electron. To simplify calculations, reaction via a tbp intermediate is assumed, but an equivalent pathway through a pentagonal bipyradmidal (pbp) intermediate is easy to imagine and may be more realistic considering the activation volume[33] evidence supporting associative photosubstitution in cationic Cr(III) complexes.

In such a seven-coordinate transition state of the (tn)₂ complex the steric crowding is severe, particularly in the equatorial plane. A model shows that as a water molecule approaches the FNFN plane of labilization, one of the two N–F equatorial edges trans to the amine ligand is blocked by a methylene group, favoring entry on the other. As the N–Cr–F angle then closes toward 70°, the axial proton on the tn α-carbon interacts strongly with the fluoride ligand trans to the entering water molecule. As this interaction occurs on only one side of the fluoride, it could promote its loss from the coordination sphere, further facilitated by the proximity of a hydrogen-bonding proton of the adjacent amine group. This provides the best explanation for the observed unusual fluoride aquation. The concept of a seven-coordinate transition state seems to be needed to explain the large excited-state effect in the absence of any ground-state enhancement of fluoride aquation.

Models show that the ring configuration of the ethanediamine analogue is such that no analogous interactions occur. Therefore, in this molecule, as in the tetraammine, the entering water molecule has easy access to the equatorial plane and the fluoride ligand does not experience any notable interactions with other ligands during the course of an expansion to a pbp intermediate.

Endicott has also proposed[34] that the photoreactions of Cr(III) occur via a seven-coordinate "associative" transition state, emphasizing its ground-state nature. While we agree that the main photochemistry in this system occurs via such a ground-state intermediate, we note that some of our earlier studies and some features of this system also require a small proportion of reaction via excited-state intermediates for consistency with the VC theory of d³ photostereochemistry.

In summary, the change in photochemical reaction mode seen on increasing the chelate ring size by one methylene group is explicable in terms of a steric effect on the lability of fluoride in the excited state, without any concomitant effect in the ground state. Although the VC theory is capable of giving good predictions of the excited-state labilizations for many molecules, steric effects can play an important part in either completely stopping photochemistry or dramatically changing its course. We have found a major photochemical effect can be induced by a structural change that, to a casual glance, may seem unimportant.

(33) Angermann, K.; Van Eldik, R.; Kelm, H.; Wasgestian, F. *Inorg. Chem.* **1981**, *20*, 955.

(34) Endicott, J. F. *J. Chem. Educ.* **1983**, *60*, 824.

(35) Sawano, M.; Yoshifuji, H.; Uehara, A.; Tsuchiya, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2106 and references therein.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. 7. Formation and Redox Reactions of Sulfur-Bonded Aqua(sulfito)- and Bis(sulfito)[bis(phenanthroline) or -bis(bipyridine)]cobalt(III) Complex Ions[1,2]

V. K. Joshi,[†] R. van Eldik,*[‡] and G. M. Harris*[†]

Unlike the case for all the other aquo amine cobalt(III) complexes so far studied, SO₂ uptake in the range 2 < pH < 7 by *cis*-[Co(phen)₂(OH₂)₂]³⁺ and the (bpy)₂ congener does not form an observable O-bonded species but goes directly to the S-bonded aqua sulfito complex at rates much too rapid to observe by stopped-flow procedure. However, the rate of the substitution by a second sulfite group of the remaining aqua ligand to form the *cis*-bis(sulfito) complexes is within stopped-flow times. This involves solely the ionic reactants HSO₃⁻ and SO₃²⁻ and appears to proceed by the S$_N$1(lim) or D mechanism. At higher pHs, the only observable products are S-bonded *cis*-[Co(phen)₂(SO₃)(OH)] and its (bpy)₂ analogue, and their formations involve reactions of SO₂, HSO₃⁻, and SO₃²⁻ with the (OH)(OH₂) and (OH)₂ forms of the diaqua species, describable by three rate constants. Internal redox reactions to yield Co(II) and SO₄²⁻ in a 2:1 ratio occur only at elevated temperatures and acidities, and only the fully protonated forms of either the bis(sulfito) or aqua mono(sulfito) complexes undergo this reaction.

Introduction

A number of earlier papers in this series[2] have demonstrated that various aqua amine cobalt(III) complex ions react with aqueous sulfur dioxide by direct addition to yield oxygen-bonded sulfito complexes. These products are unstable in acid (pH <2), reverting to the original reactants. Similar behavior has been observed for the aqua pentaammine complexes of rhodium(III), chromium(III), and platinum(IV), as well as for the hexaaquachromium(III) species.[3]

None of the O-bonded mono(sulfito) cobalt(III) compounds has been isolated due to instability factors other than acid-catalyzed decomposition. These factors are their tendencies (a) to undergo internal redox, (b) to isomerize to a stable S-bonded form,

or (c) to add a second sulfito ligand. These secondary reactivities vary considerably, depending upon the nature of the amine ligand moiety. Thus, [Co(NH₃)₅OSO₂]⁺ very rapidly undergoes intramolecular electron transfer,[4] while its long-chain tetraethylenepentamine analogue, [Co(tetren)OSO₂]⁺, isomerizes to the stable S-bonded form with no evidence for redox even at elevated temperatures.[5] Similarly, the bis(ethylenediamine) species, *cis*-[Co(en)₂OSO₂]⁺, exhibits redox[2] over the pH range 3–7 as the

(1) Based on the Ph.D. dissertation of V. K. Joshi, State University of New York at Buffalo, 1984. Copies are available from University Microfilms, Ann Arbor, MI. Detailed data for many of the experiments discussed in this paper are given in the dissertation.

