Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 5. Formation, Isomerization, and Sulfite Addition Reactions of the Oxygen-Bonded (Sulfito)pentaammineplatinum(IV) Ion and the Subsequent Intramolecular Redox Reactions of the Sulfur-Bonded Intermediate, the cis-Bis(sulfito)tetraammineplatinum(IV) Ion[1,2]

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The aquopentaammineplatinum(IV) complex ion reacts in aqueous sulfite solutions to produce the O-bonded complex ion $[Pt(NH_3)_5OSO_2]^{2+}$. Both SO_2 and HSO_3^- take part in the process, according to the expression rate = $(k_1[SO_2] + k_2[HSO_3^-])[Pt(NH_3)_5OH^{3+}]$. The relatively large rate constant values (k_1 and k_2 are 6.8×10^6 and 5.9×10^2 M^{-1} s^{-1}, respectively, at 25 °C) are consistent with a mechanism of direct S(IV) addition to the Pt–OH moiety without metal–oxygen bond rupture. The product of this reaction (which has been isolated and identified as $[Pt(NH_3)_5OSO_2]SO_3 \cdot 2H_2O$) undergoes relatively slow rearrangement in the presence of excess sulfite (but independent of its concentration) to form a bis(sulfito) complex, which was isolated and identified as cis-$[Pt(NH_3)_4(SO_3)_2] \cdot 2H_2O$. The kinetic characteristics of the reaction suggest that there is rapid cis-NH_3 replacement by water (on heating to reaction temperature) followed by rate-determining O-bonded to S-bonded sulfito isomerization ($k = 4.0 \times 10^{-5}$ s^{-1} at 25 °C), followed by rapid replacement of the cis-aquo ligand by sulfite to yield the observed bis(sulfito) complex. The cis-bis(sulfito) species is stable to internal redox in neutral solution at room temperature. However, at elevated temperatures in acidic solution, a single-step two-electron transfer takes place to yield a Pt(II) product (which was isolated and identified as $[Pt(NH_3)_3SO_3] \cdot 2H_2O$) according to the rate law rate = $k[Pt(NH_3)_4(SO_3)(SO_3H)^+]$. In this, k has the value 5.6×10^{-4} s^{-1} and the pK of cis-$[Pt(NH_3)_4(SO_3)(SO_3H)]^+$ is approximately 2 (both figures extrapolated from the 45–55 °C experimental range to 25 °C). The mechanism appears to involve simultaneous detachment of an SO_3 molecule and its trans-NH_3 ligand (accompanied by rapid hydration of SO_3 to sulfate) to generate the observed planar $Pt(NH_3)_3SO_3$ product.

Introduction

During recent years, a number of systems have been studied in our laboratory and by collaborators elsewhere that involve the reaction of various aquo transition-metal complex ions with free sulfite in aqueous solution. The studies so far reported include reactions of the aquopentaammine complexes of cobalt(III),[4] rhodium(III),[5] and chromium(III),[5] along with $(OH_2)_2(tren)Co^{III}$[2,6] (tren $\equiv$ 2,2′,2″-triaminotriethylamine), and $(\alpha\beta S)$-$(OH_2)(tetren)Co^{III}$[7] (tetren $\equiv$ tetraethylenepentamine). The kinetic data show that in each instance the most significant first step in the overall process is very rapid nucleophilic attack by ligand hydroxide on dissolved SO_2 to form an O-bonded sulfito complex, a reaction which is readily reversed by immediate acidification. Metal-to-oxygen bonding is not involved in this reversible process, as recently confirmed by NMR measurements.[8] Subsequent reactions in the cobalt(III) systems comprise O-bonded to S-bonded isomerization, internal redox, sulfite ion addition, or a combination of these processes depending on the pH and the nature of the N_4 or N_5 ligand grouping.

Platinum(IV) is found in many very stable octahedral complexes that are direct structural analogues of cobalt(III) species but contrast greatly in other chemical properties since platinum(IV) is a two-electron oxidant which on reduction produces stable square-planar platinum(II) complexes. We therefore expected aquopentaammineplatinum(IV) to behave somewhat differently from its cobalt(III) analogue mentioned above, and the purpose of our present study was to identify these contrasts. We have been able to isolate for the first time a relatively stable O-bonded sulfito complex, evaluate the mechanism of its formation and conversion to an S-bonded bis(sulfito) product, and determine the nature of the internal double-electron transfer within the latter, which yields square-planar platinum(II) final products.

Experimental Section

Materials. All chemicals used were of reagent grade. Solid $Na_2S_2O_5$ (Baker Analyzed) was the source of sulfite; this salt is very stable in the solid form but hydrates rapidly and completely when dissolved in water to yield sulfite.[4] The laboratory distilled water was further purified by passage through a mixed-bed ion-exchange column.

Preparation and Characterization of Complexes. Aquopentaammineplatinum(IV) perchlorate was prepared from H_2PtCl_6 by a method based on procedures described in ref 9, as follows: H_2PtCl_6 is dissolved in a minimum quantity of water, and ammonia solution is added to it dropwise until it is neutral. The yellow precipitate of $(NH_4)_2[PtCl_6]$ is filtered off and washed with cold water. Fifteen grams of solid $(NH_4)_2[PtCl_6]$ is mixed with 30 g of Na_2HPO_4, 300 mL of 20% ammonia, and 450 mL of water. The mixture is slowly heated to boiling. The resultant solution is cooled to room temperature, and white crystals of $[Pt(NH_3)_5Cl]PO_4$ are filtered off and washed successively with cold water, alcohol, and ether. The $[Pt(NH_3)_5Cl]PO_4$ so obtained is dissolved in a minimum quantity of warm dilute hydrochloric acid. The solution is cooled, and concentrated HCl is added dropwise until white crystals appear at the surface of the solution. The solution is further cooled, and the white needle-shaped crystals of $[Pt(NH_3)_5Cl]Cl_3$ are filtered off, washed with cold water, and dried in a desiccator. This dried solid is again dissolved in a minimum quantity of water, and 3% NaOH solution is added dropwise until the initially formed white precipitate dissolves. The colorless solution is boiled for about 5 min, and concentrated $HClO_4$ is added dropwise to this hot solution until turbidity appears. Further additions of concentrated $HClO_4$ are made until precipitation is complete. The mixture is cooled in an ice bath, and the white crystals of aquo-

(1) Preliminary reports based on this work were presented at the 182nd Meeting of the American Chemical Society, New York, Aug 1981, and at the Third International Conference on Mechanisms of Reactions in Solution, Canterbury, England, July 1982.
(2) Preceding paper in this series: El Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 4251.
(3) Present address: Department of Chemistry, University of the West Indies, Kingston 7, Jamaica.
(4) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880.
(5) van Eldik, R. *Inorg. Chim. Acta* **1980**, *42*, 49.
(6) El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 1660.
(7) Dash, A. C.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 3160.
(8) van Eldik, R.; von Jouanne, J.; Kelm, H. *Inorg. Chem.* **1982**, *21*, 2818.
(9) "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: West Berlin, 1957; Vol. 68D, pp 476–484.

