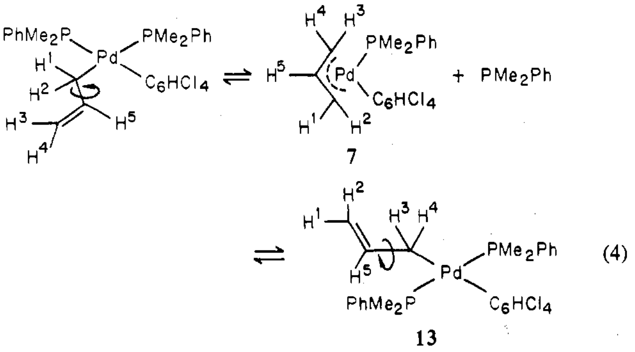

strong NMR trans influence of the C_6HCl_4 group.

Registry No. **1**, 58260-07-4; **2**, 62415-30-9; **3**, 62415-31-0; **4**, 62415-32-1; **5**, 58260-06-3; **6**, 62415-33-2; **7**, 62415-34-3; **8**, 62415-35-4; **9**, 62415-36-5; **10**, 62415-37-6; **11**, 62415-38-7; **12**, 62415-39-8; **13**, 62415-40-1; **14**, 62415-24-1; **15**, 62415-25-2; **16**, 62415-26-3; $Pt(\pi\text{-}C_3H_5)Cl(PPh_3)$, 35770-09-3.

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Oxidation of the Tetraammineplatinum(II) Cation with the Peroxodisulfate Ion and with Hydrogen Peroxide. Synthesis of Sulfatoplatinum(IV) Complexes

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Peroxodisulfate ion reacts with $Pt(NH_3)_4^{2+}$ to form primarily $Pt(NH_3)_4OHSO_4^+$ and $Pt(NH_3)_4(SO_4)_2$. The rate of reaction at 30 °C and ionic strength 1.0 is $5.1[Pt(NH_3)_4^{2+}][S_2O_8^{2-}]$. A radical mechanism involving SO_4^- and $Pt(NH_3)_4SO_4^+$ is proposed. Hydrogen peroxide reacts with $Pt(NH_3)_4^{2+}$ to produce *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ with a rate at 35 °C of $0.0010[Pt(NH_3)_4^{2+}][H_2O_2]$. A one-step two-electron oxidation mechanism is proposed. Significant amounts of *trans*-$Pt(NH_3)_4Br_2^{2+}$ are formed in both neutral and acidic $S_2O_8^{2-}$ reaction mixtures containing bromide ion but only in acidic H_2O_2 solutions.

Introduction

The oxidation of square-planar complexes of platinum(II) produces octahedral platinum(IV) complexes. The mechanisms for a variety of such reactions have been investigated in which the oxidizing agent has been another platinum(IV) complex,[2] a halogen,[3] the ions Ce^{4+}, VO_2^+, $Cr_2O_7^{2-}$, ClO_3^-, and MnO_4^-,[4] organic halides,[5] $IrCl_6^{2-}$,[6] Fe^{3+},[7] and $AuCl_4^-$.[8] Hydrogen peroxide is known to react with a variety of platinum(II) complexes to yield *trans*-dihydroxoplatinum(IV) complexes.[9] We had observed that these reactions were slow enough for convenient kinetic studies. Although studies on the rate or mechanism of peroxide oxidations of square-planar d^8 systems do not seem to have been reported, peroxide oxidations of a variety of other metal complexes have been carried out.[10-13] In most of these reactions one-electron oxidation and the formation of radicals are observed. However, hydrogen peroxide is known to oxidize many substances in a one-step two-electron process.[14]

The reactions of $Pt(NH_3)_4^{2+}$ with H_2O_2 and $S_2O_8^{2-}$ were studied in order to determine the products and mechanisms of these reactions and to enhance the understanding of the oxidation of square-planar d^8 systems.