(2) Part 6: Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* **1984**, *23*, 4399.

(3) Moritzen, P. A.; El Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1985**, *24*, 313. (See this paper for a tabulation of data for the aqua pentaammine Rh(III), Cr(III), and Pt(IV) work.)

(4) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880.

(5) Dash, A. C.; El Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 3160.

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‡University of Frankfurt.

only observable secondary process, while the tripodal triethylenetetramine congener, [Co(tren)OSO₂]⁺, undergoes[6,7] only redox for pH <5 but at higher pHs shows evidence for the disappearance of the redox reaction path while addition of a second sulfite yields a stable complex anion of stoichiometry [Co(tren)(SO₃)₂]⁻.

The purpose of this study is to investigate what differences might be observed in the sulfito complex properties when the amine ligand moiety contains aromatic groupings. It is well-known that complex ions of the form [Co(phen)₂X₂]ⁿ⁺ and [Co(bpy)₂X₂]ⁿ⁺ (phen = 1,10-phenanthroline; bpy = 2,2′-bipyridine) exist in only the *cis* configuration, notwithstanding the existence of both *cis*- and *trans*-tetrapyridyl analogues. Furthermore, earlier work[8] has demonstrated that the chelated carbonato species, [Co(phen)₂CO₃]⁺ and [Co(bpy)₂CO₃]⁺, are unusually resistant to acid-catalyzed decarboxylation. Our interest in the two aromatic ligand entities was further excited by a brief (but as yet unconfirmed) report[9] of the preparation of sulfito analogues of the above-mentioned carbonato chelates. Our study of the [Co(phen)₂(OH₂)₂]³⁺/sulfite and [Co(bpy)₂(OH₂)₂]³⁺/sulfite systems has revealed a number of startling contrasts relative to the earlier cobalt(III) sulfito complex results. The uptake of sulfur dioxide by either diaqua complex is too rapid to follow by stopped-flow procedure at pH <7, and the immediate product of this uptake appears to be solely the S-bonded aqua sulfito complex. This rapidly adds a second sulfite to yield a stable S-bonded bis(sulfito) species. However, at pH >7.5, mono(sulfito) complex formation becomes observable though formation of a bis(sulfito) complex no longer occurs. Redox is observable only in strongly acid medium at elevated temperatures. Details of the kinetic and mechanistic features of these unexpected reactivity observations follow herewith.

Experimental Section

Materials. Reagent grade 2,2′-bipyridine and 1,10-phenanthroline were obtained from Fisher Scientific Co. Analytical grade sodium metabisulfite, Na₂S₂O₅, was used as the source of sulfite; this salt is very stable in the solid state but hydrates to sulfite rapidly and almost completely when dissolved in water.[4] The laboratory distilled water was further purified by passage through a Fisher Model 9-035-25 mixed-bed ion-exchange column.

Preparation of Compounds. *cis*-[Co(phen)₂(H₂O)₂](NO₃)₃. This compound was used rather than the perchlorate due to the very low solubility of the latter. The nitrate was prepared by the literature method[10] and its purity confirmed by comparison of its UV/vis spectrum with that reported earlier.[11,12]

cis-[Co(phen)₂(SO₃H)(SO₃)]. A minimum quantity of water was used to dissolve 0.3405 g (5.025 × 10⁻⁴ mol) of [Co(phen)₂(H₂O)₂](NO₃)₃, and the pH was adjusted to 5.6. In a separate beaker, 0.2388 g (1.56 × 10⁻³ mol) of Na₂S₂O₅ was dissolved in a minimum quantity of water, and the mixture was adjusted to the same pH. The two solutions were then mixed, and the pH was readjusted to 5.6. The resulting solution was concentrated on a rotary vacuum evaporator between 50 and 60 °C. Upon cooling, a yellow solid separated. This solid was washed with ethyl alcohol and ether, recrystallized from water, and dried in a desiccator. The pure solid was further dried to a constant mass by heating it in an oven at 120 °C for 24 h. Anal.[13] Calcd for [Co(C₁₂H₈N₂)₂(SO₃H)(SO₃)]: C, 49.60; H, 2.93; N, 9.65; S, 11.80; Co, 10.15. Found: C, 48.80; H, 2.93; N, 9.42; S, 11.80; Co, 10.13.

