands in $PtBr_4^{2-}$ or $PtCl_4^{2-}$ in aqueous solutions have been reported in detail.[1,2] Because the two ammine ligands in *cis*-$Pt(NH_3)_2Cl_2$ are relatively inert[3] only two of the three nucleophilic centers in the amine would be expected to become bound to a particular platinum atom as the result of a substitution reaction. Such a product would resemble bidentate intermediates proposed for the tetrahalide substitution reactions.[1,2] Watt and Cude[4] have demonstrated that polymeric species containing platinum atoms bridged by dien groups can be obtained by the reaction of the amine with concentrated acidic solutions of $PtCl_4^{2-}$. The described *cis*-$Pt(NH_3)_2Cl_2$ reaction provides a convenient test of the tendencies for dien complexes of platinum(II) to polymerize because any monomeric product contains an unbound nitrogen center which could react with another complex ion.

Experimental Section

cis-$Pt(NH_3)_2Cl_2$ was prepared by the method of Lebedinskii

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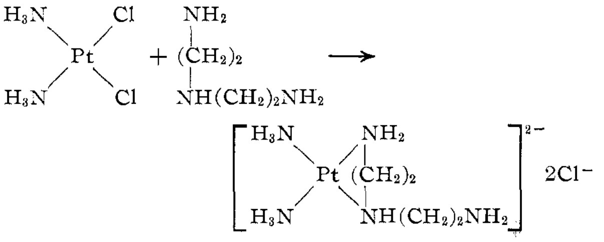
and Golovnya.[5] *Anal.* Calcd for *cis*-$Pt(NH_3)_2Cl_2$: Pt, 65.03; Cl, 23.62. Found: Pt, 65.3; Cl, 23.8. Aqueous complex solutions exhibited an absorption maximum at 300 nm and a minimum at 247 nm in agreement with the observations of Reishus and Martin.[6] Technical grade dien was vacuum distilled prior to use. The water for kinetic experiments was redistilled from alkaline permanganate solution. All other materials were of reagent grade.

Weighed amounts of finely powdered *cis*-$Pt(NH_3)_2Cl_2$ were dissolved in an aqueous dien solution which had been preequilibrated at 25°. Th pH and ionic strength of the resultant solution were controlled by the inclusion of KCl and HCl in the original amine solution. The presence of excess chloride served to inhibit the aquation of the complex.[7] The reaction was followed by a previously reported spectrophotometric procedure[1] utilizing the decrease in the absorption maximum at 300 nm as the *cis*-$Pt(NH_3)_2Cl_2$ was consumed. An isosbestic point was observed at 266 nm indicating that only two absorbing species were present in solution. A white solid was precipitated from completed reaction mixtures by the addition of an alkaline ethanol–ether mixture at 0°. Elemental analysis of this material was consistent with the simple monomeric product shown in eq 1. *Anal.* Calcd for $Pt(dien)(NH_3)_2Cl_2$: Pt, 48.28; C, 11.85; Cl, 17.28. Found: Pt, 48.2; C, 11.7; Cl, 17.1.



(1)

In all experiments dien was present in excess concentration compared to the complex ion. As previously described,[1,2] this enabled a pseudo-first-order rate constant, as defined in eq 2, to be calculated for each individual experiment.

$$\text{rate} = k_1[cis\text{-}Pt(NH_3)_2Cl_2] \qquad (2)$$

Results and Discussion

The dependence of observed first-order rate constants on reactant concentrations at constant pH is illustrated by Table I. Because of the limited solubility of the complex molecule it was not possible to vary the complex concentration by a large factor. Nevertheless, satisfactory agreement was obtained between the observed first-order constants and those predicted from the two-term law in eq 3. For the conditions in Table I k_A and k_B were equal to 2.35 × 10^{-5} sec^{-1} and