Results

The reaction of $Pt(NH_3)_4^{2+}$ with H_2O_2 has been reported to produce *trans*-$Pt(NH_3)_4(OH)_2^{2+}$.[9,15] Consistent with this is our analysis of reaction mixtures using high-pressure ion-exchange chromatography which indicates only one product which absorbs 205-nm radiation. The rate of the reaction at 35.0 °C is $d[Pt(NH_3)_4(OH)_2^{2+}]/dt = 0.0010\cdot[Pt(NH_3)_4^{2+}][H_2O_2]$. Rate data are presented in Table I. The reaction rate is insensitive to changes in ionic strength. The rate is 30% greater in 0.10 M perchloric acid than in its absence. The activation parameters are $\Delta H^* = 13.8 \pm 0.5$ kcal/mol and $\Delta S^* = -28 \pm 2$ cal/(mol deg). The disappearance of the yellow color of a colloidal solution of the

Table I. Rate Data[a] for $Pt(NH_3)_4^{2+} + H_2O_2 \rightarrow$ *trans*-$Pt(NH_3)_4(OH)_2^{2+}$

Temp, °C	$[H_2O_2]$, M	10^4k_2, $M^{-1}\ s^{-1}$	Temp, °C	$[H_2O_2]$, M	10^4k_2, $M^{-1}\ s^{-1}$
35.2	0.030	10.0[b]	40.3	0.049	14.6
	0.030	9.3[c]		0.101	14.4
	0.098	10.1			
	0.098	10.0[d]	45.1	0.027	19.3
	0.098	13.2[e]		0.050	19.5
	0.203	9.5			
			50.2	0.027	26.0
				0.051	28.7

[a] $[Pt(NH_3)_4(ClO_4)_2] = 1.08 \times 10^{-3}$ M; $k_2 = k_{obsd}/[H_2O_2]$. [b] $[NaCl] = 0.010$ M. [c] $[NaBr] = 0.010$ M. [d] $[NaClO_4] = 0.10$ M. [e] $[HClO_4] = 0.10$ M.

Table **II.** Ion-Exchange Chromatography Data for $Pt(NH_3)_4{}^{2+}$-$S_2O_8{}^{2-}$ Reaction Mixtures[a]

$10^3[S_2O_8{}^{2-}]$, M	Height of peak eluted after		
	2.28 min	3.00 min	4.80 min
0.50[b]	0.000	0.010	0.146
1.00	0.007	0.057	0.305
2.00	0.045	0.082	0.309
5.0	0.183	0.102	0.302
10.0	0.399	0.116	0.281
5.0[c]	0.154	0.160	0.245
	0.42[e]		0.37[d]

[a] $[Pt(NH_3)_4(ClO_4)_2] = 1.03 \times 10^{-3}$ M; chromatography was run on a 25-cm Reeve Angel Partisil 10 SCX column with 0.0100 M K_2SO_4 as the eluent. Detection was by UV absorbance at 210 nm. Flow rate was 1.10 mL/min at 600 psi. The reaction was complete prior to the chromatograms. The interpretation given the peaks is 2.28 min = $S_2O_8{}^{2-}$; 3.00 min = $Pt(NH_3)\ (SO_4)_2$; 4.80 min = $Pt(NH_3)_4OHSO_4{}^+$. The weak $Pt(NH_3)_4(OH)_2{}^{2+}$ peaks were not observed in these studies. [b] A peak was also observed for unreacted $Pt(NH_3)_4{}^{2+}$. [c] $[H_2SO_4] = 0.025$ M in reaction mixture. [d] $[Pt(NH_3)_4OHSO_4ClO_4] = 1.07 \times 10^{-3}$ M. [e] $[K_2S_2O_8] = 10.0 \times 10^{-3}$ M.

radical scavenger galvinoxyl[16] is not enhanced in a solution of both $Pt(NH_3)_4{}^{2+}$ and H_2O_2.

