data reflect a real difference in the properties of the NO^- intermediate produced in the $NO–NH_2OH$ reaction and in $HN_2O_3^-$ decomposition. We have previously reported that at pH 8 the $HN_2O_3^-$ decomposition product is predominantly reduced to N_2 in the presence of excess NH_2OH, whereas the intermediate produced in the $NO–NH_2OH$ reaction forms N_2O predominantly under similar conditions.[24] We have speculated that this difference may correspond to the tautomers HNO and NOH, and since recent NMR evidence suggests that $HN_2O_3^-$ is protonated at nitrogen[28] and therefore releases HNO, we believe it possible that NO abstracts a hydrogen atom from NH_2O^- (reaction 13) at oxygen to form NOH. Since HNO is known to have a singlet ground state while calculations show that the unobserved species NOH would have a triplet ground state,[29–32] the key to the differences of properties observed in our reaction settings may reside in a difference of multiplicity between the two postulated forms of NO^-.

Conclusion

This paper describes the first proven instance of synthesis of a nitrosyl complex by direct insertion of NO^- into the coordination sphere of a transition metal ion, as far as we are aware. However, our efforts to achieve similar NO^- displacement processes in $Au(CN)_2^-$, $Pd(CN)_4^{2-}$, and $Pt(CN)_4^{2-}$, employing $HN_2O_3^-$ as a source of NO^-, have not succeeded. While our combination of kinetic and stoichiometric results shows conclusively that NO^- does engage in direct reaction in the case of Ni(II), it appears likely that Veprek-Siska and Lunak are correct in concluding that the reaction between NH_2OH and $Ni(CN)_4^{2-}$ can proceed at high pH without NO^- intermediacy[10,11] and that NH_2OH disproportionation does not produce this intermediate.[12] The NO^- test proposed by Nast et al.[4] cannot be taken to be conclusive and must be applied with caution.

Registry No. $NiNO(CN)_3^{2-}$, 25703-99-5; $K_2Ni(CN)_4$, 14220-17-8; $Na_2N_2O_3$, 13826-64-7; NH_2OH, 7803-49-8; NO, 10102-43-9; N_2O, 10024-97-2; N_2, 7727-37-9.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 3. Formation, Acid-Catalyzed Decomposition, and Intramolecular Isomerization of Oxygen-Bonded (αβ*S*)-(Sulfito)(tetraethylenepentamine)cobalt(III) Ion and the Hydrolysis of Its Sulfur-Bonded Analogue[1]

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The rate of SO_2 uptake by $(\alpha\beta S)$-hydroxo(tetraethylenepentamine)cobalt(III) ion has been studied by stopped-flow technique over the ranges $5.15 \leq pH \leq 7.6$ and $0.005 \leq [\text{total sulfite}] \leq 0.2$ M ($I = 1.0$ M, 10–20 °C) in sulfite buffer medium. The rate and activation parameters for SO_2 addition to $[(\alpha\beta S)\text{-Co(tetren)OH}]^{2+}$ are $k(10\ °C) = (3.2 \pm 0.5) \times 10^8\ s^{-1}\ M^{-1}$, $\Delta H^{*} = -0.5 \pm 1.0$ kcal mol^{-1}, and $\Delta S^{*} = -21.0 \pm 3.5$ cal $K^{-1}\ mol^{-1}$. Retardation by SO_3^{2-} and SO_4^{2-} is observed, which is ascribed to the formation of nonreactive ion pairs $[(\alpha\beta S)\text{-Co(tetren)OH}_2,X]^+$ with association constants of $125 \pm 25\ M^{-1}$ ($X = SO_3^{2-}$) and $27 \pm 3\ M^{-1}$ ($X = SO_4^{2-}$) at 10 °C and $I = 1.0$ M. The product of the SO_2 uptake reaction is shown by spectral studies to be an O-bonded sulfito intermediate. At 10 °C the protonated form of such a species, $[(\alpha\beta S)\text{-Co(tetren)OSO}_2H]^{2+}$ (p$K = 3.3$), eliminates SO_2 with $k = 550 \pm 80\ s^{-1}$, $\Delta H^{*} = 7.2 \pm 2.5$ kcal mol^{-1}, and $\Delta S^{*} = -20.4 \pm 8.7$ cal $K^{-1}\ mol^{-1}$. The oxygen-bonded sulfito intermediate shows no tendency to undergo internal redox but slowly isomerizes to its sulfur-bonded analogue. This process is shown to be totally intramolecular and its rate parameters are $k(30\ °C) = (4.2 \pm 0.7) \times 10^{-4}\ s^{-1}$, $\Delta H^{*} = 13.5 \pm 0.9$ kcal mol^{-1}, and $\Delta S^{*} = -29.6 \pm 3.0$ cal $K^{-1}\ mol^{-1}$. The sulfur-bonded isomer is also very stable to reduction of the cobalt(III) center, but it does undergo second-order base hydrolysis in the range $[OH^-] = 0.2–0.8$ M with $k(25\ °C) = (0.81 \pm 0.01) \times 10^{-4}\ s^{-1}\ M^{-1}$, $\Delta H^{*} = 27.6 \pm 0.7$ kcal mol^{-1}, and $\Delta S^{*} = 15.1 \pm 2.4$ cal $K^{-1}\ mol^{-1}$. At 90 °C and $[H^+] = 0.5$ M, there is evidence for slow acid-catalyzed hydrolysis ($k_{obsd} \sim 10^{-5}\ s^{-1}$), but a detailed study of this process was not made.

Introduction

Recent investigations in this laboratory show that O-bonded sulfito complexes are formed on the stopped-flow time scale by reaction of acidic aqueous sulfite with aquopentaammine-,[4] *cis*-[5] or *trans*-diaquobis(ethylenediamine)-,[6] or diaquo(2,2′,2″-triaminotriethylamine)cobalt(III)[1] complex ions. The kinetic data demonstrate in each case that formation of the O-bonded sulfito species may be attributed to nucleophilic attack by the Co–OH moiety of the deprotonated complex ions on dissolved SO_2. The O-bonded products are all unstable, rapidly and completely reverting to the original reactants at low pH (≤2). However, at higher pH values, a much slower

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Table I. UV-Visible Absorption Spectra

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
($\alpha\beta S$)-$[Co(tetren)OH_2]^{3+}$	473, 350	120, 85	this work
	473, 350	122, 85.3	9
($\alpha\beta S$)-$[Co(tetren)OSO_2]^+$	510, 330	150, 1928	this work
$[Co(NH_3)_5OSO_2]^+$	518, 330	~88, ~2100	4
$[Co(tren)(OH_2)OSO_2]^+$	510, 325	136, 1825	1
($\alpha\beta S$)-$[Co(tetren)SO_3]^+$	444, 281	236, 16 900	this work
$[Co(NH_3)_5SO_3]^+$	456, 278	148, 19 500	12
	456, 278	150, 18 900	13
$[Co(en)_2(NH_3)SO_3]^+$	463, 272	162, 13 800	14

intramolecular redox process to produce Co^{2+}_{aq} and SO_4^{2-} becomes dominant. This is in fact the sole secondary reaction observable for $[Co(NH_3)_5OSO_2]^+$ and the *cis*- and *trans*-$[Co(en)_2(OH_2)OSO_2]^+$ species within the investigated acidity range ($3 \leq pH \leq 9$).[4-6] For $[Co(tren)(OH_2)OSO_2]^+$, however, redox[7] is the major reaction only within the range $3 \leq pH \leq 5.4$, above which addition of a second sulfite ligand appears as a dominant alternative process and in fact is the sole reaction for pH ≥7.2. The present work was undertaken to obtain further evidence concerning the apparent "multidentate effect" noted above in the contrasting behavior of $(en)_2$ and tren analogues. We have therefore investigated the sulfite-uptake behavior of the complex ion containing the long "wrap-around" ligand tetraethylenepentamine (tetren) in place of the NH_3 groups of $[Co(NH_3)_5OH_2]^{3+}$. Again, a considerable contrast turns up in that, while $[Co(tetren)OH]^{2+}$ undergoes the expected rapid reversible SO_2 uptake to form $[Co(tetren)OSO_2]^+$, the O-bonded product shows no tendency to undergo internal redox, the only secondary reaction being a relatively slow internal rearrangement to yield the S-bonded analogue. This isomer is itself very stable both to internal redox and acid hydrolysis but does undergo base hydrolysis. Rate studies have been made of the various reactions mentioned, enabling some interesting mechanistic conclusions to be drawn.