Table I. Elemental Analysis

complex	% found				% calcd			
	Pt	N	S	Cl	Pt	N	S	Cl
$[Pt(NH_3)_5(OH_2)](ClO_4)_4$	28.02	9.69		16.68^a	28.03	10.06		20.40
$[Pt(NH_3)_5OSO_2]SO_3 \cdot 2H_2O$	40.56	14.21	13.72		40.98	14.70	13.44	
cis-$Pt(NH_3)_4(SO_3)_2 \cdot 2H_2O$	42.88	12.41	14.50		42.51	12.20	13.94	
$Pt(NH_3)_3SO_3 \cdot 3H_2O^b$	51.63	12.30	9.76		51.33	11.05	8.42	
$Pt(NH_3)_3SO_3 \cdot 2H_2O^c$	53.57	11.81	9.95		53.87	11.60	8.84	

^{a} Low value may be due to presence of some $[Pt(NH_3)_5OH](ClO_4)_3$ impurity since the pK of the aquo complex is rather low (~4). ^{b} Obtained as a reduction product of cis-$Pt(NH_3)_4(SO_3)_2$. ^{c} Obtained as a product of sulfite reaction with $[Pt(NH_3)_4]Cl_2$.
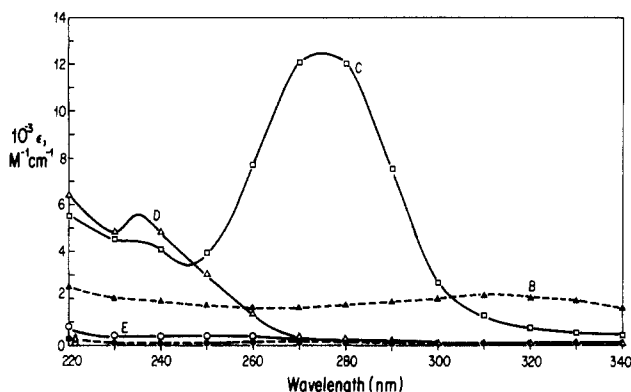

Figure 1. Spectral shifts during the reaction of $[Pt(NH_3)_5OH]^{3+}$ with aqueous sulfite: (A) original reactant; (B) $[Pt(NH_3)_5OSO_2]^{2+}$; (C) cis-$[Pt(NH_3)_4(SO_3)_2]$; (D) $[Pt(NH_3)_3SO_3]$; (E) final aquation product.

pentaammineplatinum(IV) perchlorate are filtered off, washed with cold water, and dried. The complex is recrystallized by dissolving it in a minimum amount of hot water and precipitating it with concentrated $HClO_4$, repeating the procedure outlined above.

The chloropentaammineplatinum(IV) complex obtained as an intermediate during the preparation of the aquopentaammine species gave a λ_{max} (measured by a Cary 118C spectrophotometer) at 283 nm ($\epsilon = 190$), which is in complete agreement with the literature data for this complex.[10] Aquopentaammineplatinum(IV) perchlorate shows no UV/vis spectral features. Elemental analyses[11] (Table I) for Pt, N, and Cl were in satisfactory agreement with the calculated values for $[Pt(NH_3)_5OH_2](ClO_4)_4 \cdot H_2O$.

When an aqueous solution of the aquo complex is reacted with aqueous sulfite, a series of reactions occur which differ enough in rate so that consecutive spectra can be obtained corresponding to various intermediates in the overall reaction, as shown in Figure 1. Each of the intermediates was separately synthesized and identified, the experimental details for which are given in the following paragraphs.

$[Pt(NH_3)_5(OSO_2)]SO_3 \cdot 2H_2O$ (I). A 0.125-g quantity of $[Pt(NH_3)_5OH_2](ClO_4)_4$ is dissolved in 10 mL of water by slightly warming the solution, and its pH is adjusted to 6.5 with 0.1 M NaOH. In a separate test tube is placed 1.2 mL of 0.5 M $Na_2S_2O_5$ solution, its pH also adjusted to 6.5 with 0.1 M NaOH. An almost instantaneous color change to yellow results when the two solutions are mixed. The solution is stirred for about 5 min, and 95% methanol is added with stirring until a yellowish white solid starts to precipitate. More alcohol is added to complete the precipitation, and the solid is recovered by centrifugation. This solid is washed several times with a cold 50% alcohol/water mixture and then with water containing a little ammonia until free of excess sulfite. The yellow powder obtained at this stage is dried over silica gel in a desiccator. The composition of the complex was checked by microanalysis (see Table I) and by precipitation tests with Ba^{2+} which proved that half the sulfite present is in the free ionic form. Its UV/vis spectrum (Figure 1) exhibits a broad peak at 310 nm ($\epsilon = 2090$). Its O-bonded structure was confirmed by IR data (Table II) measured with a Beckman Model 4240 spectrophotometer.

cis-$Pt(NH_3)_4(SO_3)_2$ (II). This bis(sulfito)tetraammineplatinum(IV) complex is the product of the further reaction of compound I in aqueous sulfite. To a warm 10-mL solution containing 0.125 g of $[Pt(NH_3)_5OH_2](ClO)_4$ is added 1.2 mL of 0.5 M $Na_2S_2O_5$ solution (pH

Table II. Vibrational Frequencies (cm^{-1}) of Some New Platinum(1V) and -(II) Complexes Containing the Sulfite Ligand

complex	structure	found	reported^a	
$[Pt(NH_3)_5OSO_2]SO_3$	SO_3^{2-}	1010	1010	$\nu_3(E)$
		961	961	$\nu_1(A_1)$
		633	633	$\nu_2(A_1)$
		490	496	$\nu_4(E)$
	O-bonded	955	902^b	$\}\nu_3$
		915	862	
		990	989	ν_1
		666	673	ν_2
		506	506	$\}\nu_4$
		485	460	
$[Pt(NH_3)_4(SO_3)_2]$	S-bonded	1110–	1082–	ν_3
		1090	1057^c	
		970	964	ν_1
		625	660	ν_2
		514	540	ν_4
$[Pt(NH_3)_3SO_3]$	S-bonded	1060–	1110^d	ν_3
		1040		
		955	985	ν_1
		633	633	ν_2
		520	519	ν_4

^{a} Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1970; p 177. ^{b} $Tl_2[Cu(SO_3)_2]$. ^{c} $K_6[Pt(SO_3)_4] \cdot 2H_2O$. ^{d} $[Co(NH_3)_5SO_3]Cl$.