In the absence of added acid, the rate of reaction is not altered by 0.010 M bromide or chloride ions. Moreover, the spectra of and chromatographic data on reaction mixtures indicate that there is little or no incorporation of these halide ions into the platinum(IV) products. However, when the reactions are run in 0.010 M $HClO_4$ and 0.010 M NaBr, evidence is obtained for the formation of appreciable amounts of $Pt(NH_3)_4(OH)Br^{2+}$ and *trans*-$Pt(NH_3)_4Br_2{}^{2+}$. Moreover, the rate of absorbance change becomes bromide dependent. (Data for acidic bromide solutions are not presented in Table I, since absorbance vs. time data are complicated by the presence of several reactions.) On the basis of absorbance changes at 300 nm and chromatographic data, the approximate percentages of *trans*-$Pt(NH_3)_4Br_2{}^{2+}$ ultimately formed in solutions having varying concentration of bromide and hydrogen are as follows: $[H^+] = [Br^-] = 0.010$ M, 40%; $[H^+] = 0.010$ M, $[Br^-] = 0.040$ M, 60%; $[H^+] = 0.040$ M, $[Br^-] = 0.010$ M, 55%. The $Pt(NH_3)_4Br(OH)^{2+}$ is formed as an intermediate and ultimately reacts to yield *trans*-$Pt(NH_3)_4Br_2{}^{2+}$.[3]

The products of the reaction of peroxodisulfate ion and $Pt(NH_3)_4{}^{2+}$ were determined to be $Pt(NH_3)_4(SO_4)_2$, $Pt(NH_3)_4OHSO_4{}^+$, and $Pt(NH_3)_4(OH)_2{}^{2+}$. We have isolated samples of both sulfate complexes from reaction mixtures of $Pt(NH_3)_4{}^{2+}$ and $S_2O_8{}^{2-}$. Both $Pt(NH_3)_4(SO_4)_2$ and $Pt(NH_3)_4OHSO_4{}^+$ were reported by Cleve in 1866[17] on the basis of other synthetic methods. Our samples are probably trans isomers since they hydrolyze in basic solution to give *trans*-$Pt(NH_3)_4(OH)_2{}^{2+}$. The dominant product (approximately 70% at $[Pt(NH_3)_4{}^{2+}] = 1.0 \times 10^{-3}$ M and $[S_2O_8{}^{2-}] = (1\text{–}20) \times 10^{-3}$ M) is $Pt(NH_3)_4OHSO_4{}^+$. The concentration of $Pt(NH_3)_4(SO_4)_2$ increases as the $S_2O_8{}^{2-}$ or H^+ concentration is increased. The identification of the products and the semiquantitative determination of their amounts were achieved using high-pressure cation-exchange chromatography. Fortunately anions (in this case $S_2O_8{}^{2-}$) emerge from the column before neutral molecules ($[Pt(NH_3)_4(SO_4)_2]$) and therefore the presence of the disulfato complex could be monitored. See Table II.

The reaction also generates hydrogen ion, presumably, arising from the acid dissociation of $Pt(NH_3)_4OH_2SO_4{}^{2+}$. Potentiometric titrations of concentrated solutions of $Pt(NH_3)_4OHSO_4{}^+$ and trans $Pt(NH_3)_4Cl_2{}^{2+}$ with 0.5 M perchloric acid were essentially identical, indicating that the pK_a of the aquosulfato complex is less than 2 (which is as low a pK_a as can be reliably estimated by this method). The moles of H^+ produced in the reaction of $Pt(NH_3)_4{}^{2+}$ and $S_2O_8{}^{2-}$ should therefore be a measure of the moles of $Pt(NH_3)_4OHSO_4{}^+$ produced and the values obtained were consistent with the chromatographic data. See Table III. (The formation of $Pt(NH_3)_4(OH)_2{}^{2+}$ would produce two H^+ ions; therefore the approach used in Table III would overestimate the amount of $Pt(NH_3)_4OHSO_4{}^+$.) The moles of H^+ decreased as $[S_2O_8{}^{2-}]$ was increased and when chloride or bromide ions were added to the reaction mixtures. The acidity was generated at a rate comparable with that of the absorbance change during the reaction. A slow and small subsequent increase in acidity was also noted in some instances.