Experimental Section

Materials. Tetraethylenepentamine (tetren) was used as obtained from Matheson, Coleman, and Bell. Solid $Na_2S_2O_5$ (Baker Analyzed) was the source of sulfite; this salt is very stable but hydrates rapidly and completely when dissolved in water.[4] All other chemicals were of reagent grade. The laboratory-distilled water was further purified by passing through a mixed-bed ion-exchange column.

Preparation and Characterization of Compounds. ($\alpha\beta S$)-Aquo(tetraethylenepentamine)cobalt(III) perchlorate was prepared from ($\alpha\beta S$)-chloro(tetraethylenepentamine)cobalt(III) perchlorate as described by House and Garner.[8-10] Elemental analyses[11] for C, H, N, and Co were in satisfactory agreement with the calculated values for $[Co(C_8N_5H_{23})OH_2](ClO_4)_3$. The UV-visible spectral parameters of the aquo complex measured by a Cary 118 spectrophotometer were close to those reported earlier (see Table I). ($\alpha\beta S$)-(Sulfito)(tetraethylenepentamine)cobalt(III) perchlorate (the stable S-bonded isomer) was prepared as follows. To an aqueous solution containing 1.13 g of ($\alpha\beta S$)-$[Co(tetren)OH_2](ClO_4)_3$ was added 0.22 g of $Na_2S_2O_5$. The orange-yellow color of the original solution turned red-brown almost instantaneously. This solution was allowed to sit at room temperature until a yellow solid crystallized out, which was collected on a fritted-glass funnel and washed with 95% ethanol. Recrystallization involved dissolving the sample in a minimum volume of warm water and adding a small amount of sodium perchlorate. The solution was filtered and set aside. The sulfito complex crystallizes out as orange-yellow crystals, which were collected and stored over silica gel in a desiccator. Anal. Calcd for $[Co(C_8N_5H_{23})SO_3](ClO_4)\cdot H_2O$: C, 21.55; H, 5.65; N, 15.71; S, 7.19; Co, 13.22. Found: C, 21.78; H, 5.78; N, 15.73; S, 7.42; Co, 13.38. The UV-visible spectral parameters of this complex are given in Table I and are seen to be quite similar to those for the analogous pentaammine species.

Acid-Dissociation Contants. The dissociation equilibria of SO_2 in aqueous medium may be represented as shown in eq 1 and 2. Analysis

$$SO_2 + H_2O \overset{K_1}{\rightleftharpoons} HSO_3^- + H^+ \tag{1}$$

$$HSO_3^- \overset{K_2}{\rightleftharpoons} SO_3^{2-} + H^+ \tag{2}$$

of our rate data is based on $K_2 = 5.0 \times 10^{-7}$ M (10-20 °C, $I = 1.0$ M) while the values of K_1 were taken to be 1.82×10^{-2}, 1.62×10^{-2}, and 1.41×10^{-2} M at 10, 15, and 20 °C ($I = 1.0$ M), respectively, as reported earlier.[4] The acid-dissociation constant (K_3) of the aquo cation ($\alpha\beta S$)-$[Co(tetren)OH_2]^{3+}$ was determined by titrating a 2×10^{-3} M complex solution ($I = 1.0$ M) with 0.1 M NaOH. pH measurements were made with a Fisher Accumet Model 420 pH/ion meter equipped with a Markson combination electrode. The meter was standardized against commercially available standard buffers. Values of pK_3 turned out to be 6.30 ± 0.05, 6.20 ± 0.05, and 6.10 ± 0.05 at 10, 15, and 20 °C ($I = 1.0$ M), respectively. These data are in reasonable agreement with the value of pK_3 = 6.3 ± 0.1 (15-25 °C, $I = 0.5$ M KCl) reported earlier.[15] Protonation of S-bonded ($\alpha\beta S$)-$[Co(tetren)SO_3]^+$ was not detectable by pH titration nor from spectral measurements in the wavelength range 220-600 nm at $[H^+]$ = 0.008-0.8 M ($I = 1.0$ M), so a rather small pK value must be assumed for the protonated ion.

Kinetics. All rate measurements were made at 1 M ionic strength ($NaClO_4$). The procedure for the SO_2 uptake study was essentially the same as described earlier[4] except for the fact that, when self-buffered sulfite media were used, one of the storage syringes of the automated Durrum Model 110 stopped-flow assembly contained the solution of the aquo complex 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 way with $[Co(III)]_T = (0.42-1.5) \times 10^{-3}$ M. The SO_2 elimination process was studied by acidifying the O-bonded (sulfito)(tetraethylenepentamine)cobalt(III) species with McIlvaine phosphate-citric acid buffer.[16] This complex was prepared in situ by dissolving appropriate amounts of ($\alpha\beta S$)-$[Co(tetren)OH_2](ClO_4)_3$ and $Na_2S_2O_5$ ($[Co(III)]_T$:$[S]_T$ = 1:2) and adjusting the ionic strength to 1 M and the pH to 6.0 ± 0.1. This solution was stored at 0 °C to minimize isomerization to the S-bonded form. The rates of the SO_2 uptake and elimination processes were measured at 410 nm. pH measurements were made immediately after the kinetic runs with use of a water-jacketed sample holder thermostated at the reaction temperature.

The kinetics of isomerization of ($\alpha\beta S$)-$[Co(tetren)OSO_2]^+$ to ($\alpha\beta S$)-$[Co(tetren)SO_3]^+$ was followed in the thermostated cell compartment of the Cary 118 UV-visible spectrophotometer in self-buffered sulfite media. The sulfite buffer and the aquo complex solutions were thermostated separately in 50-mL volumetric flasks. A known volume of the complex solution was then added to the sulfite buffer, and the volume was made up with distilled water at the reaction temperature. This solution was quickly transferred to the thermostated 1-cm cuvette. In a number of experiments, complete spectral curves were run at a series of times over the wavelength range 600-330 nm. For some runs the rates of isomerization were followed at 380, 410, 440, and 540 nm, and the data proved that there was no wavelength dependence of the observed rate constant. For most of the runs, however, experiments were done at 380 nm, where the transformation of the O-bonded sulfito complex to the final S-bonded sulfito product is associated with a substantial absorbance decrease. The rate of base hydrolysis of the S-bonded sulfito complex was studied spectrophotometrically at 440 nm, the experimental procedure being similar to that described for the study of the isomerization kinetics. All the tabulated pseudo-first-order observed rate constants (k_{obsd}) were calculated by means of a linear least-squares analysis of ln $|A_t - A_\infty|$