~3.5), which results in the almost instantaneous formation of the O-bonded sulfito complex (I) as indicated by its yellow color. The yellow solution is thermostated at 35 °C, and periodically small amounts are withdrawn and the growth of a sharp peak at 274 nm is monitored. As the reaction leading to the formation of the bis-(sulfito) complex is proceeding, the 274-nm peak grows in intensity until finally a maximum is reached, after which it begins to fall off, indicating the onset of a second slow reaction. At this maximum point, excess ethanol is added to the solution, which results in the precipitation of a yellow solid. This is collected on a fritted-glass funnel and washed several times with water until chemical tests for free sulfite are negative. The yellow solid is recrystallized from water to yield a bright yellow microcrystalline product. Its solution shows a sharp peak at 274 nm ($\epsilon = 12\,380$) (Figure 1). Microanalysis of this complex is given in Table I, and proof of its S-bonded nature is provided by the IR data (Table II). The rather unexpected[12] cis geometry of the above complex was established by use of Raman[13] and IR spectroscopy as follows. An authentic sample of $trans$-$[Pt(NH_3)_4(SO_3)_2]$ is prepared by the peroxide oxidation[14] of $[Pt(NH_3)_4]^{2+}$ to $trans$-$[Pt(NH_3)_4$-$(OH)_2]^{2+}$. The latter complex ion is then reacted with aqueous sulfite. The IR and Raman spectra of this product were then compared with those of compound II with the results recorded in Table III. It is clear that compound II has a much more complicated IR spectrum and fewer IR/Raman coincidences than does the trans isomer, confirming the cis geometry of the former less-symmetrical species.

$Pt(NH_3)_3SO_3$ (III). This is the reduction product of the bis-(sulfito)tetraammineplatinum(IV) complex described above. An easy method to prepare a pure sample of the species involves use of a concentrated solution of aquapentaammineplatinum(IV) perchlorate

(10) Jørgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 518.
(11) Galbraith Laboratories, Inc., Knoxville, TN 37921.

(12) Typically, Co(III) S-bonded sulfito complexes exhibit strong trans effects in subsequent substitutions. See: Spitzer, U.; van Eldik, R. *Inorg. Chem.* **1982**, *21*, 4008 and references quoted therein.
(13) Measurements made on a Spex 14018 Raman spectrophotometer, courtesy of Prof. P. Prasad of this department.
(14) Reference 9, p 486.

Table III. Comparison of Infrared and Raman Spectra of cis- and trans-$Pt(NH_3)_4(SO_3)_2$

cis		trans	
IR, cm^{-1}	Raman, cm^{-1}	IR, cm^{-1}	Raman, cm^{-1}
415	425	415	
454	454	497	
488	461		
514 (ν_4)	545	563	562
585	563		565
612	638		
625 (ν_2)	642	622	635
	660		
783			
865			
958	983	920	
970 (ν_1)		966	
1005	1005	1003	1007
1038	1018		1013
	1030		1017
1110–1090 (ν_3)		1125–1117	

into which is passed SO_2 gas. The solution turns yellow, and after about 5 min a yellow solid is found to precipitate. At this stage passage of SO_2 is discontinued and the solution is heated to 50–60 °C on a hot plate with continuous stirring. The yellow color of the solution fades slowly until it becomes colorless, and on cooling of the solution, a white solid precipitates, which is recovered by filtration. The solid is washed with ethanol and ether and then dried in a desiccator. A second crop of white solid can be recovered from the filtrate by the addition of more alcohol. Microanalysis (Table I) of the complex gives the expected Pt:N:S ratio of 1:3:1. The spectrum of the complex exhibits a UV peak at 234 nm (ϵ = 5650) (Figure 1), and its IR spectrum confirms the retention of one S-bonded sulfito ligand (Table II).

$Pt(NH_3)_3SO_3$ can also be prepared by an altogether different procedure. A 0.10-g quantity of tetraammineplatinum(II) dichloride is dissolved in 3 mL of water, and 5 mL of 0.5 M $Na_2S_2O_5$ solution is added to it. The solution is stirred and allowed to stand for 1 h, during which time needle-shaped crystals are produced. These crystals are isolated, washed with ethanol and ether, dried in a desiccator containing silica gel, and identified by analysis (Table I) and by their UV/vis and IR spectra.

During long standing in aqueous solution, $Pt(NH_3)_3SO_3$ slowly loses its spectral peak at 234 nm, ending up with nearly zero absorbance (curve E of Figure 1) over the whole range of wavelengths examined, and 1 equiv of free sulfate appears in the solution. We made no detailed kinetic or other study of this reaction, which presumably involves the hydrolysis of ligand sulfite either before, during, or after oxidation to sulfate. The final product is thus the aquotriammineplatinum(II) species, which is known to have no observable spectral peaks in the range of our measurements.

Rate Measurements. All rate measurements were made at an ionic strength of 1.0 M ($NaClO_4$) and over acidity and temperature ranges as given in the Results and Discussion section. The procedure for the SO_2-uptake study was essentially identical with that described earlier for similar systems.[2,4–6,8] When self-buffered sulfite media were used, one of the storage syringes of the automated Durrum Model 110 stopped-flow assembly contained the aquo complex solution adjusted to I = 1.0 M and the other contained the sulfite buffer adjusted to the same ionic strength. Runs were made under pseudo-first-order conditions in the usual manner, with $[Pt(IV)]_T$ = 1 × 10^{-4} M in all kinetic experiments. The SO_2-elimination process was followed by a "pH-jump" procedure.[6] In this method, the O-bonded (sulfito)pentaammineplatinum(IV) species is prepared in situ by dissolving appropriate amounts of $[Pt(NH_3)_5H_2O](ClO_4)_4$ and $Na_2S_2O_5$ in the molar ratio 1:2 and immediately adjusting the pH to 6.2 ± 0.1 and the ionic strength to 1 M. This solution is stored at 0–5 °C to minimize the isomerization reaction to form the S-bonded form. The rates of the SO_2-uptake and -elimination processes were measured at 310 nm. pH determinations were made immediately after the stopped-flow kinetic runs by mixing equal volumes of the reactants with use of the stopped-flow drive syringes and keeping the resulting product solution thermostated while pH measurements are made.

The kinetics of the formation of $Pt(NH_3)_4(SO_3)_2$ from $[Pt(NH_3)_5OSO_2]^{2+}$ was followed in citric acid/citrate buffer (phosphate/citrate buffer, used in some of the initial runs, was found to have a retarding effect on the rate) at a pH range of 2.7 to 5.5, with a Cary 118 UV/visible spectrophotometer equipped with a thermostated cell compartment. To commence kinetic runs under conditions such that half-times were long (k_{obsd} < 10^{-3} s^{-1}), known volumes of the aquo complex solution were added to an aqueous solution already containing the other reactants ($Na_2S_2O_5$, $NaClO_4$, and the buffer) at the temperature of the run. The resulting solution was made up to 10 mL and transferred quickly to a cuvette and placed in the cell compartment for observation. Similar results can be obtained by using $[Pt(NH_3)_5OSO_2]SO_3\cdot2H_2O$ instead of $[Pt(NH_3)_5OH_2](ClO_4)_4$ as the starting material. The elapsed time from mixing (t = 0) to the first measurement was approximately 2 min. Data was collected in the form of absorbance vs. time plots. In a number of runs complete spectral curves were recorded over a series of times within the wavelength range 300–240 nm. The rate of isomerization was followed at different wavelengths in this range, and it was found that there was no wavelength dependence of the observed rate constant. Therefore, all the rate data presented in this report for the formation of the bis(sulfito) complex have been collected at 274 nm, where there is a sharp increase in absorbance as the reaction proceeds.