Table III. $[H^+]$ Produced as a Result of the $Pt(NH_3)_4{}^{2+}$-$S_2O_8{}^{2-}$ Reaction[a]

$10^3[Pt(NH_3)_4{}^{2+}]$, M	$10^3[S_2O_8{}^{2-}]$, M	$10^3[H^+]$ produced, M	$Pt(NH_3)_4OHSO_4{}^+$ produced, %
5.0	25.0	2.45	49
5.0	10.0	3.16	63
5.0	2.50	1.78	71
5.0	1.20	1.00	83
1.00	1.00	0.69	69
1.00	1.00	0.36[b]	36
1.00	1.00	0.34[c]	34

[a] The pH values used to calculate $[H^+]$ were measured after the reaction was complete, about 10 min. This type of measurement would not lead to highly accurate values of % $Pt(NH_3)_4OHSO_4{}^+$. [b] Reaction mixture contained 2.0×10^{-3} M NaBr. [c] Reaction mixture contained 4.0×10^{-3} M NaBr.

Table IV. Rate Data[a] for $Pt(NH_3)_4{}^{2+} + S_2O_8{}^{2-} \rightarrow$ Products

Temp, °C	$10^3[S_2O_8{}^{2-}]$, M	k_2, $M^{-1}\ s^{-1}$	Temp, °C	$10^3[S_2O_8{}^{2-}]$, M	k_2, $M^{-1}\ s^{-1}$
12.0	1.00	1.8	21.0	5.0	34[e]
				5.0	19[f]
21.0	1.00	2.9[b]		5.0	3.4
	1.00	2.6[c]		10.0	3.3
	1.00	3.8[d]		20.0	3.4
	1.00	3.3			
	2.5	3.6	30.0	1.00	5.1

[a] $[Pt(NH_3)_4(ClO_4)_2] = (0.5\text{–}5.0) \times 10^{-4}$ M; $[NaClO_4] = 1.0$ M; $k_2 = k_{obsd}/[S_2O_8{}^{2-}]$. [b] $[H_2SO_4] = 0.010$ M. [c] $[H_2SO_4] = 0.010$ M; $[NaBr] = 0.010$ M. [d] $[NaH_2PO_4] = 0.0050$ M; $[Na_2HPO_4] = 0.0050$ M. [e] No $NaClO_4$ added; $\mu = 0.015$. [f] $[NaClO_4] = 0.061$ M; $\mu = 0.076$.

The absorbance of the reaction mixtures increases appreciably at wavelengths below 300 nm during the reaction; this absorbance increase conforms to first-order kinetics. A small subsequent decrease in absorbance was also a common feature. This feature does not occur where $S_2O_8{}^{2-}$ concentrations are lower than 0.002 M or when H_2SO_4 is added to reaction mixtures. It seems likely that this feature is due to the hydrolysis of $Pt(NH_3)_4(SO_4)_2$. This would also explain the larger absorbance increases observed in acidified solutions and slow increases observed in solution acidity in reaction mixtures to which no acid was added. Insoluble $Pt(NH_3)_4(SO_4)_2$ samples react rapidly at room temperature with barium ions to produce $BaSO_4$ and $Pt(NH_3)_4OHSO_4{}^+$.

The reaction has the rate law r (rate) $= 3.3[Pt(NH_3)_4{}^{2+}][S_2O_8{}^{2-}]$ at 21.0 °C in a 1.0 M $NaClO_4$ solution. Rate data are presented in Table IV. The reaction rate decreases significantly as the ionic strength is increased, a result consistent with a reaction between 2+ and 2− charged ions. The rate changed little over a pH range from about 2 to 7. The presence of 0.010 M NaBr had little effect on the reaction rate. The activation parameters are $\Delta H^* = 9.1 \pm 0.7$ kcal/mol and $\Delta S^* = -25 \pm 3$ cal/(mol deg).