$$\text{rate} = (k_A + k_B[\text{dien}])[Pt(NH_3)_2Cl_2] \qquad (3)$$

3.90 × 10^{-4} M^{-1} sec^{-1}, respectively. This type of rate law has been interpreted many times in terms of two concurrent mechanisms.[8] The proposed path corresponding to k_A involves initial slow attack of $Pt(NH_3)_2Cl_2$ by solvent followed by a relatively rapid reaction of the resultant aquo complex with amine to produce the final product. The other term in the rate law is consistent with direct reaction between dien and $Pt(NH_3)_2Cl_2$. The agreement between the value of k_A in alkaline solution (2.35 × 10^{-5} sec^{-1}) and the values reported by Martin[6] (2.5 × 10^{-5} sec^{-1}) and Pearson[9] (3.8 × 10^{-5} sec^{-1}) for the first-order rate constant for aquation of *cis*-$Pt(NH_3)_2Cl_2$ at 25° provides support for the aquation mechanism for the amine-substitution reaction. The direct substitution of $Pt(NH_3)_2Cl_2$ by dien proceeds at approximately 10% of the rate of the substitution of $PtCl_4^{2-}$ by the same amine under comparable conditions at pH 9.6.[1] However, it has been reported that 1,10-phenanthroline reacts approximately 200 times faster with $PtCl_4^{2-}$ than with $Pt(NH_3)_2Cl_2$.[10] It would appear, therefore, that the steric restrictions imposed by the presence of two rather than four equivalent labile groups per complex molecule inhibit attack by the rigid 1,10-phenanthroline molecule to a greater extent than for the more flexible dien molecule.

TABLE I

DETERMINATION OF FIRST-ORDER RATE CONSTANTS (pH 9.6, 25.0°, μ = 0.318)

Molar concn × 10^3		10^4k_1, sec^{-1}	
$Pt(NH_3)_2Cl_2$	dien	Obsd	Calcd[a]
2.50	50	4.30[b]	4.30
...	...	4.22[b]	...
1.25	50	4.35[b]	...
...	...	4.17[b]	...
2.50	40	4.00	3.91
2.50	30	3.59	3.52
2.50	25	3.28[b]	3.33
...	...	3.39[b]	...
1.25	25	3.48[b]	...
...	...	3.27[b]	...
2.50	20	3.06	3.13
2.50	10	2.74[b]	2.74
...	...	2.77[b]	...
1.25	10	2.68[b]	...
...	...	2.68[b]	...

[a] From k_1 = 2.35 × 10^{-5} sec^{-1} + (3.90 × 10^{-4} M^{-1} sec^{-1})·[dien]. [b] Results of duplicate experiments.

The reaction rate for the substitution of *cis*-$Pt(NH_3)_2Cl_2$ by dien decreases with decreasing pH. This behavior differed from that reported for the $PtCl_4^{2-}$ and $PtBr_4^{2-}$ substitutions in that the reaction rate was too slow to follow at pH 7 whereas the tetrahalide reactions proceeded at a measurable rate down to pH 4.[1,2] It should be pointed out, however, that the rates for the reactions of dien with $PtCl_4^{2-}$ and $PtBr_4^{2-}$ also decreased with decreasing pH. Typical results are shown in Table II for a constant dien concentration. Because reaction rates for mixtures containing low dien concentrations become very slow below pH 8.5, it is difficult to estimate accurate numerical values for the individual rate constants in eq 3 for the more acidic solutions. However, the relative reaction rates for solutions containing 5 × 10^{-2} and 10^{-2} M amine are approximately constant down to pH 8. This suggests that a two-term rate law still applies under these circumstances. The concentrations of the various amine species listed in Table II are calculated from pK values quoted in a previous report.[1] It is interesting to note that the experimental rate constants parallel the total concentrations of unprotonated and monoprotonated