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Table II. Dependence of k_{obsd} on pH and [Total Sulfite] for SO_2 Uptake by ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$ in Sulfite Buffer

temp, °C	pH	$[S]_T$	k_{obsd}, s^{-1}	k_b, s^{-1} [a]	$10^{-8}k_1$, s^{-1} M^{-1} [b]
10.0	5.15	0.04	290 ± 10	8.5	4.5 (2.9)
	5.31	0.04	217 ± 5	5.9	3.3 (2.3)
	5.44	0.10	277 ± 16	4.4	3.0 (1.3)
	5.63	0.05	141 ± 4	2.8	2.8 (1.5)
	5.64	0.10	196 ± 15	2.8	2.9 (1.0)
	5.66	0.10	170 ± 10	2.7	2.6 (0.9)
	5.49	0.04	195 ± 3	3.9	3.6 (2.3)
	5.72	0.04	130 ± 4	2.3	3.4 (1.9)
	5.89	0.04	102 ± 3	1.6	3.5 (1.6)
	5.80	0.10	135 ± 14	1.9	2.7 (0.84)
	5.93	0.10	103 ± 3	1.4	2.7 (0.76)
	6.03	0.05	86.4 ± 2.2	1.1	3.5 (1.5)
	6.05	0.10	79.5 ± 2.2	1.1	2.7 (0.70)
	6.06	0.10	68.1 ± 1.9	1.0	2.3 (0.60)
	6.05	0.05	80.4 ± 3.1	1.1	3.4 (1.4)
	6.17	0.04	56.8 ± 1.1	0.8	3.4 (1.5)
	6.24	0.10	50.1 ± 1.3	0.7	2.6 (0.63)
	6.25	0.10	44.1 ± 4.9	0.7	2.3 (0.56)
	6.38	0.005	8.93 ± 0.26	0.5	3.4 (3.0)
	6.40	0.01	16.1 ± 0.7	0.5	3.8 (2.9)
	6.40	0.02	25.0 ± 0.8	0.5	3.6 (2.3)
	6.43	0.03	28.1 ± 0.8	0.4	3.0 (1.3)
	6.40	0.04	33.9 ± 0.5	0.5	3.4 (1.5)
	6.47	0.04	32.1 ± 1.0	0.4	3.8 (1.8)
	6.42	0.05	36.3 ± 1.1	0.5	3.5 (1.4)
	6.45	0.06	36.0 ± 1.4	0.4	3.5 (1.3)
	6.45	0.08	35.8 ± 1.9	0.4	3.2 (0.95)
	6.43	0.10	31.6 ± 2.1	0.4	2.5 (0.62)
	6.45	0.10	34.5 ± 1.2	0.4	2.8 (0.73)
	6.44	0.10	33.3 ± 3.7	0.4	2.7 (0.67)
	6.46	0.15	35.1 ± 3.5	0.4	2.7 (0.50)
	6.49	0.20	35.1 ± 3.7	0.4	2.8 (0.41)
	6.62	0.04	18.0 ± 0.2	0.3	3.2 (1.5)
	6.81	0.04	11.4 ± 0.2	0.2	3.6 (1.9)
	6.92	0.04	7.93 ± 0.11	0.15	3.3 (1.9)
	7.13	0.05	4.91 ± 0.17	0.09	3.6 (2.1)
	7.60	0.05	0.98 ± 0.04	0.03	3.8 (3.0)
15.0	6.26	0.005	14.4 ± 0.5	1.0	3.2 (2.8)
	6.32	0.005	10.3 ± 0.4	0.92	2.6 (2.3)
	6.30	0.01	24.0 ± 0.4	0.96	3.4 (2.7)
	6.35	0.02	36.1 ± 0.8	0.86	3.6 (2.3)
	6.34	0.03	48.0 ± 2.4	0.87	3.7 (2.0)
	6.36	0.04	56.8 ± 0.8	0.84	3.9 (1.9)
	6.36	0.05	60.4 ± 1.7	0.84	3.8 (1.6)
	6.39	0.06	63.5 ± 1.0	0.78	4.0 (1.5)
	6.40	0.08	69.0 ± 1.1	0.76	4.0 (1.3)
	6.40	0.10	68.6 ± 1.9	0.73	3.9 (1.1)
	6.43	0.15	68.0 ± 2.0	0.71	3.6 (0.73)
	6.40	0.20	69.3 ± 1.1	0.76	3.3 (0.51)
	6.44	0.20	68.4 ± 1.3	0.70	3.5 (0.57)
	6.51	0.20	60.5 ± 1.2	0.59	3.7 (0.61)
	5.76	0.10	251 ± 6	3.3	3.4 (1.1)
	6.05	0.10	143 ± 3	1.7	3.5 (0.97)
	6.60	0.10	34.2 ± 2.8	0.48	3.1 (0.91)
	6.78	0.10	19.1 ± 0.5	0.32	2.7 (0.93)
	7.04	0.10	10.1 ± 1.0	0.17	3.0 (1.3)
	7.43	0.10	2.95 ± 0.07	0.07	3.2 (1.9)
20.0	5.62	0.10	374 ± 8	6.9	4.3 (0.96)
	5.95	0.10	235 ± 17	3.2	3.3 (0.95)
	6.39	0.005	12.6 ± 0.2	1.18	3.0 (2.6)
	6.34	0.010	26.2 ± 0.5	1.33	3.1 (2.4)
	6.28	0.010	30.7 ± 0.7	1.53	3.2 (2.4)
	6.28	0.020	52.4 ± 1.0	1.53	3.3 (2.1)
	6.28	0.030	65.4 ± 1.5	1.53	3.2 (1.8)
	6.29	0.040	72.5 ± 2.2	1.49	3.1 (1.5)
	6.31	0.050	77.9 ± 2.4	1.42	3.2 (1.4)
	6.36	0.060	79.9 ± 1.7	1.27	3.4 (1.3)
	6.37	0.080	89.9 ± 3.3	1.24	3.5 (1.18)
	6.38	0.10	90.5 ± 3.0	1.21	3.4 (0.98)
	6.42	0.15	88.5 ± 3.3	1.10	3.3 (0.71)
	6.39	0.20	89.5 ± 3.4	1.18	2.9 (0.50)
	6.41	0.02	38.4 ± 0.6	1.13	3.4 (2.2)
	6.40	0.03	53.4 ± 0.9	1.15	3.6 (2.0)
	6.39	0.04	64.0 ± 0.8	1.18	3.5 (1.8)
	6.56	0.10	58.2 ± 1.7	0.80	3.4 (1.1)
	7.05	0.10	14.1 ± 0.2	0.26	3.3 (1.6)
	7.42	0.10	3.80 ± 0.06	0.11	3.1 (2.0)

[a] Calculated rate constant for SO_2 elimination reaction (eq 4). [b] Values in parentheses are calculated by using eq 5. Unparenthesized values are calculated from a rearranged form of eq 8 with $Q_1 = 125$ M^{-1} (10–20 °C). These yielded $10^{-8}k_1$(av) = 3.2 ± 0.5, 3.4 ± 0.3, and 3.3 ± 0.3 s^{-1} M^{-1} at 10, 15, and 20 °C, respectively.

vs. t data, where A_t and A_∞ are the absorbances at time t and infinity, respectively. These plots were in general linear at least up to 3 half-lives.