It will be noted that the formulas for this compound and for that of its (bpy)₂ congener are given with the proton within the complex. Evidence for this conclusion is given later.

cis-[Co(phen)₂(SO₃)(OH)]·3H₂O. A minimum amount of water was used to dissolve 0.6848 g (1.012 × 10⁻³ mol) of [Co(phen)₂(H₂O)₂](NO₃)₃, and the pH was adjusted to 9.2. In a separate beaker, 0.4810 g (2.53 × 10⁻³ mol) of Na₂S₂O₅ was similarly dissolved in a minimum

Table I. Acid Dissociation Constants

compd	temp, °C	pK₃	pK₄
[Co(phen)₂(H₂O)₂]³⁺	15	4.31 ± 0.11	7.06 ± 0.15
	25	3.97 ± 0.06	7.05 ± 0.05
	35	3.69 ± 0.09	6.94 ± 0.15
[Co(bpy)₂(H₂O)₂]³⁺	15	4.07 ± 0.06	7.02 ± 0.05
	25	3.87 ± 0.03	6.93 ± 0.02
	35	3.65 ± 0.13	6.79 ± 0.24

compd	temp, °C	pK₁	pK₂
SO₂(aq)	15	1.80	6.3
	25	1.90	6.3
	35	2.00	6.3

quantity of water, and the mixture was adjusted to the same pH. The two solutions were then mixed, and the pH was readjusted to 9.2. The resulting solution was concentrated on a rotary vacuum evaporator as before. Upon cooling, a yellow solid was obtained. The solid was filtered off and washed with ethyl alcohol and ether. It was then reprecipitated from aqueous solution and was dried, first in a desiccator and then in an oven at 120 °C until a constant weight was obtained. Anal. Calcd for [Co(C₁₂H₈N₂)₂(SO₃)(OH)]·3H₂O: C, 50.53; H, 4.06; N, 9.82; S, 5.62; Co, 10.33. Found: C, 49.98; H, 4.00; N, 9.01; S, 5.84; Co, 9.62.

cis-[Co(bpy)₂(H₂O)₂](NO₃)₃. This compound rather than the perchlorate was used because of its greater solubility. It was prepared from *cis*-[Co(bpy)₂Cl₂]Cl by the reported method.[12,14] The purity of the compound was confirmed by comparison of the UV/vis spectrum with that reported earlier.[11,12]

[Co(bpy)₂(SO₃H)(SO₃)]·3H₂O. A weighed quantity of the diaquo nitrate (0.7520 g, 1.23 × 10⁻³ mol) was dissolved in a minimum amount of water, and the pH was adjusted to 6.0. In a separate beaker, 0.5856 g (3.08 × 10⁻³ mol) of Na₂S₂O₅ was similarly dissolved in a minimum quantity of water, and the pH of the resultant mixture was also adjusted to 6.0. The two solutions were then mixed, and the pH was readjusted to 6.0. The resulting yellow solution was concentrated on a rotary vacuum evaporator as before. On cooling, a yellow solid separated, which was washed with ethyl alcohol and ether, reprecipitated from water, dried in a desiccator, and further dried to a constant weight by heating it in an oven at 120 °C for 24 h. Anal. Calcd for [Co(C₁₀H₈N₂)₂(SO₃H)(SO₃)]·3H₂O: C, 40.96; H, 3.95; N, 9.55; S, 10.93; Co, 10.05. Found: C, 40.42; H, 3.51; N, 10.09; S, 10.35; Co, 9.81.

It was found to be impossible to prepare a pure solid sample of the hydroxo sulfito (bpy)₂ congener due to solubility problems. However, aqueous solutions usable in the UV/vis spectral and kinetic studies were readily prepared.

Determination of Acid Dissociation Constants. The pK's of the diaquo complex ions were determined at 15, 25, and 35 °C by potentiometric titration using a Fisher Accumet Model 420 pH meter and combination electrode. This was calibrated against commercially available standard buffers. The samples were thermostated at ±0.1 °C and maintained at an ionic strength of 1.0 M (NaNO₃). The data were treated by the curve-fitting procedure of Rossotti and Rossotti,[15] assuming two independent protonation steps. The results of this treatment are summarized in Table I as pK₃ and pK₄. For the sulfite system, pK₁ and pK₂ were deduced from the data recorded in our earlier paper,[6] and these are also given in Table I.

Spectra. The visible spectra of the various species were obtained with a Cary 118 spectrophotometer. The [Co(LL)₂(H₂O)₂]³⁺ spectra[16] were run in 1.0 M HNO₃ and those of [Co(LL)₂(OH)₂]⁺ in 1.0 M NaOH. The spectra of the species [Co(LL)₂(H₂O)(OH)]²⁺ were obtained in buffered solutions at pHs close to 5.5, where over 90% of the complexes are in the aqua hydroxo form. The spectra of the bis(sulfito) and hydroxo sulfito complexes were determined at pHs of ~5 and ~9, respectively. The results of the various UV/vis spectral measurements are presented in Figures 1 (phen complexes) and 2 (bpy complexes). Rapid-scan spectral measurements were performed on an OMA II instrument (Princeton Applied Research) combined with a Durrum Model 110 stopped-flow assembly. The IR spectra mentioned later were run on either a Perkin-Elmer 621 or a Beckman Accu Lab 4 using the KBr pellet technique.