The kinetics of the reduction of $Pt(NH_3)_4(SO_3)_2$ to the Pt(II) complex, $Pt(NH_3)_3SO_3$, was studied spectrophotometrically at 274 nm, where the Pt(II) complex formation is associated with a substantial decrease in absorbance. The experimental procedure of the rate measurement is very similar to that employed for the study of the isomerization kinetics. The observed pseudo-first-order rate constants were calculated from ln ($A_t - A_\infty$) vs. t data (A_t and A_∞ are the absorbances of the solutions at times t and infinity, respectively) by using a least-squares program. In general the plots were linear up to at least 3 or 4 half-times.

Determination of the Acid Dissociation Constants. The values of the acid dissociation constant of $[Pt(NH_3)_5OH_2]^{4+}$, K_3, were determined by titrating a 4 × 10^{-3} M complex solution of ionic strength I = 1.0 M ($NaClO_4$) with 0.1 M NaOH. The pH measurements were made with a Fisher Accumet Model 420 digital pH/ion meter equipped with a Fisher combination electrode. The pH meter was standardized against commercially available Fisher standard buffers. The values of pK_3 were found to be 4.10 ± 0.05, 4.17 ± 0.04, and 4.23 ± 0.05 at 25, 20, and 15 °C, respectively, which are in good agreement with values reported elsewhere.[15] For the analysis of our rate data the values of the first and second dissociation constants of "sulfurous acid" were taken to be 1.79, 1.85, and 1.90 at 15, 20, and 25 °C (I = 1.0 M), respectively, for pK_1, and pK_2 = 6.3 ± 0.1 (15–25 °C), as reported in the literature.[6,7]

Results and Discussion

The formation and decomposition reactions of the O-bonded (sulfito)pentaammineplatinum(IV) ion were studied by stopped-flow procedure under pseudo-first-order conditions ([complex] = 1.0 × 10^{-4} M). Data for the formation reaction were obtained within the ranges 5.0 < pH < 7.5, 15 °C < T < 25 °C, and 0.005 M < S_T < 0.20 M (S_T = total sulfite concentration), at an ionic strength of 1.0 M ($NaClO_4$). In a few initial experiments the values of k_{obsd} obtained with use of phosphate/citric acid buffer[16] and sulfite self-buffering were compared and found to be essentially identical. All succeeding experiments were performed in sulfite buffer as done previously.[7] The reaction was first studied as a function of total sulfite ($[S]_T$) at fixed pH of 6.1. These data appear as plots (Figure 2) of k_{obsd} vs. $[S]_T$ and are seen to be linear at all temperatures with a zero intercept.[17] The slopes of these lines

(15) Bjerrum, J.; Schwarzenbach, G.; Sillen, L. G. "Stability Constants"; The Chemical Society: London, 1957. Sillen, L. B.; Martell, A. E. "Stability Constants"; The Chemical Society: London, 1964.

(16) Elving, P. J.; Markowitz, J. M.; Rosenthal, L. *Anal. Chem.* **1956**, *28*, 1179.

(17) Least-squares analyses showed correlation coefficients of 0.998 or greater and intercepts of −0.35 ± 0.37, −0.66 ± 0.77, and 0.65 ± 0.48 s^{-1} at 15, 20, and 25 °C, respectively.

(18) Fowless, A. D.; Stranks, D. R. *Inorg. Chem.*: (a) **1977**, *16*, 1276; (b) **1977**, *16*, 1282; (c) **1977**, *16*, 1276.

Table IV. Dependence of k_{obsd} on pH for SO_2 Uptake by $[Pt(NH_3)_5OH]^{3+}$ in Sulfite Buffer[a]

temp, °C	pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}
15	5.32	77.6 ± 1.6	6.70	8.9 ± 0.1
	5.85	32.2 ± 1.0	6.82	7.0 ± 0.1
	6.05	25.4 ± 0.8	7.12	3.8 ± 0.1
	6.27	18.2 ± 0.2	7.27	2.8 ± 0.1
	6.48	12.9 ± 0.2	7.43	2.0 ± 0.1
20	5.34	154.8 ± 3.0	6.48	21.8 ± 0.8
	5.72	81.3 ± 2.7	6.72	13.8 ± 0.4
	6.00	47.3 ± 1.8	6.97	8.3 ± 0.2
	6.16	39.8 ± 1.1	7.20	5.1 ± 0.1
	6.38	25.7 ± 1.0	7.41	3.3 ± 0.1
25	5.48	198.5 ± 2.9	6.52	28.2 ± 0.8
	5.78	112.3 ± 2.7	6.71	19.3 ± 0.2
	6.00	75.1 ± 1.6	7.02	10.3 ± 0.2
	6.20	52.8 ± 1.8	7.20	7.0 ± 0.1
	6.28	44.5 ± 1.2	7.40	4.5 ± 0.1

[a] $[S]_T = 0.1$ M.

Table V. Rate Constants for Sulfite Reaction with the $Pt(NH_3)_5OH^{2+}$ Complex Ion

temp, °C	$10^{-6}k_1$, M^{-1} s^{-1}	$10^{-2}k_2$, M^{-1} s^{-1}	$10^{-6}(k_1 + k_2K_2/[H^+])$, M^{-1} s^{-1}	
			calcd	obsd[a]
15	2.1 ± 0.2	2.8 ± 0.1	7.8	9.2
20	4.4 ± 0.2	4.4 ± 0.1	12.2	13.1
25	6.8 ± 0.2	5.9 ± 0.1	16.2	13.7
$\Delta H^{\ddagger}$, kcal mol^{-1}	21.0 ± 2.2	13.0 ± 1.1		
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	43.2 ± 7.3	−2.5 ± 3.8		

[a] Determined by dividing the values of the slopes of Figure 2 by the fraction $[SO_2]/[S]_T$ at the various temperatures.

may be equated to an overall second-order rate constant that has the values (M^{-1} s^{-1}) of 277 ± 3, 452 ± 7, and 531 ± 5 at 15, 20, and 25 °C, respectively, at the prevailing pH (6.1 ± 0.1). A second set of data, given in Table IV, shows the effect of changes in pH of the system at a fixed $[S]_T$ (0.1 M) on the values of k_{obsd}. These values decrease steeply as the pH is increased as was previously observed for the aquo-cobalt(III) analogue.[4] However, the decrease does not parallel the decrease in $[SO_2]$, since a 1000-fold decrease in the latter (pH decrease from 5.4 to 7.4) results in a less than 50-fold decrease in k_{obsd}. It is also readily deduced that at high pH (7.0-7.4) the rate constant roughly parallels $[HSO_3^-]$ but bears no relation to $[SO_3^{2-}]$.