The absorbance of a yellow colloidal solution of the free radical galvinoxyl in reaction mixtures decreases rapidly. This yellow color fades only very slowly in solutions containing only one of the reagents $S_2O_8^{2-}$, H_2O_2, or $[Pt(NH_3)_4](ClO_4)_2$. When galvinoxyl solutions were added at intervals after the $Pt(NH_3)_4^{2+}$ and $S_2O_8^{2-}$ solutions were mixed, the absorbance change (due to the fading of the yellow color of galvinoxyl) became smaller until no absorbance change was observed when the galvinoxyl was added several minutes after the $S_2O_8^{2-}$–$Pt(NH_3)_4^{2+}$ reaction had begun.

Bromide ion was incorporated into platinum(IV) products from both neutral (0.0050 M NaH_2PO_4 and 0.0050 M Na_2HPO_4) and acidic (0.010 M H_2SO_4) 0.010 M NaBr solutions. Approximately 25% of the product was *trans*-$Pt(NH_3)_4Br_2^{2+}$ on the basis of the absorbance of the reaction solutions at the 238- and 318-nm absorption maxima of this complex.

Sulfate ion is difficult to remove from $Pt(NH_3)_4OHSO_4^+$. Heating a solution containing barium ions at 90 °C for 0.5 h produces little $BaSO_4$. Hydrolysis is achieved with hot aqueous ammonia or hot dilute NaOH. The complex reacts only slowly with 2 M NaBr ($t_{1/2} \approx 20$ h at 60 °C) and the spectrum of the product does not correspond to that of *trans*-$Pt(NH_3)_4Br_2^{2+}$, the ultimate product expected from substitution of the sulfate ion.

Discussion

The collected data provide evidence that the mechanisms for the oxidation of $Pt(NH_3)_4^{2+}$ by H_2O_2 and $S_2O_8^{2-}$ are significantly different. We propose that the $S_2O_8^{2-}$ oxidation occurs by two one-electron steps and short-lived SO_4^- and $Pt(NH_3)_4SO_4^+$ intermediates. The H_2O_2 oxidation is proposed to occur in a single two-electron step. The rate laws for the reactions are consistent with either model.

Several pieces of evidence support a one-electron radical mechanism for the $S_2O_8^{2-}$ oxidation. (1) A reactive intermediate is present during the reaction which will decolorize the free radical galvinoxyl and also pH indicators added to monitor pH changes. The most plausible reactive intermediates are SO_4^- and a platinum(III) species. (2) The reaction produces $Pt(NH_3)_4(SO_4)_2$, a product which is difficult to explain in terms of a two-electron oxidation step. Although concerted addition of $S_2O_8^{2-}$ across $Pt(NH_3)_4^{2+}$ is possible, there is little precedent for such a reaction.[18] The more plausible product of a two-electron oxidation is $Pt(NH_3)_4OHSO_4^+$, and it does not react with sulfate ion to form $Pt(NH_3)_4(SO_4)_2$. (3) The formation of $Pt(NH_3)_4(OH)_2^{2+}$ is also difficult to explain on the basis of a two-electron oxidative step. An inner-sphere process without coordination of SO_4^{2-} seems implausible as is an outer-sphere two-electron transfer. The hydrolysis of $Pt(NH_3)_4OHSO_4^+$ is too slow to account for the $Pt(NH_3)_4(OH)_2^{2+}$. (4) In previous studies of oxidations of metal complexes by $S_2O_8^{2-}$ the mechanisms proposed have involved one-electron radical mechanisms.[11,14] The reaction rate and activation parameters for the oxidation of $Pt(NH_3)_4^{2+}$ have values which lie comfortably within the range of values reported for the other complexes.

