$$(\mathrm{edtaH})\mathrm{TiOHCo(NH_3)_5}^{2+} \xrightarrow{k_2} \text{products} \qquad (5)$$

known whether k_1 or k_2 is rate determining. However clearly k_1 must be equal to or greater than the rate constant (ca. 10^7 M^{-1} s^{-1}). Since K for outer-sphere association of the reactants in k_1 is unlikely to be >1 M^{-1}, the water-exchange rate constant is >ca. 10^7 s^{-1}. The rate constant for water exchange on $Ti(H_2O)_6^{3+}$ is ca. 10^5 s^{-1} [17] so that the edta appears to have a strong labilizing effect. This could well result from the presence of the uncoordinated carboxylate arm of the edta which is capable of forming a transient seven-coordinate Ti(III) species, with resultant labilization of the H_2O. An analogous mechanism has been suggested to explain the rapid complexation (replacement of H_2O) of the Cr(III)–edta complex $Cr(edta)H_2O^-$ by acetate, azide, chromate(VI), molybdate(VI), and tungstate(VI).[18,19] A similar, quite remarkable labilization has been observed also for the Ru(III)–edta complex $Ru(edta)H_2O$.[20] Whether this is a feature to be expected of all such complexes having fewer than six d electrons requires further substantiating.

Other features to note in these reactions are that the Ti(III)–edta complex is a more effective reductant than the aquo ion. Thus rate constants for the reaction of $Ti(H_2O)_5OH^{2+}$ with $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ are 0.015 and 0.95 M^{-1} s^{-1}, respectively,[21] whereas corresponding values for $Ti(edtaH)H_2O$ are 0.165 and 9.6 M^{-1} s^{-1}, i.e., a factor of ca. 10 greater. We also note that rate constants for the $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5Cl^{2+}$ oxidations of the Ti(III)–edta complex remain unaffected by $[H^+]$ down to 0.010 M. This suggests, since the first pK_a value is 2.02, that the reactions are insensitive as to whether the free carboxylate of the edta is protonated or not. Finally, with the presumed linear relationship in Figure 2 and a value for $k_{Ru} = 3$ M^{-1} s^{-1} for the $Ru(NH_3)_6^{2+}$ reduction of $Co(NH_3)_5H_2O^{3+}$,[22] an outer-sphere contribution to the Ti(III)–edta reduction of $Co(NH_3)_5H_2O^{3+}$ of 1–2 M^{-1} s^{-1} is obtained. It is possible that such a pathway is a dominant, or the only, contributor to the rate constant a in eq 2.

Acknowledgment. We are grateful to Dr. C. Creutz and Professor J. E. Earley for communicating results to us prior to publication. The award of a Science Research Council CASE Studentship (to G.A.K.T.) in collaboration with Tioxide International is gratefully acknowledged.

Registry No. Ti(III)-edta, 69897-19-4; $Co(NH_3)_6^{3+}$, 14695-95-5; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5H_2O^{3+}$, 14403-82-8.

References and Notes

(1) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975); **15**, 1934 (1976).

(2) M. Orhanović and J. E. Earley, *Inorg. Chem.*, **14**, 1478 (1975).

(3) J. P. Birk, *Inorg. Chem.*, **14**, 1724 (1975).

(4) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).

(5) A. Bakač and M. Orhanović, *Inorg. Chim. Acta*, **21**, 173 (1977).

(6) M. Hery and K. Wieghardt, *Inorg. Chem.*, **17**, 1130 (1978).

(7) J. Podlahova and J. Podlaha, *J. Inorg. Nucl. Chem.*, **28**, 2267 (1966).

(8) M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2730 (1973).

(9) I. Baldea, K. Wieghardt, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 78 (1977).

(10) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973).

(11) T. D. Hand, M. R. Hyde, and A. G. Sykes, *Inorg. Chem.*, **14**, 1720 (1975), and references therein.

(12) Alternatively, using the point for $Co(bpy)_3^{3+}$ (a revised rate constant of 1.1×10^4 M^{-1} s^{-1} has been obtained for the $Ru(NH_3)_6^{2+} + Co(bpy)_3^{3+}$ reaction[13]) and reassigning the μ-superoxo point as outer-sphere, we observe that this plot may curve upward at log $k_{Ru} > 4.0$ and assume a slope approaching 1.0. An outer-sphere assignment for the $TiOH^{2+}$ reduction of the μ-superoxo complex is consistent with previous assignments with Fe^{2+}, Cr^{2+}, and V^{2+} as reductant.[11] The previous suggestion that the $TiOH^{2+}$ reaction was inner-sphere was based on the lack of correlation with other data at log $k_{Ru} < 4.0$. We now feel that this possibility should be further considered. The correlation in ref 11 provides another possible example of a nonlinear log–log plot of rate constants.