A mechanism that adequately accounts for the data so far presented takes the form shown in Scheme I. As will be discussed later, there is no evidence for the decomposition reaction k_{-1} at pH >4. Also, since $pK_3 \approx 4$, the aquo form
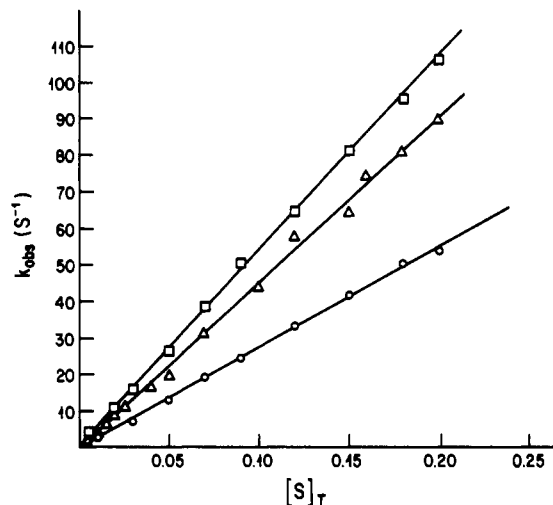
Figure 2. Plot of k_{obsd} vs. $[S]_T$ at pH 6.1 for the SO_2-uptake reaction by $[Pt(NH_3)_5OH]^{3+}$: (O) 15 °C; (△) 20 °C; (□) 25 °C.

Scheme I
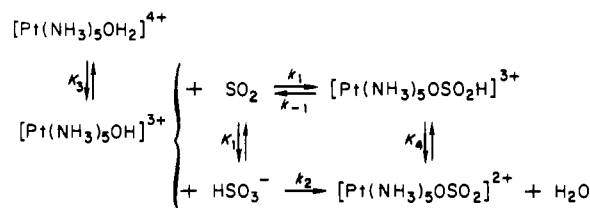
of the reactant complex is a minor constituent under the experimental conditions so that the rate equation for the formation reaction takes the form

$$k_{obsd} = \left(k_1 + \frac{k_2K_1}{[H^+]} \right)[SO_2] \qquad (1)$$

The concentration of SO_2 at various pHs and $[S]_T$ values is given by the expression

$$[SO_2] = [H^+]^2[S]_T/([H^+]^2 + K_1[H^+] + K_1K_2) \qquad (2)$$

One can now plot the data of Table III according to the rearranged form of eq 1:

$$k_{obsd}/[SO_2] = k_1 + k_2K_1/[H^+] \qquad (3)$$

Linear least-squares analyses for the intercepts and slopes of the plots of $k_{obsd}/[SO_2]$ vs. $1/[H^+]$ lead to the figures given in Table V for k_1 and k_2 (M^{-1} s^{-1}) (using the known K_1 values at each temperature to calculate the latter) with a very acceptable degree of precision (the correlation coefficients are 0.9999 for all three sets of data). The quantities derived from Figure 2 for the overall rate constants in terms of $k_{obsd}/[S]_T$ at pH 6.1 yield the values for $k_1 + k_2K_1/[H^+]$, quoted in Table

Table VI. Rate Constants and Activation Parameters for the Reactions of Various Aquo Transition-Metal Complex Ions with Sulfite in Aqueous Solution at 25 °C

| no.	complex ion	reactant	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	ref
1	$[Co(NH_3)_5]OH^{2+}$	SO_2	4.7×10^8	9.8 ± 0.3	14.0 ± 0.4	4
2	$[Co(tetren)OH]^{2+}$	SO_2	3.3×10^8	−0.5 ± 1.0[a]	−21.0 ± 3.5	7
3	$[Co(tren)(OH_2)(OH)]^{2+}$	SO_2	5.3×10^7	4.5 ± 0.1	−8.0 ± 0.3	6
4	$[Rh(NH_3)_5OH]^{2+}$	SO_2	1.8×10^8			5
5	$[Cr(NH_3)_5OH]^{2+}$	SO_2	2.9×10^8			5
6	$[Pt(NH_3)_5OH]^{3+}$	SO_2	6.8×10^6	21.0 ± 2.2	43.2 ± 7.3	this work
7	$[Pt(NH_3)_5OH]^{3+}$	HSO_3^-	590	13.0 ± 1.1	−2.5 ± 3.8	this work
8	$[Co(NH_3)_5(OH_2)]^{3+}$	$HSeO_3^-$	147	13.5 ± 0.5	−9.0 ± 1.0	18
9	$[Co(NH_3)_5OH]^{2+}$	CO_2	220	15.3 ± 0.9	3.6 ± 3.0	19

[a] Ion-pairing complications in the interpretation of these data probably invalidate the apparent zero value for $\Delta H^{\ddagger}$, which, however, is undoubtedly quite low, as found for the tren analogue (entry no. 3).

V, which are seen to agree satisfactorily with those calculated from the k_1 and k_2 values as derived above, attesting to the inner consistency of the experiments.

The data concerning a number of aquo complex/sulfite reaction systems are collected in Table VI. It is noted that all the direct SO_2 additions to the monohydroxo forms of the various species are very rapid, ranging from a low of 6.8×10^6 M^{-1} s^{-1} for the Pt(IV) complex (entry no. 6) to a high of 4.7×10^8 M^{-1} s^{-1} to the corresponding Co(III) complex (no. 1), only 2 or 3 orders of magnitude slower than the diffusion-controlled limit for such reactions in aqueous systems. The Co(III) species exhibit rather low ΔH^* and ΔS^* values, in contrast to the considerably larger values for the Pt(IV) complex. The other reactions listed (nos. 7, 8, and 9) involve HSO_3^-, $HSeO_3^-$, and CO_2, respectively, with rate constants and temperature parameters within a narrow range of values. It has been fully documented[19,20] that the CO_2 reaction involves rapid nucleophilic attack by coordinated hydroxide on the carbon atom of the CO_2. It appears likely, therefore, that both the HSO_3^- and the $HSeO_3^-$ reactions proceed by a similar "add-on" mechanism as suggested earlier for the selenite system.[18a] An unusual feature of the selenite study is that the authors concluded that the most reactive form of the complex was the aquo species, with a considerably lower rate constant (8 M^{-1} s^{-1}) for the hydroxo analogue.[18b]