Results and Discussion

Qualitative Observations. Addition of $Na_2S_2O_5$ to a buffered aqueous solution of ($\alpha\beta S$)-$[Co(tetren)OH_2]^{3+}$ causes an instantaneous color change from light orange to red-brown. This is presumed on the basis of our previous evidence[1,4] to be characteristic of the formation of the O-bonded $[Co(tetren)OSO_2]^+$ cation, as is also evident from its spectral characteristics (Table I). The extent of this color change is dependent upon the concentration of the aquo complex, total sulfite, and pH of the medium. Maximum buildup of the intermediate occurs at $5 < pH < 7$. Acidification of the red-brown solution to pH 2 results in rapid regeneration of the aquo complex. Attempts to isolate the O-bonded sulfito complex in the solid state proved unsuccessful. The red-brown solution, however, slowly changes to bright yellow, the spectral features of which are similar to those of other S-bonded sulfito complexes (see Table I). Tests for cobalt(II) in the form of $[Co(NCS)_4^{2-}]$[17] after the buffered mixtures of the aquo complex and sulfite had been left at room temperature for several weeks were negative. This is in contrast with the earlier observations of facile intramolecular electron transfer[4–7] of $[Co(NH_3)_5OSO_2]^+$, *cis*- and *trans*-$[Co(en)_2(OH_2)OSO_2]^+$, and $[Co(tren)(OH_2)OSO_2]^+$ ions in acidic sulfite media.

SO_2 Uptake and Elimination Reactions. The observed rapidity and reversibility of the formation of (sulfito-*O*)(tetraethylenepentamine)cobalt(III) ion is consistent with SO_2 uptake by ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$ and with SO_2 elimination from the product species in an acid-catalyzed step, in both cases without breakage of the Co–O bond. Earlier studies have shown that aquation of $[Co(tetren)X]^{2+}$ ($X = Cl^-$, N_3^-, and NCS^-) and anation of $[Co(tetren)OH_2]^{3+}$ by N_3^- and NCS^- proceed extremely slowly,[18,19] which is typical of reactions involving Co–X or Co–OH_2 bond fission.

Table II presents the rate data for the formation of the O-bonded sulfito complex measured in sulfite buffer. Some rate data at 10 °C measured in phosphate–citric acid buffer under similar conditions of pH and total sulfite concentration revealed a strong buffer effect, which will be discussed later. The observed rate constants of Table II may be treated as done in our previous studies[1,4] as the sum of the overall rate constants for SO_2 uptake by $[Co(tetren)OH]^{2+}$ (k_f) and SO_2 elimination (k_b) from $[Co(tetren)OSO_2H]^+$:

$$k_{obsd} = k_f + k_b \qquad (3)$$

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[17] Hughes, R. G.; Endicott, J. F.; Hoffman, M. Z.; House, D. A. *J. Chem. Educ.* **1969**, *46*, 440.

[18] El-Awady, A. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1463; **1974**, 1265.

[19] Ni, T.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1071.

Table III. Effect of Sulfate on the Rate of SO_2 Uptake by ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$ at 10 °C and I = 1.0 M

pH	$[SO_4^{2-}]_T$	k_{obsd}, s^{-1} [a]
5.63	0	141 ± 4
5.65	0.025	121 ± 5
5.65	0.05	106 ± 2
5.70	0.075	87.8 ± 3.5
5.71	0.10	74.6 ± 3.1
5.70	0.125	61.1 ± 3.5

[a] Sulfite buffer; $[S]_T$ = 0.05 M.

The value of k_b at each pH was calculated from the relationship

$$k_b = \frac{k_2[H^+]}{[H^+] + K_4} \tag{4}$$

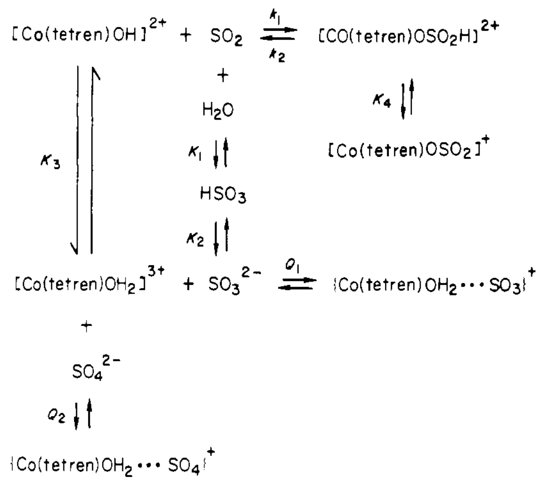
where k_2 is the first-order rate constant for loss of SO_2 from $[Co(tetren)OSO_2H]^{2+}$ and K_4 is its acid-dissociation constant. Values of k_2 and K_4 at different temperatures were obtained from the independent rate study of the SO_2 elimination process (see below). With the assumption that $[Co(tetren)OH]^{2+}$ and SO_2 are the reactant species, the expression for k_f takes the form

$$k_f = k_1\left(\frac{K_3}{K_3 + [H]^+]}\right)f_1S_T \tag{5}$$

where k_1 is the second-order rate constant for SO_2 uptake by $[Co(tetren)OH]^{2+}$, $f_1 = [H^+]^2/([H^+]^2 + K_1[H^+] + K_1K_2)$ (the fraction of total sulfur in the form of SO_2), and all other constants are as defined earlier. Values of k_1 calculated from eq 5 utilizing the known values of k_{obsd}, k_2, and K_4 are given in Table II. One notes that k_1 calculated in this way is not constant but decreases with pH. This variation is inconsistent with simultaneous rate-determining addition[20] of SO_2 to $[Co(tetren)OH_2]^{2+}$ and $[Co(tetren)OH]^{2+}$, as proposed[1] in the SO_2 uptake study of $[Co(tren)(OH_2)_2]^{3+}$. An attempt to fit the data to a two-term rate expression involving simultaneous addition of HSO_3^- and SO_2 to $[Co(tetren)OH]^{2+}$ also fails.[21] However, the slow rate of isomerization of $[Co(tetren)OSO_2]^+$ to $[Co(tetren)SO_3]^+$ (see below) and the slow rates of anation[18] of $[Co(tetren)OH_2]^{3+}$ by NCS^- and N_3^- rule out the possibility of formation of O-bonded sulfito complexes via conventional HSO_3^- or SO_3^{2-} substitution for ligand water. Rate-limiting addition of HSO_3^- to $[Co(tetren)OH_2]^{3+}$ without Co–O bond fission remains a possibility. This process is kinetically indistinguishable from SO_2 addition to $[Co(tetren)OH]^{2+}$, but our study[7] of the sulfite reaction with $[Co(tren)(OH_2)OSO_2]^+$ shows that this type of HSO_3^- or SO_3^{2-} addition is several orders of magnitude slower than the reaction presently under consideration.