(13) M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).

(14) K. M. Davies and J. E. Earley, *Inorg. Chem.*, in press.

(15) M. B. Stevenson, R. D. Mast, and A. G. Sykes, *J. Chem. Soc. A*, 941 (1969).

(16) N. Sutin, *Acc. Chem. Res.*, **1**, 227 (1968).

(17) A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, **51**, 4238 (1969).

(18) H. Ogino, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, **14**, 2093 (1975).

(19) Y. Sulfab, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **15**, 2388 (1976).

(20) T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, **100**, 6255 (1978).

(21) The acid dissociation constant for $Ti(H_2O)_6^{3+}$ is assumed to be ca. 2×10^{-3} M; see ref 4.

(22) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

Contribution from the Department of Chemistry,
Emory University, Atlanta, Georgia 30322

Hydrolysis of the *trans*-Hydroxo(sulfato)tetraammineplatinum(IV) Cation and Synthesis of *cis*-Dihydroxotetraammineplatinum(IV) Sulfate

Ronald C. Johnson* and Charles G. Widmer

Received July 5, 1978

Sulfato complexes of platinum(IV) are rare,[1] and data on the hydrolysis of the platinum(IV)–sulfate bond are not available. In cationic ammine complexes of platinum(IV) hydrolysis of anionic ligands is quite slow and normally requires strongly alkaline conditions.[2,3] We report here an isomerization which accompanies the hydrolysis of a platinum(IV)–sulfate bond, a type of behavior which had not been previously reported for ammine complexes of platinum(IV).

Results and Discussion

The hydrolysis of *trans*-$Pt(NH_3)_4(OH)SO_4^+$ (reaction 1)

$$trans\text{-}Pt(NH_3)_4(OH)SO_4^+ + OH^- \rightarrow Pt(NH_3)_4(OH)_2^{2+} + SO_4^{2-} \qquad (1)$$

was studied in alkaline solution. High-pressure cation-exchange chromatograms of hydrolyzed solutions had two peaks, both at retention volumes corresponding to 2+ ions. The relative sizes of the two peaks was a function of the pH at which the *trans*-$Pt(NH_3)_4(OH)SO_4^+$ was hydrolyzed. The major product when hydrolysis was carried out in an ammonia solution (pH 11.1) eluted before the second component and had the same retention volume as *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ (made by the reaction of H_2O_2 with $Pt(NH_3)_4^{2+}$).[4,5] The percentage of trans compound was approximately 30 at pH 13.2, 60 at pH 12.2, and 80 at pH 11.1. The hydrolysis was run on a synthetic scale in 0.3 M NaOH. From this solution a sparingly soluble sulfate salt could be isolated which had a retention volume identical to the more strongly retained ion in the chromatogram of the hydrolysis solution. The analysis of this compound corresponds to the formula $Pt(NH_3)_4(OH)_2SO_4$. This compound and *trans*-$[Pt(NH_3)_4(OH)_2]SO_4$ have ultraviolet spectra with different shapes; however, neither has a maximum at wavelengths longer than 200 nm; both do absorb strongly below 240 nm. (At 220 nm their molar absorptivities are 1.5×10^3 and 2.0×10^3 (trans).) The infrared spectra of the two compounds have peaks in the same regions but are different in the placement and intensities of the peaks. On the basis of this data it seems that the new compound is *cis*-$[Pt(NH_3)_4(OH)_2]SO_4$. The cation is quite unreactive; for example, it reacts only very slowly with 2 M HBr at 25 °C.