We attempted to study the acid-catalyzed SO_2-elimination process governed by the k_{-1} path defined above. The O-bonded sulfito complex was made in situ at pH >4 (where formation of this complex is complete) and then mixed with phosphate/citrate buffer of the desired lower pH in the stopped-flow setup. Little spectral evidence of SO_2 elimination is observed until the pH is lowered to 2.5, when about 20% hydrolysis of O-bonded sulfite is observed. At pH 1.8, about 50% is hydrolyzed, while complete hydrolysis is found to occur only for pH <1.3. In each case, the attainment of equilibrium was too rapid to observe in the stopped-flow procedure, indicating that $k_{-1} \gg k_1[SO_2]$. It thus was impossible in our experiments to evaluate k_1 at pH values such that the available complex for SO_2 uptake is largely $[Pt(NH_3)_5OH_2]^{4+}$, but the rapid equilibrations at low pH clearly indicate that the aquo form is indeed reactive to SO_2, as mentioned above in the case of the $[Co(NH_3)_5OH_2]^{3+}/HSeO_3^-$ system. The extreme instability of the protonated complex $[Pt(NH_3)_5OSO_2H]^{3+}$ as compared to $[Co(NH_3)_5OSO_2H]^{2+}$ (for which[4] k_{-1} is ~4 $\times$ 10^4 s^{-1} at 10 °C) may be ascribed to the 2-unit difference in the pK's of the corresponding aquo complexes, 4.3[21] and 6.3,[4] respectively, indicative of a considerably weaker O–H (or O–S) bond in the Pt(IV) as compared to the Co(III) species.

Formation of the *cis*-Bis(sulfito)tetraammineplatinum(IV) Ion. The rate of the reaction

$$[Pt(NH_3)_5(OSO_2)]^{2+} \xrightarrow[\text{sulfite}]{\text{excess}} cis\text{-}[Pt(NH_3)_4(SO_3)_2] \quad (4)$$
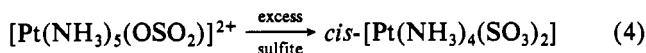
was found to proceed at rates readily determined by conventional spectrophotometric procedures in the ranges 30 °C < T < 40 °C and 2.5 < pH < 5.5. Under the excess sulfite conditions of all our experiments the reaction at a fixed pH was totally independent of $[S]_T$ (see Table VII). However, the variation of the rate of reaction with pH takes the form of a bell-shaped curve, as illustrated in Figure 3. This kind of variation is frequently observed for dibasic acid systems where only the monoprotonated species is reactive. One can

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(21) Extrapolated from the data for pK_3 given in the Experimental Section.
(22) Deduced from the data of: Thacker, M. A.; et al. *J. Chem. Soc., Dalton Trans.* **1974**, 647. These data were recently confirmed by: van Eldik, R., personal communication.

Table VII. Dependence of k_{obsd} on $[S]_T$ for the Formation of *cis*-$Pt(NH_3)_4(SO_3)_2$[a]

temp, °C	$10^3 \times$ $[S]_T$, M	$10^4 \times$ k_{obsd}, s^{-1}	$10^3 \times$ $[S]_T$, M	$10^4 \times$ k_{obsd}, s^{-1}
30	2	4.42	5	4.55
	2.5	3.50	6	4.81
	3	3.89	7	4.47
	3.5	3.72	8	3.92
	4	4.41	9	3.46
			av	4.1 ± 0.5
35	2	5.31	5	4.93
	2.5	4.97	6	5.11
	3	4.82	7	4.89
	3.5	5.40	8	5.26
	4	5.18	9	4.72
			av	5.1 ± 0.2
40	2	6.93	5	7.20
	2.5	7.13	6	7.18
	3	6.81	7	6.41
	3.5	6.21	8	7.18
	4	6.39	9	6.58
			av	6.8 ± 0.4

[a] pH 3.2 ± 0.1.
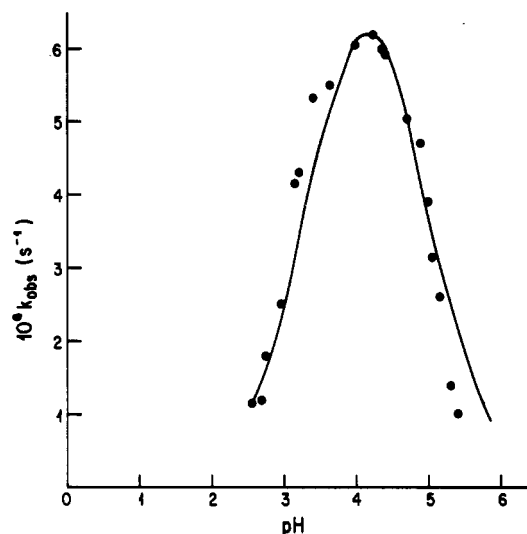
Figure 3. Variation of k_{obsd} for the formation of $[Pt(NH_3)_4(SO_3)_2]$ with pH at 30 °C ($[S]_T = 0.05$ M).

achieve such a situation in the present system if it is assumed that, on heating to reaction temperature, there occurs cis-NH_3 replacement by water as a result of the sulfito ligand proximity. The product complex then can take three equilibrium forms:

$$cis\text{-}[Pt(NH_3)_4(OH_2)(OSO_2H)]^{3+} \underset{K_4}{\rightleftharpoons}$$
$$cis\text{-}[Pt(NH_3)_4(OH_2)(OSO_2)]^{2+} \underset{K_5}{\rightleftharpoons}$$
$$cis\text{-}[Pt(NH_3)_4(OH)(OSO_2)]^+ \quad (5)$$
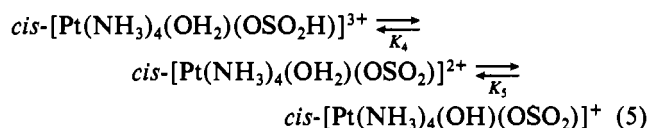
With the assumption that only the monoprotonated central species is reactive and that it undergoes rate-determining O-bonded to S-bonded isomerization, followed by rapid replacement of the cis-aquo ligand by sulfite, the reaction scheme becomes

$$cis\text{-}[Pt(NH_3)_4(OH_2)(OSO_2)]^{2+} \xrightarrow{k_s}$$
$$cis\text{-}[Pt(NH_3)_4(OH_2)(SO_3)]^{2+} \xrightarrow[\text{fast}]{+SO_3^{2-}}$$
$$cis\text{-}[Pt(NH_3)_4(SO_3)_2] \quad (6)$$
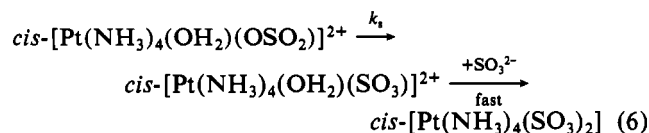
The corresponding rate law for the overall process is thus