Because of the above consideration, we have looked at other possible explanations of the falloff of k_1 with pH. Examination of selected rate data from Table II ($[S]_T$ = 0.005—0.2 M and almost constant pH values of 6.44 ± 0.05, 6.36 ± 0.05, and 6.38 ± 0.04 at 10, 15, and 20 °C) reveals that k_{obsd} increases with total sulfite concentration and levels off to a constant value at $[S]_T \geq 0.08$ M. Under these conditions, the calculated $k_b << k_{obsd}$, so k_{obsd} essentially represents the observed rate constant for the SO_2 uptake reaction, k_f. The k_{obsd} vs. $[S]_T$ profile at constant pH can be ascribed to the rate-retarding influence of SO_3^{2-} due to the formation of a nonreactive ion pair, $[Co(tetren)OH_2^{3+},SO_3^{2-}]$. To test this assumption, we made some rate measurements at pH 5.68 ± 0.03 and $[S]_T$ = 0.05 M (10 °C), adjusting ionic strength to 1 M with varying amounts of Na_2SO_4 and $NaClO_4$, as shown in Table III. A reaction scheme that will account for both the SO_3^{2-} and SO_4^{2-} retardation of the rate of SO_2 uptake by $[Co(tetren)OH]^{2+}$ is presented in Scheme I (excluding the various H^+ additions and dissociations for the sake of simplicity). For such a scheme the observed rate constant takes the form

Scheme I



$$k_{obsd} = \frac{k_1K_3f_1[S]_T}{[H^+] + K_3 + Q_1[H^+]f_2[S]_T + Q_2[H^+][SO_4^{2-}]} + k_b \tag{6}$$

where f_1 is already defined, $f_2 = K_1K_2/([H^+]^2 + K_1[H^+] + K_1K_2)$, $[S]_T$ = [total sulfite], and Q_1 and Q_2 are the association constants of SO_3^{2-} and SO_4^{2-} ion pairs of the aquo complex (see Scheme I), respectively. All other terms of eq 6 are as defined earlier. Equation 6 can be rearranged to a reciprocal form:

$$\frac{1}{k_{obsd} - k_b} = \frac{([H^+] + K_3 + [H^+]Q_1f_2[S]_T)}{k_1K_3f_1[S]_T} + \left(\frac{Q_2[H^+]}{k_1K_3f_1[S]_T}\right)[SO_4^{2-}] \tag{7}$$

The rate data at constant pH and $[S]_T$ but varying concentration of SO_4^{2-} (Table III) fit eq 7 satisfactorily. The linear least-squares best fit plot of $10^3/(k_{obsd} - k_b)$ against $[SO_4^{2-}]$ yields intercept = 6.03 ± 0.51 s and slope = 77 ± 9 M^{-1} s. The value of Q_2 (27.3 ± 3.2 M^{-1}) calculated from the slope and utilizing the corrected value of $k_1 = 32 \times 10^8$ s^{-1} M^{-1} (see below) and the other known constants is in satisfactory agreement with the published value[22] of the association constant of a typical complex ion/sulfate ion pair, $[Co(NH_3)_5OH_2^{3+},SO_4^{2-}]$ (Q = 16 M^{-1} at I = 1 M, 31.1 °C).

The rate data measured in sulfite buffer (Table II) were analyzed in a similar manner but in the absence of added SO_4^{2-}. In this event, eq 6 can be recast as

$$\frac{[H^+]}{k_{obsd} - k_b} = \left(\frac{1}{k_1}\right)\left\{\left(\frac{K_3 + [H^+]}{K_3}\right)\frac{[H^+]}{f_1[S]_T}\right\} + \frac{Q_1K_1K_2}{k_1K_3} \tag{8}$$

Values of k_1 (s^{-1} M^{-1}) and Q_1 (M^{-1}) obtained from the linear least-squares best-fit plots of $10^8[H^+]/(k_{obsd} - k_b)$ against $(K_3 + [H^+])[H^+]/(K_3f_1[S]_T)$ are as follows: (3.7 ± 0.2) × 10^8, 158 ± 11; (3.1 ± 0.1) × 10^8, 103 ± 7; (3.0 ± 0.4) × 10^8, 116

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(20) Simultaneous SO_2 uptake by ($\alpha\beta S$)-$[Co(tetren)OH_2]^{3+}$ (k_0) and ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$ (k_1) will have $k_f = \{(k_0/K_3)[H^+] + k_1\}\{K_3/(K_3 + [H^+])\}f_1[S]_T$.

(21) For SO_2 and HSO_3^- addition to ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$ $k_f = \{(k_1 + k_{HSO_3}K_1/[H^+])K_3/(K_3 + [H^+])\}f_1[S]_T$ where

$$[Co(tetren)OH]^{2+} + HSO_3^- \xrightarrow{k_{HSO_3}} [Co(tetren)OSO_2]^+ + H_2O$$

(22) Taube, H.; Posey, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 1463.

Table IV. Comparison of the Rates and Activation Parameters for SO_2 and CO_2 Uptake by Some Aquoaminecobalt(III) Ions in Aqueous Solution at 25 °C

complex ion	reactant	k, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	ref
$[Co(NH_3)_5OH]^{2+}$	SO_2	4.7×10^8	9.8 ± 0.3	14.0 ± 0.4	4
cis-$[Co(en)_2(OH)OH_2]^{2+}$	SO_2	1.0×10^8	6.0 ± 0.1	−1.6 ± 0.2	5
$[Co(tren)(OH)OH_2]^{2+}$	SO_2	5.3×10^7	4.5 ± 0.1	−8.0 ± 0.3	1
$[Co(tetren)OH]^{2+}$	SO_2	3.3×10^8	−0.5 ± 1.0	−21.0 ± 3.5	this work
$[Co(NH_3)_5OH]^{2+}$	CO_2	220	15.3 ± 0.9	3.6 ± 3.0	*a*
cis-$[Co(en)_2(OH)OH_2]^{2+}$	CO_2	280	14.8 ± 0.2	2.0 ± 0.8	*b*
$[Co(tren)(OH)OH_2]^{2+}$	CO_2	44	14.7 ± 0.1	−1.9 ± 0.2	*c*
$[Co(tetren)OH]^{2+}$	CO_2	166	15.4 ± 1.2	3.3 ± 4.1	15

[a] Chaffee, E.; Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4169. [b] DeJovine, J. M.; Wan, W. K.; Harris, G. M., unpublished work. [c] Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1975**, *97*, 1733.

± 24; at 10, 15, and 20 °C, respectively. These plots were good straight lines as indicated by the correlation coefficients (r = 0.987 (10 °C), 0.995 (15 °C), and 0.973 (20 °C)). It may be noted that the parameters k_1 and Q_1 do not show a measurable trend with temperature in the range studied. We, therefore, choose constant values for $Q_1 = 125 \pm 25$ M^{-1} (average of values at 10–20 °C), and k_1 can now be calculated for all the data of Table II by use of a rearranged form of eq 8. The corrected values of k_1 (see Table II) do not show pH and sulfite dependence and average out to $(3.2 \pm 0.5) \times 10^8$, $(3.4 \pm 0.3) \times 10^8$, and $(3.3 \pm 0.3) \times 10^8$ s^{-1} M^{-1} at 10, 15, and 20 °C, respectively. The data utilizing phosphate–citrate buffers exhibit a much more pronounced pH effect than do those given in Table II. For example, at 10 °C, k_1 calculated by means of eq 5 decreases from 2.7×10^8 M^{-1} s^{-1} at pH = 3.2 and $[S]_T$ = 0.04 to 9×10^6 M^{-1} s^{-1} at pH = 6.8 and the same $[S]_T$. In view of the complexity of this buffer, which contains various types and fractions of phosphate and citrate ions at various pHs, no attempt was made to analyze these data in terms of ion-pairing phenomena.