A simple mechanism follows which is consistent with the rate law and the major products (the four ammonias in the coordination sphere of platinum are omitted).

$$Pt^{2+} + S_2O_8^{2-} \xrightarrow{\text{slow}} PtSO_4^+ + SO_4^- \tag{1}$$

$$H_2O + PtSO_4^+ + SO_4^- \xrightarrow{\text{fast}} HOPtSO_4^+ + HSO_4^- \tag{2}$$

$$PtSO_4^+ + S_2O_8^{2-} \xrightarrow{\text{fast}} Pt(SO_4)_2 + SO_4^- \tag{3}$$

$$SO_4^- + Pt^{2+} \xrightarrow{\text{fast}} PtSO_4^+ \tag{4}$$

The small amount of $Pt(NH_3)_4(OH)_2^{2+}$ observed could be produced in reactions such as

$$PtSO_4^+ + H_2O \rightarrow PtOH_2^{3+} + SO_4^{2-} \tag{5}$$

$$H_2O + PtOH_2^{3+} + SO_4^- \rightarrow HOPtOH^{2+} + HSO_4^- + H^+ \tag{6}$$

or could result from OH radicals from the reaction of sulfate radicals with water.[19] Steps 1 and 2 constitute a simple two-step redox process for the major product, $Pt(NH_3)_4OHSO_4^+$. Steps 3 and 4 introduce chain character to the reaction. This is not the only mechanism consistent with our data; in particular $Pt(NH_3)_4OHSO_4^+$ could be produced in a chain process. Any valid mechanism should be consistent with an increase in $[Pt(NH_3)_4(SO_4)_2]$ as $[S_2O_8^{2-}]$ is increased.

There are several pieces of evidence that indicate that H_2O_2 and $S_2O_8^{2-}$ oxidize $Pt(NH_3)_4^{2+}$ by significantly different mechanisms. (1) Hydrogen peroxide reacts much more slowly than $S_2O_8^{2-}$. This is in contrast to data in the literature which indicate that H_2O_2 and $S_2O_8^{2-}$ react at similar rates with metals ions such as Fe^{2+} or Cr^{2+}.[10-12] For these reactions, one-electron steps have been postulated. (2) The incorporation of bromide ion into platinum(IV) products is different in the oxidations by $S_2O_8^{2-}$ and H_2O_2. The absence of bromide incorporation in neutral H_2O_2 solutions is one striking feature. Bromide ion is an efficient scavenger for OH and SO_4^- radicals.[19] The presence of OH radicals should generate bromine atoms, which we would expect to add rapidly to $Pt(NH_3)_4^{2+}$. (Bromine reacts very rapidly with $Pt(NH_3)_4^{2+}$ to yield $Pt(NH_3)_4(OH)Br^{2+}$.[3]) The formation of significant amounts of *trans*-$Pt(NH_3)_4Br_2^{2+}$ in neutral solutions containing Br^- and $S_2O_8^{2-}$ ions is also striking. $Pt(NH_3)_4Br(OH)^{2+}$ cannot be an intermediate in this reaction since it reacts negligibly slowly with bromide ion in neutral solution. Radical mechanisms involving $Pt(NH_3)_4Br^{2+}$ and Br can account for this product as could the plausible reaction of Br^- with this unknown complex, $Pt(NH_3)_4Br(SO_4)^+$. The formation of *trans*-$Pt(NH_3)_4Br_2^{2+}$ in acidic bromide solutions of H_2O_2 is probably a consequence of the acid-catalyzed reaction of H_2O_2 with Br^- to yield Br_2. Preliminary studies indicate this reaction is fast enough to account for our results. (3) The absence of evidence for reactive intermediates suggests that OH radicals and Pt(III) complexes are not produced by oxidation with H_2O_2. (4) The rate of oxidation by H_2O_2 is much slower than most studied one-electron oxidations of metal ions by peroxides.[10-12] The inability of H_2O_2 to react rapidly with $Pt(NH_3)_4^{2+}$ by a one-electron process could lead to the domination of a two-electron mechanism. We do not have an explanation for why the one-electron mechanism is so slow in this case and the resulting marked difference in reactivities of H_2O_2 and $S_2O_8^{2-}$.