$$k_{obsd} = k_s K_4[H^+]/[H^+]^2 + K_4[H^+] + K_4 K_5 \quad (7)$$

Using values for pK_4 and pK_5 of 3.4 and 5.0, respectively, one

Table VIII. Dependence of k_{obsd} on [S]$_T$ for the Reduction of cis-Pt(NH$_3$)$_4$(SO$_3$)$_2$[a]

temp, °C	$10^3 \times$ [S]$_T$, M	$10^4 \times$ k_{obsd}, s^{-1} [b]	$10^3 \times$ [S]$_T$, M	$10^4 \times$ k_{obsd}, s^{-1}
45	2	1.99	6	2.17
	2.5	2.18	7	2.32
	3	1.72	8	1.68
	4	1.85	10	1.95
	5	2.23	av	2.0 ± 0.2
50	2	4.52	6	4.55
	2.5	4.83	7	4.67
	3	4.31	8	4.21
	4	4.48	10	4.98
	5	4.57	av	4.6 ± 0.2
55	2	8.90	6	8.19
	2.5	9.31	7	9.23
	3	9.00	8	8.42
	4	9.75	10	9.45
	5	8.40	av	9.0 ± 0.5

[a] The pH of the system was maintained constant at 2.9 ± 0.1.

Table IX. Dependence of k_{obsd} on pH for the Reduction of cis-Pt(NH$_3$)$_4$(SO$_3$)$_2$[a]

temp, °C	pH	$10^4 \times$ k_{obsd}, s^{-1}	pH	$10^4 \times$ k_{obsd}, s^{-1}
45	2.66	2.97	3.63	0.48
	2.75	2.60	3.75	0.41
	2.89	2.21	3.99	0.26
	3.02	1.88	4.11	0.20
	3.12	1.63	4.32	0.13
	3.41	0.67		
50	2.68	10.01	3.48	1.64
	2.85	6.20	3.62	1.24
	3.00	4.99	3.80	1.01
	3.12	4.36	4.00	0.82
	3.29	3.39	4.19	0.50
	3.38	2.30	4.41	0.34
55	2.82	14.23	3.47	3.23
	2.89	13.29	3.81	2.27
	3.00	10.79	4.12	1.46
	3.09	9.59	4.26	1.25
	3.12	7.74	4.43	0.92
	3.31	4.12		

[a] [S]$_T$ was maintained constant at 2.5×10^{-3} M.

Table X. Rate Data for the Intramolecular Reduction of cis-[Pt(NH$_3$)$_4$(SO$_3$)$_2$]

temp, °C	$10^4 k$, s^{-1}	$10^{-3} K$, M^{-1}	p(1/K)
45	3.5 ± 0.8	0.8 ± 0.2	2.9 ± 0.1
50	6.6 ± 1.6	1.4 ± 0.4	3.1 ± 0.1
55	9.5 ± 2.4	2.7 ± 0.7	3.4 ± 0.1

$\Delta H^{\ddagger} = 20.2 \pm 3.1$ kcal mol^{-1}
$\Delta S^{\ddagger} = -11.3 \pm 9.5$ cal deg^{-1} mol^{-1}

can achieve a very satisfactory fit to the experimental data, as shown in Figure 3.

The pK values are in the range to be expected, since studies of an analogous cobalt(III) system[2] suggest a similar order

of magnitude for pK_4, while one would expect pK_5 to be at least 1 unit larger than pK_3, due to the considerably decreased positive charge on the (sulfito)aquotetraammine species as compared to the aquopentaammine parent compound. Data at several temperatures were obtained at pH ∼4.2, where k_3 ≈ k_{obsd}, with values for $10^4 k_s$ (s^{-1}) of 6.2, 7.1, and 7.6 at 30, 35, and 40 °C, respectively. These lead to figures for $\Delta H_s^{\ddagger}$ and $\Delta S_s^{\ddagger}$ of 3.6 ± 0.5 kcal mol^{-1} and −61.3 ± 1.6 cal deg^{-1} mol^{-1}, respectively.

Reduction of Pt(NH$_3$)$_4$(SO$_3$)$_2$. As mentioned earlier the cis-bis(sulfito)tetraammineplatinum(IV) complex undergoes a two-electron reduction to yield (sulfito)triammineplatinum(II). Although the formation of this complex is associated with the growth of a peak at 234 nm, this increase in absorbance was not accessible to kinetic studies because of the difficulty in selecting a buffer that does not absorb appreciably at 234 nm. Hence, the decrease in absorbance at 274 nm associated with the reduction process was followed for kinetic purposes and the rate data were obtained under pseudo-first-order conditions. One notices (Table VIII) that the k_{obsd} is independent of changes in the total sulfite concentration at constant pH, as expected for an internal redox mechanism in which one SO$_3^{2-}$ is oxidized to SO$_4^{2-}$ with simultaneous reduction of Pt(IV) to Pt(II). In contrast, k_{obsd} sharply decreases with increasing pH at a given total sulfite concentration (Table IX). The observed [H$^+$] dependence is best treated by assuming proton preequilibration of the cis-bis(sulfito)tetraammineplatinum(IV) ion prior to reduction as in the scheme

$$Pt(NH_3)_4(SO_3)_2 + H^+ \overset{K}{\rightleftharpoons} Pt(NH_3)_4(SO_3)(SO_3H)^+ \overset{k}{\longrightarrow}$$
$$\text{products} \quad (8)$$
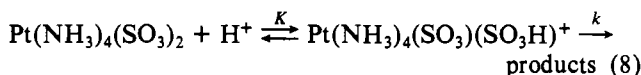
According to this mechanism, the observed rate constant, k_{obsd}, is given by the equation
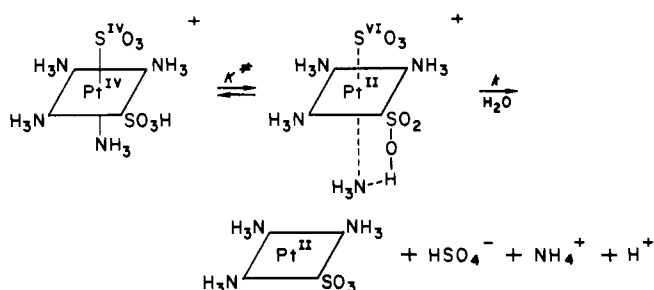
$$k_{obsd} = \frac{kK[H^+]}{1 + K[H^+]} \quad (9)$$

or, in the inverse form

$$\frac{1}{k_{obsd}} = \frac{1}{k} + \frac{1}{kK[H^+]} \quad (10)$$

Thus, plots of $1/k_{obsd}$ vs. $1/[H^+]$ should give straight lines of slope $1/kK$ and intercept $1/k$. Such plots are indeed satisfactorily linear (correlation coefficients for the least-squares analysis are all >0.98), and the values of k and K calculated at 45, 50, and 55 °C are given in Table X, together with the appropriate temperature parameters. The detailed mechanism by which the intramolecular redox reaction can best be visualized in keeping with the above kinetic observations is one in which the reactive protonated bis(sulfito) complex undergoes electron transfer, as shown in Scheme II. A summary of data concerning the various redox, isomerization, and sulfite addition reactions of a selection of sulfito complexes is presented in Table XI. It is notable that the redox reactions of the Co(III) species, which must initially take place by rate-determining one-electron transfer, are at 25 °C in the range of