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TABLE II
pH DEPENDENCE OF REACTIONS AT 25°
([COMPLEX] = 2.5 mM, [dien] = 50 mM, μ = 0.318)

pH	10^5k_1, sec^{-1}	% concn[a] dien + dienH$^+$	% concn[a] dienH$_2$$^{2+}$
9.6	4.33	88	12
9.2	3.89	70	30
8.9	3.28	52	47
8.6	2.15	35	65
8.2	1.18	17	83
7.8	0.6[b]	8	92
7.0	<0.1[b]	1.2	99
6.0	No reaction in 1 week		

[a] Calculated from data in ref 1. [b] Estimated from initial rates.

amine. This observation can be explained by assuming that only amine species containing at least two unprotonated nitrogens are reactive. A possible mechanism consistent with these data could involve the initial formation of an axial bond from a nucleophilic nitrogen to platinum followed by attack by another unprotonated nitrogen site in the same amine molecule with resultant displacement of the first equatorial halide ligand. The geometrical situation would now be favorable for the rapid displacement of the second chloride ligand by a terminal nitrogen in the amine. Concurrent breakage of the initial weak axial bond would result in the product indicated in eq 1.

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Correspondence

Stereochemistry and the *cis* and *trans* Influences of Methido and Hydrido Ligands[1]

Sir:

The experimental evidence for the *trans* effect, *i.e.*, the effect of a coordinated ligand L upon the rate of substitution reactions of the ligand Y *trans* to L,[2-4] for platinum(II) complexes is overwhelming. There also is a good deal of extrakinetic structural evidence for bond-weakening effects in the ground state of complexes in which the ligands fall in essentially the same order of effectiveness as they do in their ability to labilize ligands in substitution reactions.

This communication is concerned primarily with observations on the ground states of complexes, and the assignment by Pidcock, *et al.*,[5,6] of a *trans* "influence" to a ligand, *i.e.*, the ability to weaken a *trans* bond, will be adopted.

Briefly, the various explanations for the *trans* influence of ligands may be described as (a) σ-orbital rehybridization where the platinum–L bond has a greater share of the platinum 6s orbital than the platinum–Y bond *trans* to it,[5] (b) σ-orbital rehybridization where the platinum–L bond has a greater share of a 6p orbital than the platinum–Y bond *trans* to it,[7,8] (c) the classical polarization theory,[9] and (d) the π-bonding theory.[10]

The cases to be considered here involve alkyl ligands they can be considered to be similar to the case where hydride is a ligand, and the π-acceptor model can be eliminated.

Effects analogous to those reported for the ground state of platinum(II) complexes recently have been observed with the complexes of the isoelectronic gold(III). Replacement of two halides of the square-planar anions AuX_4^- ($X^- = Cl^-, Br^-$) with two CH_3^- leads to complexes which have exclusively the *cis* structure and to a decrease in the Au–X stretching force constants by more than 30%.[11]

The ligands, L, *trans* to the methyl groups decrease in their effectiveness in reducing the gold–carbon stretching frequencies in the sequence $(CH_3)_2S > Br^- > Cl^- >$ en $> OH^- > H_2O$. Substitution of these ligands also proceeds very rapidly in the positions *trans* to the methyl groups. Oxygen-17 nmr spectra indicate that the average lifetime of a water molecule bound to $(CH_3)_2Au^+$ in aqueous solution is only *ca.* 2×10^{-5} sec.[12]

Alkylation of these d^8 transition metals is stereospecific, for not only are the gold(III) dialkyls exclusively *cis* but also only *cis*-dialkylplatinum(II) complexes seem to have been isolated. Traces of the *trans* platinum compounds have been suggested only as impurities in the main (*cis*) product.[13]

Rather similar bond-weakening effects also are found with octahedral complexes of the heavy representative elements, *e.g.*, tin(IV), but they are directed differently. Stereochemically, a *cis* effect is observed. Replacement of two halide ions of SnX_6^{2-} ($X^- = F^-, Cl^-, Br^-$) by methide ions gives complexes which have exclusively the *trans* structure and leads to a decrease in the Sn–X stretching force constants by up to 50%.[14]

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