Rate Measurements. The kinetics of the reactions with sulfite were studied under pseudo-first-order conditions by using the same stopped-

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(9) Schiavon, G.; Marehatti, F.; Paradisi, C. *Inorg. Chim. Acta* **1971**, *33*, L101.
(10) Ablov, A. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1961**, *6*, 157.
(11) Francis, D. J. Ph.D. Dissertation, University of Alberta, 1972.
(12) Palade, D. M. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1969**, *14*, 231.
(13) All reported analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY 11377.

(14) Vlcek, A. A. *Inorg. Chem.* **1967**, *6*, 1425.
(15) Rossotti, F. J. C.; Rossotti, H. *The Determination of Stability Constants*; McGraw-Hill: New York, NY, 1961; Chapter 5.
(16) The formulas in which the aromatic amine ligands are given as (LL)₂ are used throughout this paper whenever the (phen)₂ or (bpy)₂ species need not be specified separately.
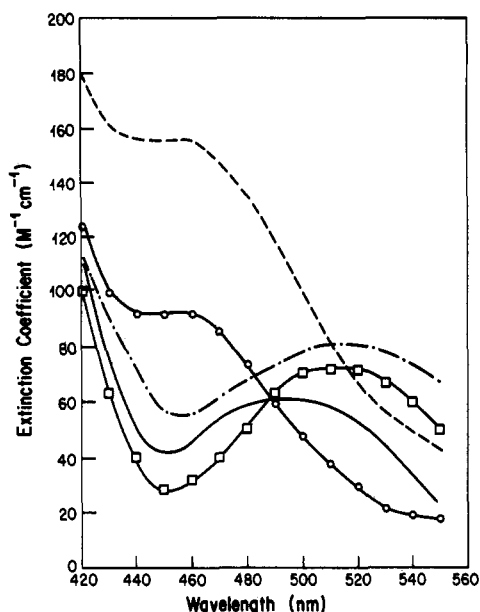
Figure 1. Spectra of some bis(phenanthroline)cobalt(III) complexes: (—) $[Co(phen)_2(H_2O)_2]^{3+}$; (−·−) $[Co(phen)_2(H_2O)(OH)]^{2+}$; (□) $[Co(phen)_2(OH)_2]^+$; (---) $[Co(phen)_2(SO_3)(OH)]$; (O) $[Co(phen)_2(SO_3)_2]^-$.
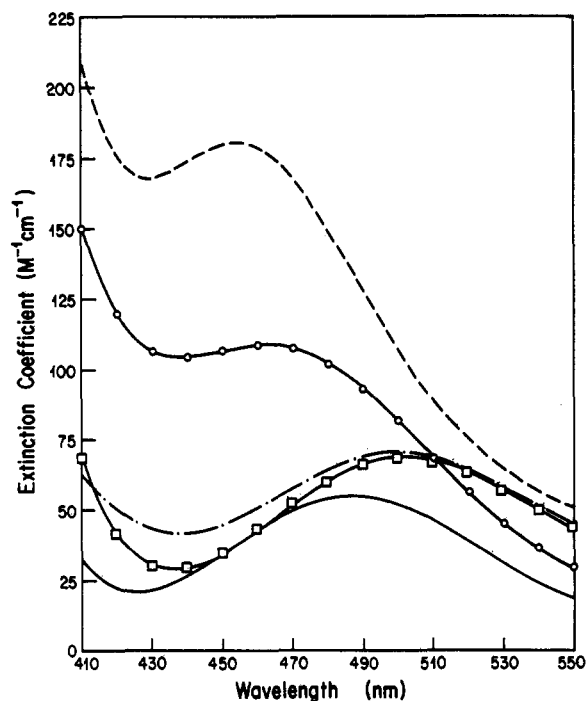
Figure 2. Spectra of some bis(pyridine)cobalt(III) complexes: (—) $[Co(bpy)_2(H_2O)_2]^{3+}$; (−·−) $[Co(bpy)_2(H_2O)(OH)]^{2+}$; (□) $[Co(bpy)_2(OH)_2]^+$; (---) $[Co(bpy)_2(SO_3)(OH)]$; (O) $[Co(bpy)_2(SO_3)_2]^-$.

flow technique described previously.[4] The kinetics of the redox reactions in the high acid range, also studied under pseudo-first-order conditions, were determined by means of a Cary 118 spectrophotometer. All the reactions were studied in the range 450–460 nm. The ionic strength of the solutions was maintained at 1.0 M ($NaNO_3$). Various buffers were used to adjust the pH in the stopped-flow runs, namely Na_2HPO_4/citric acid for pH 2–8, Tris/HCl for pH 8–9, and borax/NaOH for pH 9.5–10.5. The SO_2, HSO_3^-, and SO_3^{2-} concentrations were calculated from the pK values given in Table I. A series of experiments were performed on a double-mixing stopped-flow instrument at the Max Planck Institute for Biophysics, Frankfurt am Main, FRG.