In a recent study Farrell and Murray[23] interpreted the rate data for the sulfite substitution reaction of S-bonded *trans*-aquo(sulfito)bis(ethylenediamine)cobalt(III) ion in terms of the S_N1 (IP) mechanism. Ion pairing of *trans*-$[Co(en)_2(SO_3)OH_2]^+$ was believed to occur through hydrogen bonding of the aquo ligand with SO_3^{2-}. They reported a value of K_{IP} = 30 ± 1 M^{-1} at 25 °C (I = 1 M) for the ion pair *trans*-$\{Co(en)_2(SO_3)(OH_2)\cdots SO_3\}^-$. The association constant of the ($\alpha\beta S$)-$\{Co(tetren)(OH_2)\cdots SO_3\}^+$ ion pair is 4 times larger than the figure just quoted. This difference is attributable to both charge and relative hydrogen-bonding ability of the cobalt(III)-bound aqua ligand with SO_3^{2-}. The pK of the aqua ligand of $[Co(tetren)OH_2]^{3+}$ is at least 3 units lower than that of *trans*-$[Co(en)_2(SO_3)OH_2]^+$. It is, therefore, quite understandable that the hydrogen-bonding possibility in $(en)_2$ complex/sulfite will be somewhat less pronounced than for the $\{Co(tetren)OH_2\cdots SO_3\}^+$ ion pair. It is also evident from the relative stabilities of the SO_3^{2-} and SO_4^{2-} ion pairs that specific hydrogen-bonding effects strongly influence the stability of $\{Co(tetren)OH_2\cdots SO_3\}^+$. It is also noteworthy that, while the ion pair is the reactive species in the *trans*-$[Co(en)_2(SO_3)OH_2]^+$ reaction, it is totally inactive in the $[Co(tetren)OH_2]^{3+}$ reaction. However, this contrasting behavior is to be expected, since in the former instance, the reaction is conceived as a total *substitution* of SO_3^{2-} for the trans-labilized OH_2 ligand to which it is hydrogen bonded in the ion pair. In our case, SO_2 *addition* must take place at a site already blocked by either SO_3^{2-} or SO_4^{2-} ion, which is firmly H bonded to the rather inert aqua ligand.

Table V. Dependence of k_{obsd} on pH and Temperature for the SO_2 Elimination Reaction of ($\alpha\beta S$)-$[Co(tetren)(OH_2)OSO_2]^+$ ($[Co]_T = 1.5 \times 10^{-3}$ and $[S]_T = 3.0 \times 10^{-3}$ M)

temp, °C	pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}	pH	k_{obsd}, s^{-1}
10.0	3.03	485 ± 27	3.68	156 ± 6	4.17	77.3 ± 2.7
	3.14	366 ± 12	3.76	164 ± 10	4.29	54.0 ± 0.6
	3.23	347 ± 31	3.78	137 ± 3	4.35	49.5 ± 1.5
	3.25	309 ± 24	3.92	135 ± 2	4.40	46.6 ± 0.5
	3.32	294 ± 20	3.98	113 ± 4	4.53	34.0 ± 0.5
	3.38	276 ± 16	4.12	71.8 ± 1.7	4.78	23.0 ± 0.1
	3.42	267 ± 24	4.12	79.4 ± 2.1	5.33	7.22 ± 0.06
	3.54	220 ± 12	4.16	64.5 ± 2.5	5.47	4.80 ± 0.12
	3.66	146 ± 4	4.17	65.0 ± 0.7		
15.0	3.34	426 ± 28	3.73	228 ± 10	4.36	72.0 ± 1.6
	3.43	333 ± 16	3.89	173 ± 17	4.28	83.8 ± 6.6
	3.68	258 ± 31	4.11	111 ± 6	4.44	64.3 ± 1.7
	3.73	215 ± 12	4.13	108 ± 3		
20.0	3.28	655 ± 20	3.64	363 ± 8	4.28	132 ± 6
	3.37	585 ± 30	3.76	323 ± 8	4.40	96.8 ± 3.8
	3.46	511 ± 16	4.05	192 ± 6	4.45	84.4 ± 5.1
	3.47	528 ± 18	4.15	159 ± 5	4.73	52.3 ± 2.3
	3.54	433 ± 23	4.25	138 ± 2		

temp, °C	k_2, s^{-1} [a]	$10^4 K_4$, M [b]	temp, °C	k_2, s^{-1} [a]	$10^4 K_4$, M [b]
10.0	550 ± 80	4.5 ± 0.7	20.0	885 ± 117	3.0 ± 0.4
15.0	614 ± 75	3.2 ± 0.4			

[a] $\Delta H^{\ddagger} = 7.2 \pm 2.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -20.4 \pm 8.7$ cal K^{-1} mol^{-1}. [b] Temperature parameters for K_4 are $\Delta H = -6.2 \pm 2.8$ kcal mol^{-1}, $\Delta S = -37 \pm 10$ cal K^{-1} mol^{-1}.

A comparison of the rate parameters for SO_2 and CO_2 uptake reactions of several cobalt(III) complexes is made in Table IV. The SO_2 uptake process is ~10^6 times faster than the CO_2 uptake reaction. This large rate difference is due to a combination of both activation enthalpy and entropy differences. It is interesting to note that $\Delta H^{\ddagger}$ for SO_2 addition decreases down the series $[Co(NH_3)_5OH]^{2+}$ > *cis*-$[Co(en)_2(OH)OH_2]^{2+}$ > $[Co(tren)(OH)OH_2]^{2+}$ > ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$. For ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$ the rate would reach the diffusion-controlled limit but for the high negative value of $\Delta S^{\ddagger}$. This large negative value suggests that the solvation spheres of the reactants are least perturbed in the transition state when SO_2 adds to ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$. In such a situation, the energy requirements of the process are likely to be a minimum, as reflected in the zero value for $\Delta H^{\ddagger}$.

The rate data for the SO_2 elimination reaction measured in phosphate–citric acid buffer appear in Table V. k_{obsd} increases with hydrogen ion concentration. $1/k_{obsd}$ vs. $1/[H^+]$ plots in the pH ranges 3.03–4.53, 3.34–4.44, and 3.46–4.73 at 10, 15, and 20 °C, respectively, yielded good straight lines (Figure 1) with positive intercepts and gradients in accordance with eq 4. The validity of eq 4 suggests the following facts: (i) The SO_2 elimination process involves rapid proton preequilibration of $[Co(tetren)OSO_2]^+$ followed by rate-determining loss of SO_2 from the protonated species. (ii) There is no detectable catalysis by citrate and phosphate species. (iii) The SO_2 uptake rate does not contribute significantly to the observed pseudo-first-order rate constant (eq 3), not only because the pH and total sulfite concentration are low ($[Co]_T/[S]_T$ = 1/2) but also because the buffer anions tie up

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[23] Farrell, S. M.; Murray, R. S. *J. Chem. Soc., Dalton Trans.* **1977**, 322.

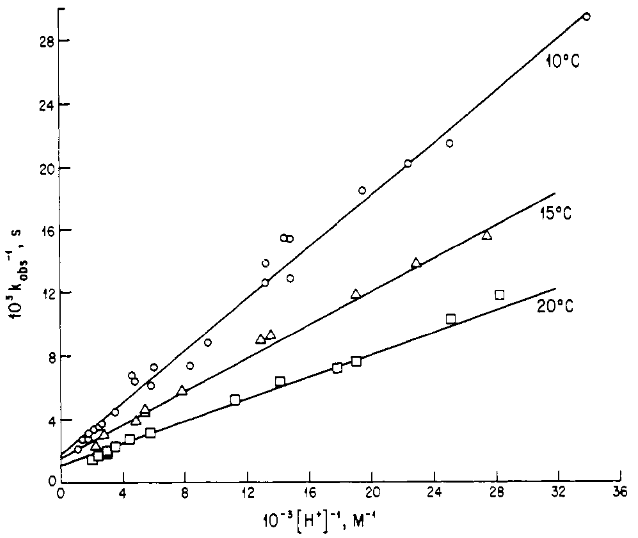

Figure 1. $10^3 k_{obsd}^{-1}$ (s^{-1}) vs. 10^{-3} $[H^+]^{-1}$ (M^{-1}) plot for the SO_2 elimination reaction.

a considerable fraction of the aquo cations. Values of k_2 and K_4 obtained from the least-squares gradient and the intercept of $1/k_{obsd}$ vs. $1/[H^+]$ plots are incorporated in Table V.