The chromatogram of an aged solution of *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ in 0.2 M NaOH does not exhibit a peak characteristic of the cis isomer. This suggests that the cis product is formed directly from the sulfato complex. Since there are two products of the reaction, the relative concen-

0020-1669/79/1318-2027$01.00/0 © 1979 American Chemical Society

Table I. Rate Data[a]

	$10^5 k_{\text{obsd}}$, s^{-1}		
$[OH^-]$, M	34.3 °C	43.5 °C	53.0 °C
0.0095		6.0	
0.0189		8.0	
0.0473	3.5	10.9	28
0.0945	4.3	14.9	38
0.0945		15.4[b]	
0.0945		15.7[c]	
0.142	5.3	18.8	48
0.189		20.9	

[a] $[[trans\text{-}Pt(NH_3)_4(OH)SO_4](ClO_4)] = 1.0 \times 10^{-3}$ M. [b] $[NaClO_4] = 0.15$ M. [c] $[[Pt(NH_3)_4](ClO_4)_2] = 1.1 \times 10^{-3}$ M. Rate parameters evaluated from eq 2 for 43.5 °C: $a = 1.36 \times 10^{-16}$ M s^{-1}, $b = 9.0 \times 10^{-30}$ M^2 s^{-1}, and $c = 1.4 \times 10^{-12}$ M.

trations of which change with hydroxide concentration, there must be at least two routes to the formation of products. The route which forms the cis product must produce little or no trans product, since 70% of the product is cis at pH 13.2 and it seems probable that the trans-producing reaction is still operative.

A determination of the K_a (1.0×10^{-12} at 25 °C) of *trans*-$Pt(NH_3)_4(OH)SO_4^+$ indicates that in the pH 12–13 range the conjugate base $Pt(NH_3)_3NH_2(OH)SO_4^0$ is the predominant species. Since the cis complex is formed only in very alkaline solution, we would speculate that the most reasonable mechanism for the formation of the cis compound is a displacement of sulfate ion from the conjugate base of *trans*-$Pt(NH_3)_4(OH)SO_4^+$ by hydroxide ion. The dissociative hydrolysis of the conjugate base could provide the pathway to the trans product. The absence of catalysis by $Pt(NH_3)_4^{2+}$ indicates that a platinum(II)-catalyzed mechanism does not play a role in this hydrolysis.

Some rate data for reaction 1 were collected and are cited in Table I. The rate of reaction is relatively insensitive to changes in ionic strength; a slight increase in rate accompanies a substantial change in ionic strength. The presence of 0.001 M $Pt(NH_3)_4^{2+}$ has little effect on the rate. The hydroxide dependence is complex. The rate is negligible in a 0.010 M Na_2HPO_4 solution (pH ~9). An equation of the form (2)

$$k_{\text{obsd}} = (a + b/[H^+])/(c + [H^+]) \qquad (2)$$

can be used to fit the data. However, it is probable that other functions with three parameters could fit the limited data equally well. One mechanism consistent with such a rate law involves the conjugate base $Pt(NH_3)_3NH_2(OH)SO_4^0$ in both hydroxide-dependent and -independent steps (in agreement with our suggestion in the previous paragraph). Hydroxide-dependence data is not sufficient to permit one to confirm this mechanism or to elaborate on its details. Moreover mechanistic interpretation is further complicated by the presence of two products.

It would be of interest to compare the rate of hydrolysis of *trans*-$Pt(NH_3)_4(OH)SO_4^+$ with that of other *trans*-$Pt(NH_3)_4(OH)X^{n+}$ complexes. However, no data of this kind has been published. Our preliminary data on the hydrolysis of *trans*-$Pt(NH_3)_4(OH)Cl^{2+}$ and *trans*-$Pt(NH_3)_4(OH)Br^{2+}$ indicate they react appreciably more slowly than the sulfate complex. It will be of interest to see whether isomerization accompanies these reactions.

Experimental Section

Preparation of Compounds. Tetraammineplatinum(II) perchlorate,[6] *trans*-$[Pt(NH_3)_4(OH)SO_4]ClO_4$,[1] $Pt(NH_3)_4(SO_4)_2$,[1] and *trans*-$[Pt(NH_3)_4(OH)_2]SO_4$[4] were prepared by published procedures.

***cis*-Dihydroxotetraammineplatinum(IV) Sulfate.** A 0.68-g sample of *trans*-$Pt(NH_3)_4(SO_4)_2$ was suspended in 50 mL of 0.3 M NaOH at 45 °C for 36 h. A white solid (0.12 g) was removed by filtration. Concentrated sulfuric acid was added dropwise to the solution until its yellow color faded and a slight white permanent suspension formed (pH was 4–5). The precipitate (0.02 g) was removed and the solution evaporated on a steam bath to 15 mL. A white crystalline precipitate formed after the solution stood for 24 h. The product was washed with water and acetone and dried under vacuum at room temperature (0.25 g, 43% yield). Most of the product dissolved slowly in 100 mL of hot water. Undissolved solid was removed. The volume was reduced to 10 mL. White crystals formed and were recovered (0.16 g). The high-pressure cation-exchange chromatogram of a solution of the product has a single peak. The soluble complex *trans*-$[Pt(NH_3)_4(OH)SO_4]ClO_4$ also works well as the starting material in this synthesis.