Results and Discussion

Preliminary Experiments. When buffered $Na_2S_2O_5$, $NaHSO_3$, or Na_2SO_3 solution (Na_2HPO_4/citric acid buffer) is added to buffered $[Co(LL)_2(H_2O)_2]^{3+}$, there is an instantaneous change in color from red to yellow within the range 2 < pH < 7. This
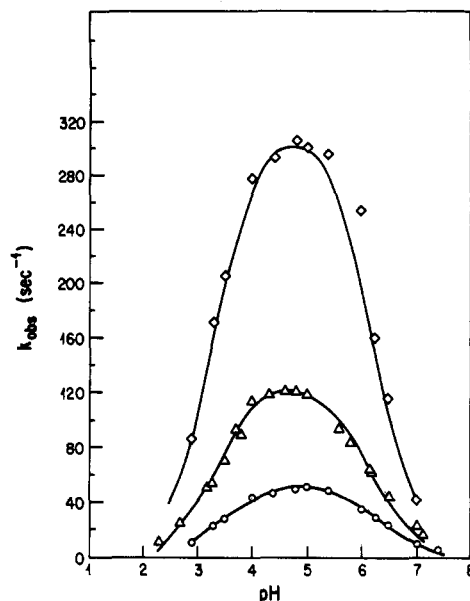

Figure 3. Plots of k_{obsd} vs. pH for the formation of $[Co(phen)_2(SO_3)_2]^-$ ([sulfite] = 0.05 M; 2 < pH < 7.5): (O) 15 °C; (△) 25 °C; (□) 35 °C.

change in color was followed spectrophotometrically. It was observed that the concentration of these yellow species depended upon the amount of sulfite added and the pH of the solution. Acidification of the product did not give $[Co(LL)_2(H_2O)_2]^{3+}$, suggesting thereby that they are S-bonded sulfito Co(III) complexes rather than O-bonded since generally the latter are quite unstable in acid, as pointed out in the Introduction. Microanalysis (see above) revealed the Co:S:N ratio to be 1:2:4, so the compounds can be formulated as either $H[Co(LL)_2(SO_3)_2]$ or $[Co(LL)_2(SO_3)(SO_3H)]$. That they are cis S-bonded species was confirmed by comparison of their IR spectra with that of cis-$[Co(en)_2(SO_3)_2]Na$[17] and by the absence of band splitting in the UV/vis spectrum.[19] Some NMR spectra obtained in D_2O (t-butyl alcohol internal standard, JEOL Model FX90 instrument) were also consistent with the cis structure, as was clear from comparison to previous NMR data for the diaquo parent complex.[11] To determine which external proton formulation of the protonated complex was correct, a 1.2×10^{-3} M solution of pure compound was prepared and found to have a pH of 3.05. A simple equilibrium calculation shows that the protonated complex has a pK of 2.6. This is reasonably consistent, though not unequivocally so, with attachment of the proton to one of the sulfito ligands, since such a species is analogous to "sulfurous acid" (hydrated sulfur dioxide), which has a pK of 1.9 at 25 °C (see Table I). The IR spectrum of $[Co(phen)_2(SO_3)(OH)]$ was compared with those of cis-$[Co(en)_2(SO_3)(OH)]$ and cis-$[Co(phen)_2(SO_3)(CN)]$. All three showed close parallelism,[20] confirming the cis geometry of the (phen)$_2$ congener.

Kinetics of Formation of $[Co(LL)_2(SO_3)_2]^-$. The first identifiable stable product of the reaction of $[Co(LL)_2(H_2O)_2]^{3+}$ with sulfite at pH ~5 is the bis(sulfito) species, as noted above. The spectra (Figures 1 and 2) of the various compounds involved show that there should be a substantial *increase* in absorbance in the range 450–460 nm when the reactants are mixed. However, stopped-flow runs show a moderately rapid *decrease* in absorbance after an immeasurably rapid initial increase to a value close to that ex-

(17) The (en)$_2$ complex has bands[18] at 1095, 1018, 943, and 625 cm^{-1}, with the corresponding bands for the (phen)$_2$ analogue at 1195, 1062, 940, and 620 cm^{-1} and for the (bpy)$_2$ analogue at 1382, 995, 965, and 635 cm^{-1}. Other bands are present, of course, in the (LL)$_2$ complexes due to their aromaticity.
(18) Baldwin, M. E. *J. Chem. Soc.* **1961**, 3123.
(19) Figgis, B. N. *Introduction to Ligand Fields*; 1st ed.; Wiley: New York, NY, 1966; p 234.
(20) The hydroxo sulfito (en)$_2$ complex[18] has bands at 1117, 1062, 972, and 625 cm^{-1}, while for the cyanosulfito (phen)$_2$ species[9] they appear at 1145, 1090, 990, and 620 cm^{-1}. The corresponding band for our hydroxo sulfito (phen)$_2$ complex are at 1140, 1095, 980, and 620 cm^{-1}.
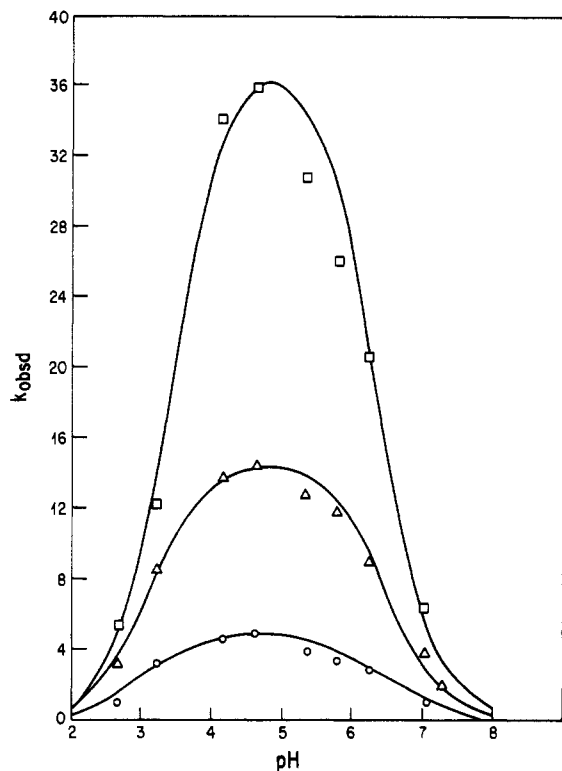
Figure 4. Plots of k_{obsd} vs. pH for the formation of $[Co(bpy)_2(SO_3)_2]^-$ ([sulfite] = 0.05 M; 2 < pH < 7.5): (O) 15 °C; (△) 25 °C; (□) 35 °C.