Elimination of SO_2 from the protonated sulfito-*O* complex occurs $\sim 10^3$ times faster than that of CO_2 from the corresponding bicarbonato complex (see Table VIII). Like the SO_2 uptake process, loss of SO_2 from ($\alpha\beta S$)-$[Co(tetren)OSO_2H]^{2+}$ is associated with low activation enthalpy and entropy. A comparison shows that S–O bond breaking is energetically more favorable than C–O and Se–O bond cleavage (see Table VIII). Low negative values of ΔS^* for SO_2 elimination from ($\alpha\beta S$)-$[Co(tetren)OSO_2H]^{2+}$ and related species may be due to intramolecular proton rearrangement and appreciable solvation of the leaving group in the transition state of the process.

Isomerization of ($\alpha\beta S$)-$[Co(tetren)OSO_2]^+$. Transformation of the O-bonded sulfito complex to the S-bonded isomer is associated with persistent isosbestic points at 487 nm ($\epsilon = 129$ M^{-1} cm^{-1}) and 431 nm ($\epsilon = 202$ M^{-1} cm^{-1}) (see Figure 2).[24] The rate data are presented in Table VI. One notes that the pseudo-first-order rate constant at a constant total sulfite concentration sharply increases with pH and attains a limiting value at pH >6. This is best explained as due to incomplete conversion of the aquo complex to the O-bonded sulfito complex at low pH. It is, however, significant that k_{obsd} is independent of wavelength, total sulfite concentration ($[S]_T$ = 0.02–0.3 M), and acidity of the medium at pH >6. Under these conditions the aquo complex is fully transformed to the O-bonded sulfito complex, which exists in the deprotonated form. The rate law for the isomerization of $[Co(tetren)OSO_2]^+$ to its S-bonded analogue is, therefore, best represented as

$$-\frac{d[CoOSO_2^+]}{dt} = k_{iso}[CoOSO_2^+]_T \qquad (9)$$

As seen in Table VI, the isomerization of ($\alpha\beta S$)-$[Co(tetren)OSO_2]^+$ to ($\alpha\beta S$)-$[Co(tetren)SO_3]^+$ is associated with $\Delta H^* = 13.5 \pm 0.9$ kcal mol^{-1} and $\Delta S^* = -29.6 \pm 3$ cal K^{-1} mol^{-1}. In comparison to these values, Adamson and coworkers[25] report $\Delta H^* = 22.6$ kcal mol^{-1} and $\Delta S^* = -15.6$ cal K^{-1} mol^{-1} for intramolecular O to S isomerization of *cis*-$[Co(en)(O\text{–}S\text{–}CH_2CH_2\text{–}NH_2)]^{2+}$. Lack of dependence on $[SO_3^{2-}]$ and $[H^+]$ on the rate of isomerization of our complex (at pH >6 and high $[SO_3^{2-}]$) suggests that the process is totally

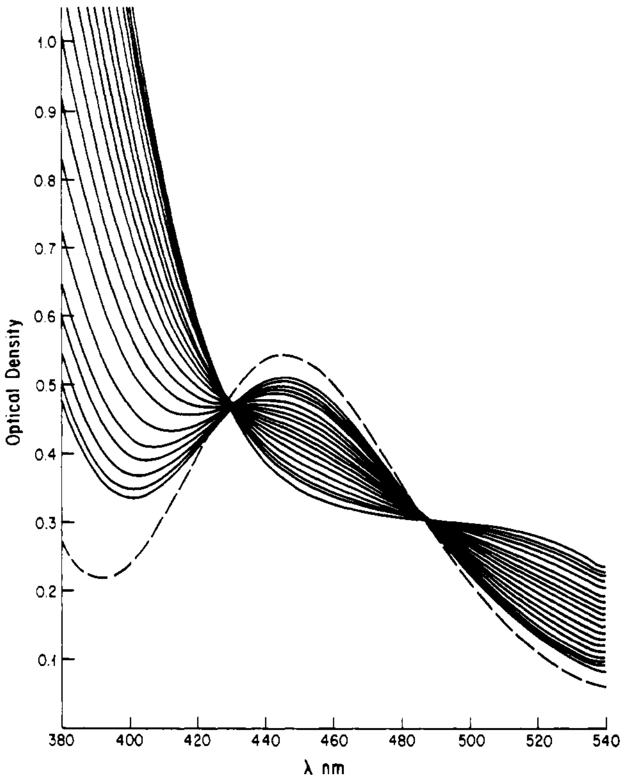

Figure 2. Successive scans of the spectral changes during the isomerization of ($\alpha\beta S$)-$[Co(tetren)OSO_2]^+$ to its S-bonded form: [complex] = 2.4×10^{-3} M, $[S]_T = 0.3$ M, pH = 6.33, temperature = 25 °C, $I = 1$ M ($NaClO_4$). Time in seconds reading downward at 400 nm: 117, 350, 500, 720, 1000, 1340, 1600, 1920, 2160, 2460, 2870, 3300, 3800, 4390, 5330, 6190, 6910, 7980, 9050, 9830. Last spectrum (dashed line) is after 20 h.

Table VI. Rate Data for the Isomerization of $[(\alpha\beta S)\text{-}Co(tetren)OSO_2]^+$

temp, °C	pH	$[S]_T$, M	$10^4 k_{obsd}$, s^{-1} [a]	pH	$[S]_T$, M	$10^4 k_{obsd}$, s^{-1} [a]
25.6	6.12	0.02	2.7[b]	6.52	0.30	2.6[b]
	6.33	0.3	2.7	6.83	0.20	2.7[b]
	6.42	0.15	3.1	7.09	0.20	2.8[b]
	6.45	0.2	3.1[b]	7.26	0.20	2.7[b]
	6.47	0.25	2.8[b]			
30.2	6.45	0.2	3.5	7.58	0.2	4.7
	7.15	0.2	5.1	7.52	0.2	3.5
	7.15	0.2	4.4			
34.2	6.47	0.2	4.3	7.53	0.2	4.8
	6.47	0.2	6.8	7.53	0.2	4.7
	7.50	0.2	5.6			
38.7	3.38	0.2	0.11[c]	7.28	0.2	7.9
	5.37	0.2	4.1[c]	7.46	0.2	8.9
	5.93	0.2	5.3[c]	7.52	0.2	7.5
	6.45	0.2	7.0	6.36	0.05	7.4
	6.87	0.2	8.1	6.28	0.02	7.7
	7.13	0.2	7.9			

temp, °C	$10^4 k_{iso}$, s^{-1} [d]	temp, °C	$10^4 k_{iso}$, s^{-1} [d]
25.6	2.8 ± 0.2	34.2	5.2 ± 0.9
30.2	4.2 ± 0.7	38.7	7.8 ± 0.5

[a] $[Co]_T = (1.2\text{–}2.4) \times 10^{-3}$, $I = 1.0$ M. [b] Average of rate constants at 400, 410, 450, and 530 nm. All other rate constants were obtained at 380 nm. [c] Excluded from average values of $k_{obsd} = k_{iso}$ given in the bottom section of the table, since pH values < 6. [d] $\Delta H^{\ddagger} = 13.5 \pm 0.9$ kcal mol^{-1}; $\Delta S^{\ddagger} = -29.6 \pm 3.0$ cal K^{-1} mol^{-1}.