Table XI. Rate Constant Data for Various Redox, Isomerization, and Sulfite Addition Reactions of Selected Cobalt(III) and Platinum(IV) Sulfito Complex Ions in Aqueous Solution at 25 °C

no.	reactant	product(s)	rate const	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	ref
1	Co(NH$_3$)$_5$OSO$_2$$^+$	Co(II), SO$_4^{2-}$, etc.	1.4×10^{-2} s^{-1}	26.9 ± 0.2	23.1 ± 4.2	4
2	Co(NH$_3$)$_5$SO$_3$$^+$	Co(II), SO$_4^{2-}$, etc.	∼1×10^{-4} s^{-1}			22
3	Co(tetren)OSO$_2$$^+$	Co(tetren)SO$_3$$^+$	2.7×10^{-4} s^{-1}	13.5 ± 0.9	−29.6 ± 3.0	8
4	Co(tren)(OH$_2$)(OSO$_2$)$^+$	Co(II), SO$_4^{2-}$, etc.	1.0×10^{-3} s^{-1}	24.2 ± 2.0	8.2 ± 6.6	7
5	Co(tren)(OH)(OSO$_2$)	Co(tren)(SO$_3$)(OSO$_2$)$^-$	0.40 M^{-1} s^{-1}	12 ± 1	19 ± 2	7
6	Pt(NH$_3$)$_5$(OSO$_2$)$^{2+}$	cis-Pt(NH$_3$)$_4$(SO$_3$)$_2$	5.6×10^{-4} s^{-1}	3.6 ± 0.5	−61.3 ± 1.6	this work
7	cis-Pt(NH$_3$)$_4$(SO$_3$)$_2$	Pt(NH$_3$)$_3$SO$_3$, SO$_4^{2-}$	4.0×10^{-5} s^{-1}	20.2 ± 3.1	−11.3 ± 9.5	this work

Scheme II

10^{-3} s^{-1} for the S-bonded (sulfito)pentaammine and the O-bonded tren species (entry no. 4) to 10^{-2} s^{-1} for the O-bonded pentaammine complex. The only platinum (IV) species for which we observed redox is no. 7, the S-bonded bis(sulfito) congener, with a rate about 2.5-fold slower than that of the S-bonded cobalt(III) example (no. 2). This somewhat slower electron transfer for the Pt(IV)/S(IV) system is most likely a result of differences in reactivity of Pt(IV) and Co(III) as oxidants, since theory predicts a decrease by a factor of only 2–4 in going from a one-electron to a comparable two-electron transfer system,[23] though this figure is derived for gaseous systems only. There is also the necessity of drastic stereochemical rearrangement in the Pt(IV) to Pt(II) conversion unlike the case for the Co^{III}/Co^{II} system.

Another comparison of interest concerns the reactions which clearly involve O-bonded to S-bonded sulfito isomerization, nos. 3 and 6 (Table XI). These have very similar rate constants at 25 °C, although the temperature parameters are rather different. It is noteworthy that reaction no. 5, which we have concluded previously[7] does *not* involve sulfito isomerization but only S-bonded addition, is the only clearly second-order process in the tabulation. It also has a pseudo-first-order rate constant much in excess of the simple first-order isomerization rate of no. 3 even in sulfite as dilute as 0.01 M ($k \cong 4 \times 10^{-3}$ s^{-1}, as compared to $\sim3 \times 10^{-4}$ s^{-1}). It is of further interest that reaction no. 6, in which S-bonded sulfite replacement of NH_3 occurs accompanied by O- to S-bonded isomerization, is rate limited by the latter process, since no sulfite concentration dependence is observed. The above discussion thus suggests that sulfite replacement of normally "stable" cis ligands such as OH^- (reaction no. 5) or NH_3 (reaction no. 6) can take place much more rapidly than isomerization in systems of this type.

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Notes

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Redox Potentials of Bis(1,4,7-triazacyclononane) Complexes of Some First Transition Series Metals(II, III). Preparation of Bis(1,4,7-triazacyclononane)nickel(III) Perchlorate

Karl Wieghardt,* Wilfried Schmidt, Willy Herrmann, and Heinz-Josef Küppers

Since its original preparation in 1972[1] and the subsequent synthesis of a series of transition-metal complexes,[2] it has been recognized that the cyclic amine 1,4,7-triazacyclononane ([9]aneN$_3$) is a strong tridentate chelating ligand.[3] To date,

[9]aneN$_3$ dien   dpt

ptn
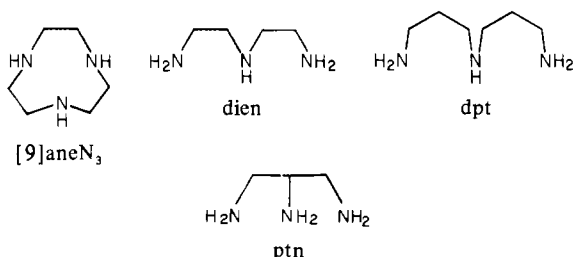
only octahedral complexes containing two such ligands of

cobalt(III),[1] nickel(II),[2–4] and copper(II)[2] have been isolated and characterized. The three N donors can only coordinate facially, which is in contrast to the well-known open-chain amines (2-aminoethyl)-1,2-ethanediamine (dien) and (3-aminopropyl)-1,3-propanediamine (dpt), the cobalt(III) species of which are dominated by the meridional structures.[5,6] Recently, the facially coordinating ligand 1,2,3-triaminopropane (ptn) has become available in good yields,[7] and the [Co(ptn)$_2$]$^{3+}$ and [Ni(ptn)$_2$]$^{2+}$ complexes[7,8] have been isolated. We have now extended the series of bis(triamine)metal(II, III) complexes and have studied their relationship in aqueous solution, determining formal redox potentials of the couples [([9]aneN$_3$)$_2$M]$^{3+/2+}$ (M = Mn, Fe, Co, Ni).

Results and Discussion

Syntheses of Complexes. A series of bis(1,4,7-triazacyclononane)metal(II) complexes have been synthesized by following a procedure described by Pedersen[9] for the preparation of chromium(III)–amine complexes in excellent yields. The appropriate metal chloride, MCl$_2$·xH$_2$O (M = Mn, Fe, Co, Ni), was dissolved in dimethyl sulfoxide at 190 °C. At this

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