pected for the high-pH mono(sulfito) product $[Co(LL)_2(SO_3)-(OH)]$. This suggests that the initial very rapidly formed species in the lower pH range is $[Co(LL)_2(SO_3)(H_2O)]^+$, so that the reaction actually followed on the stopped-flow assembly is the substitution of a second sulfite for ligand water. Data were obtained for this reaction at 15, 25, and 35 °C by using fixed concentrations of $[Co(LL)_2(H_2O)_2]^{3+}$ (1.0×10^{-3} M) and total sulfite (0.05 M) over the range 2 < pH < 7. The results are given in the form of k_{obsd} vs. pH plots in Figure 3 (phen) and Figure 4 (bpy). These curves have the typical bell shape noted for reactions in which one reactant is a diprotic acid with the monoprotic intermediate species very much more reactive than either of the other two. In the present instance, it appears that the aqua sulfito reactant is the monoprotic intermediate acid, according to the equation

$$[Co(LL)_2(SO_3H)(H_2O)]^{2+} \xrightleftharpoons{K_5} [Co(LL)_2(SO_3)(OH_2)]^+ \xrightleftharpoons{K_6} [Co(LL)_2(SO_3)(OH)] \quad (1)$$
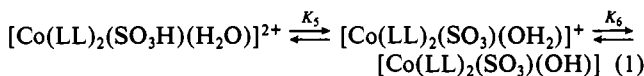
Some experiments were performed to prove that the data just presented refer indeed to the reaction of $[Co(LL)_2(SO_3)(H_2O)]^+$ with sulfite to give $[Co(LL)_2(SO_3)_2]^-$. In the first of these, rapid-scan spectral studies were carried out in the range 400–500 nm. The first spectrum recorded within 10 ms after mixing $[Co(LL)_2(H_2O)_2]^{3+}$ with sulfite exhibits a significantly higher absorbance around 460 nm, which decreases during the subsequent step, in agreement with the stopped-flow observations. The rapidly produced mono(sulfito) species has spectral properties very similar to those of $[Co(LL)_2(SO_3)OH]$ in Figures 1 and 2. The spectrum of the bpy intermediate complex could be recorded more accurately than that of the phen complex since the subsequent substitution reaction is significantly slower (compare Figures 3 and 4). To prove that this intermediate mono(sulfito) species is indeed S-bonded, it was synthesized within the double-mixing stopped-flow instrument and immediately acidified with 2 M $HClO_4$. No spectral change could be observed during acidification, from which it follows that the sulfite must be S-bonded. In the case of an O-bonded species the diaqua complex would have been generated during acidification.

In a second series of experiments, the observed rates of reaction, k_{obsd}, of sulfite with $[Co(phen)_2(H_2O)_2]^{3+}$ and $[Co(phen)_2$-

Table II. Observed Rate Constants for the Reaction of Aqueous Sulfite with Aquo(sulfito)bis(phenanthroline)cobalt(III) Ion[a]

pH	k_{obsd}, s^{-1}	k_{obsd},[b] s^{-1}
3.54	75.3 ± 1.2	76.0
4.63	115 ± 2	122
5.37	103 ± 3	109
6.52	45.3 ± 2.1	40.0