Another result which surprised us was the inertness of the platinum–sulfate bond in $Pt(NH_3)_4OH(SO_4)^+$. Simple displacement by bromide ion is very slow if it occurs at all. Even hydrolysis in 0.1 M NaOH is not rapid at 25 °C.

Experimental Section

Preparation of Compounds. Tetraammineplatinum(II) perchlorate and its precursors were prepared by published methods.[20]

Disulfatotetraammineplatinum(IV). Aqueous solutions (20 mL containing 2.70 g (8.08 mmol) of $[Pt(NH_3)_4]Cl_2$ and 180 mL containing 2.52 g (8.09 mmol) of Ag_2SO_4) were mixed with stirring. The filtrate from this solution was mixed with 1.92 g (8.4 mmol) of $(NH_4)_2S_2O_8$ dissolved in a minimum volume of water. After 5 min the solution became cloudy. The volume of the solution was reduced to 25 mL at room temperature under vacuum. The precipitate was collected and dried under vacuum (1.48 g). This product was suspended in water; the solution pH was adjusted to 4 with NH_3. After 30 min the precipitate was collected and dried overnight under vacuum. The yield was 1.26 g (34%) of white insoluble powder. Anal. Calcd for $[Pt(NH_3)_4(SO_4)_2]$: Pt, 42.84; N, 12.30; H, 2.66; S, 14.08. Found: Pt, 42.78; N, 12.31; H, 2.70; S, 13.96.

Hydroxosulfatotetraammineplatinum(IV) Perchlorate. Saturated solutions of 2.84 g (8.49 mmol) of $[Pt(NH_3)_4]Cl_2$ and 3.52 g (17.0 mmol) of $AgClO_4$ were mixed. To the filtrate from this solution was added 2.86 g (8.49 mmol) of $Ba(ClO_4)_2$. To this solution was added a solution of 1.95 g (8.55 mmol) of $(NH_4)_2S_2O_8$. The 200 mL of solution had a pH of 1.3 and slight precipitate which was removed by filtration after 5 min. The pH of the filtrate was adjusted to 6 with NH_3 and the volume reduced to 50 mL under a vacuum. A slight precipitate was removed. The volume was then reduced to 20 mL and the product collected and dried under vacuum. The yield was 1.68 g (42%) of a white crystalline product. Anal. Calcd for $Pt(NH_3)_4OHSO_4ClO_4$: Pt, 41.01; N, 11.78; H, 2.76; S, 6.74; Cl, 7.45. Found: Pt, 41.0; N, 11.95; H, 2.81; S, 6.49; Cl, 7.62.

Analyses were done by Atlantic Microlab, Inc. Chemicals used in kinetic studies were reagent grade. Deionized water was used in all studies.

Kinetic Measurements. Kinetics were followed spectrophotometrically. The H_2O_2 reactions were monitored primarily at 260 nm with a Beckman DU instrument modified with a Gilford 220 absorbance indicator. The $S_2O_8^{2-}$ reactions were monitored at 240, 260, and 280 nm with a Durrum stopped-flow spectrometer. Reactions in which *trans*-$Pt(NH_3)_4Br_2^{2+}$ was a significant product were often studied at 318 nm. The temperature of the cell compartment varied less than ±0.02 °C. Reaction solutions were prepared in normal room light and no attempt was made to exclude air. Several studies at each set of conditions were generally made and average results are reported. Duplicate results reproduced well with deviations seldom being as large as 10%. Infinite-time absorbances of kinetic solutions were consistent with those expected for the reaction products; however $Pt(NH_3)_4OHSO_4^+$ and $Pt(NH_3)_4(OH)_2^{2+}$ do not have distinctive spectra.