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(24) After several more half-times, the isosbestic point at 431 nm is seen to shift slightly, possibly due to some further isomerization of the $\alpha\beta S$ S-bonded product to a different tetren geometry. A similar effect was noted after several half-times of base hydrolysis at the 484-nm isosbestic point.

(25) Maecke, H.; Houlding, V.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6888.

Table VII. Rate Data for Base Hydrolysis of ($\alpha\beta S$)-[Co(tetren)SO$_3$]$^{+}$ [a]

temp, °C	$[OH^-]_T$, M	$10^4 k_{obsd}$, s^{-1}	$10^4 k$, M^{-1} s^{-1}
25.3	0.8	0.652 ± 0.006	0.815 ± 0.007
29.5	0.8	1.18 ± 0.02	1.47 ± 0.03
34.7	0.8	2.69 ± 0.05	3.36 ± 0.06
37.9	0.2	1.14	5.53 ± 0.25
	0.4	2.11	
	0.4	2.23	
	0.5	2.69	
	0.6	3.21	
	0.8	4.74	

[a] $\Delta H^\ddagger = 27.6 \pm 0.7$ kcal mol^{-1}; $\Delta S^\ddagger = 15.1 \pm 2.4$ cal K^{-1} mol^{-1}.

Table VIII. Rate Parameters for the Aquation Reactions of Various Protonated Sulfito, Selenato, and Carbonato Complex Ions in Aqueous Solutions at 25 °C

complex	k, s^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal K^{-1} mol^{-1}	ref
$[Co(NH_3)_5OSO_2H]^{2+}$	2.0×10^{3} [a]			4
$[Co(tetren)OSO_2H]^{2+}$	1.1×10^{3}	7.2 ± 2.5	−20.4 ± 8.7	this work
$[Co(NH_3)_5OSeO_2H]^{2+}$	0.28	12.3 ± 0.8	−19.5 ± 2.7	*b*
$[Co(NH_3)_5OCO_2H]^{2+}$	1.1	16.8 ± 0.2	−2 ± 1	*c*
$[Co(tetren)OCO_2H]^{2+}$	0.51	15.6 ± 1.9	−8.6 ± 4.4	15

[a] Extrapolated from the data at 10 °C by using the same $\Delta H^\ddagger$ value and the same acid dissociation constant as for the "tetren" analogue of the $(NH_3)_5$ species. [b] Fowless, A. D.; Stranks, D. R. *Inorg. Chem.* 1977, *16*, 1276. [c] Palmer, D. A.; Harris, G. M. *Ibid.* 1974, *13*, 965.

intramolecular. The low values of the activation parameters may be due to concerted Co–O bond breaking and Co–S bond formation, a process which may be visualized as internal S_N2. This process is similar to spontaneous intramolecular nitrito to nitro isomerization of $[(NH_3)_5CoONO]^+$ for which ΔH^* (kcal mol^{-1}) and ΔS^* (cal deg^{-1} mol^{-1}) are reported to be as follows: 22, −5;[26] 22.0 ± 0.2, −3.5 ± 0.7;[27] 22.7 ± 0.9, −1 ± 3.[28]

Base Hydrolysis of [Co(tetren)SO$_3$]$^+$. In basic medium the yellow S-bonded sulfito complex is observed to undergo base hydrolysis to $[Co(tetren)OH]^{2+}$ and SO_3^{2-}. This is evident from the absorption maximum (490 nm) of the product, which coincides with that of ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$.[9] Clean pseudo-first-order kinetics is observed up to 3 half-times of reaction, with a persistent isosbestic point[24] at 484 nm. The observed pseudo-first-order rate constants exhibit first-order dependence in $[OH^-]$ in the range 0.2–0.8 M. Tests for cobalt(II) after more than 10 half-lives were negative. The rate parameters are collected in Table VII.

Table IX. Comparison of Rate Parameters for Base Hydrolysis of ($\alpha\beta S$)-$[Co(tetren)X]^{(3-n)+}$ Species at 25 °C and $I = 1.0$ M

X^{n-}	k, s^{-1} M^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal K^{-1} mol^{-1}	ref
SO_3^{2-}	0.8×10^{-4}	27.6 ± 0.7	15 ± 2.4	this work
NCS^-	88			18
N_3^-	3.2×10^2	26.4	41	18
Cl^-	3.5×10^4	24	41	19

A comparison of base hydrolysis data for $[Co(tetren)X]^{n+}$ ($n = 2$ for X = Cl^- or N_3^-, $n = 1$ for X = SO_3^{2-}) is made in Table IX. It is evident that the reactivity decreases by a factor of ~10^7 when Cl^- or N_3^- is replaced by SO_3^{2-}. The activation enthalpy values for these complexes are comparable; the observed rate differences reside predominantly on the ΔS^* factor. Rate-limiting loss of SO_3^{2-} from the amine conjugate base ($\alpha\beta S$)-Co(tetren-H)SO$_3$ is most likely. The low value of ΔS^* is presumably due to solvation (through hydrogen bonding) of SO_3^{2-} in the transition state. This assumption is reasonable as the p*K* of SO_3^{2-} increases at least by a factor of 5 when it is released from the cobalt(III) center.

The S-bonded complex is very stable to acid-catalyzed decomposition. Spectral scans at various time intervals in a preliminary run at 90 °C in 0.5 M $HClO_4$ ($I = 1.0$ M) medium with [complex] = 2.43×10^{-3} M exhibited an isosbestic point at 495 nm ($\epsilon = 90.5$ M^{-1} cm^{-1}). Absorbance at the wavelength maximum (445 nm) of the complex decreased with time. After 21 h the NCS^- test for cobalt(II)[17] was negative, indicating extremely slow reduction of the cobalt(III) center. Absorbance vs. time data at 440 nm gave a good first-order plot (using A_∞ computed from the extinction coefficient of the assumed aquo complex final product.) A value of $k_{obsd} = (1.3 \pm 0.1) \times 10^{-5}$ s^{-1} was obtained. Attempts were made to study the redox decomposition of the yellow complex at 90 °C, in phosphate–citric acid buffer of pH 5.65 ($I = 1.0$ M) and in unbuffered medium. Spectral scans over 330–600 nm at various times and tests for cobalt(II) indicated that the redox decomposition of the complex is insignificant over an extended period of time (~15 h). No further attempts were made to study the extremely slow acid hydrolysis or redox decomposition of [Co(tetren)SO$_3$]$^+$.

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Registry No. ($\alpha\beta S$)-$[Co(tetren)OH]^{2+}$, 78183-89-8; ($\alpha\beta S$)-$[Co(tetren)OSO_2]^+$, 78109-44-1; ($\alpha\beta S$)-$[Co(tetren)SO_3]^+$, 78109-34-9; ($\alpha\beta S$)-$[Co(tetren)OH_2]^{3+}$, 78183-90-1; ($\alpha\beta S$)-$[Co(tetren)OSO_2H]^{2+}$, 78109-45-2; ($\alpha\beta S$)-$[Co(tetren)OH_2](ClO_4)_3$, 78184-49-3; ($\alpha\beta S$)-$[Co(tetren)SO_3]ClO_4$, 78109-35-0; SO_2, 7446-09-5; SO_3^{2-}, 14265-45-3; SO_4^{2-}, 14808-79-8; $Na_2S_2O_5$, 7681-57-4.

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