[a] [Complex] = 1.0×10^{-3} M; I = 1.0 M (NaNO$_3$); [total S] = 0.5 M; temp = 25 °C. [b] Interpolated from Figure 3.
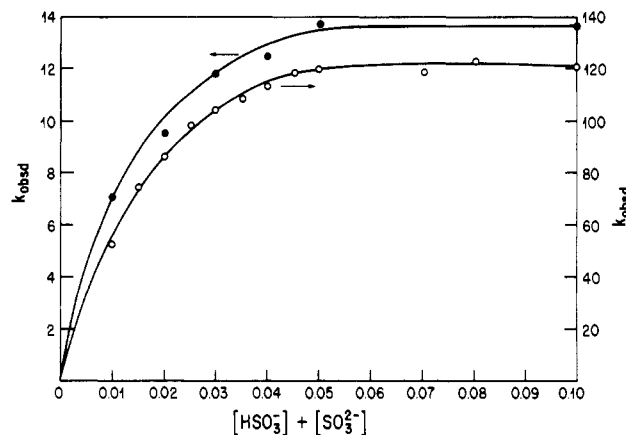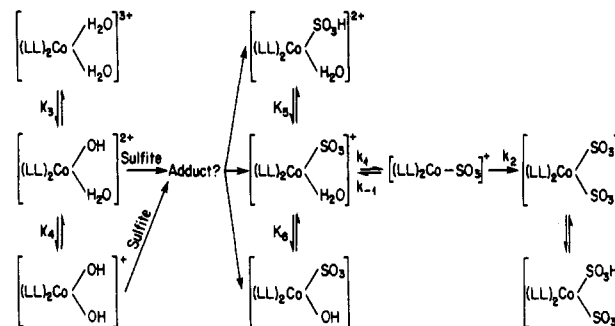

Figure 5. Plots of k_{obsd} vs. {[HSO$_3^-$] + [SO$_3^{2-}$]} for the formation of $[Co(LL)_2(SO_3)_2]^-$: (O) (phen)$_2$ (pH 4.8, 25 °C); (●) (bpy)$_2$ (pH 4.6, 25 °C).

Scheme I. Mechanism of Formation of $[Co(LL)_2(SO_3)_2]^-$

$(SO_3)(H_2O)]^+$, respectively, were compared.[21] Separate stopped-flow experiments were performed by utilizing the aqua sulfito complex as the starting material under the same conditions as already given for the diaqua data (Figure 3). The results are presented in Table II. It is seen that the two sets of k_{obsd} values agree very well, further confirming the assumptions as to the nature of the reaction with the diaqua complexes.

Finally, the values of pK_5 and pK_6 (see eq 1) were estimated for the (phen)$_2$ species by performing a spectral titration at 25 °C over the range 2 < pH < 7. Taking into account mass balance and Beer's law, one can derive an equation[22] by means of which the equilibrium constants can be extracted by least-squares analysis. By means of this procedure, values for pK_5 and pK_6 for the (phen)$_2$ system were determined to be 3.2 and 6.2, respectively. These are to be compared to the values derivable for this compound from the bell-shaped curve (see below) of 3.3 and 6.2, respectively, at 25 °C.

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(21) The aquo sulfito complex is formed when the hydroxo sulfito solution of the required concentration is acidified in the stopped-flow runs using the "pH jump" procedure.[2] It should be noted that when a solution of the mono(sulfito) complex is acidified to pH ≤2 (when it is presumably nearly all in the form $[Co(phen)_2(SO_3H)(OH_2)]^{2+}$ and sulfite is added, no appreciable spectral change is observable. A similar observation is made when the same experiment is performed at pH ≥9, where the complex is in the form $[Co(phen)_2(SO_3)(OH)]$. This confirms that only the half-acid $[Co(phen)_2(SO_3)(OH_2)]^+$ is highly reactive with sulfite in forming the bis(sulfito) product.

(22) Ashley, K. R.; Shyu, S.-B.; Leipoldt, J. G. *Inorg. Chem.* **1980**, *19*, 1913.

Table III. Governing Kinetics of Formation of $[Co(LL)_2(SO_3)_2]^-$ Ion as a Function of pH[a]

complex ion	temp, °C	pK_5	pK_6	k_1, s^{-1}
$[Co(phen)_2(SO_3)(H_2O)]^{2+}$	15	3.40	6.30	57
	25	3.30 (3.20)[b]	6.20 (6.20)[b]	131
	35	3.30	6.20	326
ΔH_1^*, kcal mol^{-1}				14.8 ± 0.7
ΔS_1^*, cal deg^{-1} mol^{-1}				0.8 ± 2.3
$[Co(bpy)_2(SO_3)(H_2O)]^{2+}$	15	3.00	6.40	5.1
	25	3.10	6.50	15
	35	3.40	6.30	39
ΔH_1^*, kcal mol^{-1}				17.3 ± 0.3
ΔS_1^*, cal deg^{-1} mol^{-1}				5.0 ± 1.0

[a] [Sulfite] = 0.05 M; I = 1.0 M (NaNO$_3$); $[[Co(LL)_2(SO_3H)(H_2O)]^{2+}]$ = 1.0 × 10^{-3} M. [b] Value obtained from spectrophotometric titration.

The variation of k_{obsd} for the bis(sulfito) complex formation with [total sulfite] was studied at 15, 25, and 35 °C in the range 0.01 M < [total sulfite] < 0.10 M at various fixed pH values in the 3–7 range, where nearly all the sulfite is in the form of HSO$_3^-$ or SO$_3^{2-}$. In each case, plots of k_{obsd} vs. {[HSO$_3^-$] + [SO$_3^{2-}$]} produce curves that rise steeply at low values of [total sulfite] but flatten out to a constant value beyond ~0.04 M (see Figure 5 for typical data at 25 °C). Such behavior is consistent with the S$_N$1(lim) or D mechanism[23] of octahedral substitution.