Reactions were studied under pseudo-first-order conditions. Rate data were analyzed by a Gauss–Newton nonlinear least-squares fit to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-kt)$. Absorbance vs. time data covering 3–4 half-lives were in general used and the fit to the equation was normally within the uncertainty of the absorbance measurements.

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Registry No. $Pt(NH_3)_4(SO_4)_2$, 62623-71-6; $[Pt(NH_3)_4OHSO_4]ClO_4$, 62571-46-4; *trans*-$Pt(NH_3)_4(OH)_2^{2+}$, 62623-70-5; $[Pt(NH_3)_4]Cl_2$, 13933-32-9; $S_2O_8^{2-}$, 15092-81-6; H_2O_2, 7722-84-1.

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Kinetics of the Displacement of Chloride by Amine under the Trans Effect of Dimethyl Sulfide in Square-Planar Platinum(II) Complexes

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The kinetics of the reaction $Pt(SMe_2)Cl_3^- + am \rightarrow$ *trans*-$Pt(SMe_2)(am)Cl_2 + Cl^-$ (am is one of a series of 15 amines covering a wide range of basicity) have been studied in methanol at 30.0 °C at $\mu = 0.505$ ($LiClO_4$). The reaction follows the usual two-term rate law $-d \ln [Pt(SMe_2)Cl_3^-]/dt = k^f_1 + k^f_2[am]$. k^f_1 ($= 1.2 \times 10^{-3}\ s^{-1}$) is essentially independent of the nature of the amine, while k^f_2 is not very sensitive to the properties of the monofunctional amines. Bifunctional amines, such as morpholine, ethylenediamine, piperazine, and ethanolamine are considerably more reactive. The replacement of the amine in *trans*-$Pt(SMe_2)(am)Cl_2$ by chloride in the presence of acid is too slow to follow, except in the case of the weakest bases. The properties of the dimethyl sulfide system are compared with those previously reported for the analogous dimethyl sulfoxide system. Dimethyl sulfoxide is some 10–20 times more effective as a trans-labilizing ligand when chloride is being replaced by amine but the difference is much greater in the reverse reaction.

Introduction

Some time ago we reported the kinetics of a series of reactions involving the replacement of chloride by amines (and the reverse reaction) in complexes containing dimethyl sulfoxide.[2,3] Although our interest was directed toward the ways in which the nature of the amines affected the rates and equilibria, the strong trans-labilizing effect of S-bonded dimethyl sulfoxide was recognized and discussed. In an extension of these studies of the *trans effect* in complexes where steric effects are minimized, we wish to compare the sulfoxide with a thioether which we expect to exert a weaker transition-state *trans effect* (due to its lower π-acceptor capacity) perhaps coupled with a marginally increased ground-state *trans effect* (*trans influence*). To this end we report the kinetics of the reaction $Pt(Me_2S)Cl_3^- + am \rightarrow$ *trans*-$Pt(Me_2S)(am)Cl_2 + Cl^-$ where am represents an amine.

Experimental Section

Preparations. Tetraethylammonium trichloro(dimethyl sulfido)platinate(II) was prepared by a modification of the method of Goodfellow, Goggin, and Duddell[4] in which $Pt_2Cl_4(Me_2S)_2$, prepared by the method of Chatt and Venanzi[5] but not isolated, was treated with Et_4NCl. $Pt_2Cl_4(C_2H_4)_2$[6] (1.0 g, 1.7 mmol) was dissolved in dichloromethane (60 cm^3) and the solution cooled to −70 °C. Dimethyl sulfide (0.25 cm^3, 3.4 mmol) was added, and the solution was shaken and allowed to warm up to room temperature. $Et_4NCl \cdot H_2O$ (0.63 g, 3.4 mmol) was added, and the solution was stirred for 2 days and