Anal. Calcd for $[Pt(NH_3)_4(OH)_2]SO_4$: Pt, 49.61; N, 14.24; S, 8.15. Found: Pt, 49.5; N, 14.22; S, 8.15.

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

Determination of K_a for *trans*-$[Pt(NH_3)_4(OH)SO_4]ClO_4$ (Reaction 3). A spectrophotometric determination of K_a was used. Equation

$$Pt(NH_3)_4(OH)SO_4^+ \rightleftarrows Pt(NH_3)_3NH_2(OH)SO_4^0 + H^+ \qquad (3)$$

4 was used to evaluate our data; it was derived from a more general

$$[H^+](A_{HA} - A) = K_aA - K_aA_{A^-} \qquad (4)$$

equation.[7] (A is the solution absorbance, A_{HA} is the absorbance when the acid is all undissociated, and A_{A^-} is the absorbance when only A^- is present in significant quantity.) All solutions contained 5.0×10^{-4} M $[Pt(NH_3)_4(OH)SO_4]ClO_4$, NaOH, and $NaClO_4$ to maintain a constant ionic strength of 0.080. Hydroxide concentrations used were 0.0783, 0.0261, 0.00870, and 0.00301 M. Absorbances were measured at 270 and 300 nm. Absorbance measurements were made first at 15.0, then at 24.5, and finally at 34.0 °C. Hydrolysis was sufficiently slow that the absorbances of the solutions at the three lower hydroxide concentrations had not changed when the solutions were cooled back to 15.0 °C. The changes in the 0.0783 M solution were small, and results based on calculations in which these data were not used were not significantly different from results based on all data. Linear plots were obtained; K_a values from data at the two wavelengths deviated from each other by less than 10%. The K_a values are 8.7×10^{-13} (15.0 °C), 1.00×10^{-12} (24.5 °C), and 1.16×10^{-12} (34.0 °C). Thermodynamic parameters are $\Delta H = 2.7$ kcal mol^{-1} and $\Delta S = -46$ cal deg^{-1} mol^{-1}.

Kinetic Measurements. The kinetics of the hydrolysis were followed spectrophotometrically at 290 nm. The temperature of the cell compartment varied less than 0.02 °C. Reaction solutions were prepared in room light, and air was not excluded. 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 uncertainity of the absorbance measurements.

Chromatographic Measurements. A 25 cm long, 4.6-mm i.d. column was packed with Vydac 401 TPx cation-exchange resin. The eluent was 0.060 M K_2SO_4 at a typical flow rate of 2.0 mL/min and 2000 psi pressure. Retention volumes of *cis*- and *trans*-$Pt(NH_3)_4(OH)_2^{2+}$ were about 7.8 and 6.5 mL, respectively (with a column volume of 2.85 mL). The effluent was monitored with a UV detector at 205 nm. Typical platinum concentrations in solution were 10^{-3}–10^{-4} M.

Registry No. *trans*-$[Pt(NH_3)_4(OH)SO_4]ClO_4$, 62571-46-4; *trans*-$[Pt(NH_3)_4(OH)_2]SO_4$, 70006-08-5; *cis*-$[Pt(NH_3)_4(OH)_2]SO_4$, 70006-10-9; *trans*-$Pt(NH_3)_4(SO_4)_2$, 62623-71-6.

References and Notes

(1) T. D. Harrigan and R. C. Johnson, *Inorg. Chem.*, **16**, 1741 (1977).
(2) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 59 (1962).
(3) A. A. Grinberg and Y. N. Kukushkin, *Dokl. Akad. Nauk SSSR*, **132**, 1071 (1960).
(4) "Gmelins Handbuch der anorganischen Chemie", No. 68D, Verlag Chemie, Weinheim/Bergstr., Germany, 1957, pp 487–488.
(5) S. E. Livingstone and R. E. Plowman, *J. Proc. R. Soc. N. S. W.*, **84**, 107 (1950).
(6) R. R. Rettew and R. C. Johnson, *Inorg. Chem.*, **4**, 1565 (1965); R. N. Keller, *Inorg. Synth.*, **2**, 251 (1963); W. E. Cooley and D. H. Busch, *ibid.*, **5**, 208 (1957).
(7) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants", McGraw-Hill, New York, 1961, p 275.