A reaction pattern for $[Co(LL)_2(SO_3)_2]^-$ formation that incorporates the mechanistic ideas touched upon so far is presented in Scheme I. Whether any of the three possible aquo forms is favored in the first step of the reaction is impossible to determine. All three are certainly present to varying extents in the pH range of the experiments (2–7) since pK$_3$ and pK$_4$ have values of ~4 and ~7 (Table I) for both types of complex over the whole temperature range. As explained earlier, the first product seen in the stopped-flow experiments is the aqua sulfito species, which is present in the three forms indicated as governed by the magnitudes of K_5 and K_6. We have no hard evidence concerning the mechanism of this extremely rapid reaction. It may take place according to the conventional SO$_2$ addition to the aqua hydroxo (or dihydroxo) parent species, followed by almost instantaneous isomerization from O-bonded to S-bonded aqua sulfito complex. An alternative view is that HSO$_3^-$ or SO$_3^{2-}$ forms an adduct with the aromatic ligand, followed immediately by displacement of an aqua ligand. Some support for the adduct concept derives from UV spectra of the free amine ligands, in the presence and absence of sulfite at pH 5, the region of most rapid mono(sulfito) formation. These spectra,[24] given in Figure 6, provide unmistakable evidence for chemical interaction between sulfite and the free ligand. Perhaps some kind of π-interaction is occurring, as has been reported previously[25] for various phenanthrolines.

Whatever the mechanism of the first step, the suggested mechanism for addition of the second sulfite group is amply supported by the data. Assuming that the HSO$_3^-$ and SO$_3^{2-}$ substituents are equally effective competitors for the 5-coordinate mono(sulfito) intermediate, one readily derives the rate expression

$$\text{rate} = \left(\frac{k_1 k_2 \{[HSO_3^-] + [SO_3^{2-}]\}}{k_{-1} + k_2 \{[HSO_3^-] + [SO_3^{2-}]\}} \right) [Co(LL)_2(SO_3)(H_2O)^+]$$

$$= \left(\frac{k_1 k_2 [\text{total sulfite}] f_1}{k_{-1} + k_2 [\text{total sulfite}] f_1} \right) [\text{total complex}] f_2$$

where $f_1 = (K_1 h + K_1 K_2)/(h^2 + K_1 h + K_1 K_2)$ (~1 for pH ≥3) and $f_2 = K_5 h/(h^2 + K_5 h + K_5 K_6)$. Thus

$$k_{obsd} = \frac{k_1 k_2 [\text{total sulfite}] f_1 f_2}{k_{-1} + k_2 [\text{total sulfite}] f_1} \qquad (2)$$

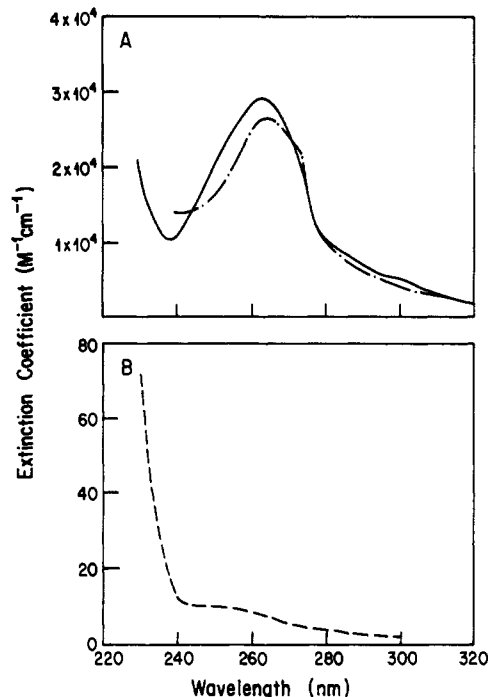**Figure 6.** UV spectra at pH 5 and 25 °C: (A) (—·—) phen only, (—) phen + [sulfite] = 0.05 M; (B) sulfite only.

Table IV. Rate Parameters for the Formation of $[Co(phen)_2(SO_3)_2]^-$ as a Function of [Sulfite][a]

temp, °C	pH	k_1, s^{-1}	k_2/k_{-1}, M^{-1}
15	3.55	55.0	34
	4.80	54.0	37
	6.22	57.0	41
25	3.29	132	48
	3.55	135	60
	4.01	136	75
	4.80	132	67
	5.30	130	67
	6.03	132	77
	6.22	138	67
35	3.55	340	73
	4.08	340	80
	6.22	335	81

[a] I = 1.0 M (NaNO$_3$); [complex] = 1.0 × 10^{-3} M.

In the case of the bell-shaped curves, [total sulfite] = 0.05 M, at which point the reaction has become independent of sulfite concentration (see Figure 5) and eq 2 reduces to $k_{obsd} = k_1 f_2$. The solid curves of Figures 3 and 4 were obtained by a nonlinear least-squares procedure, adjusting k_1, K_5, and K_6 for the best fit. The values obtained for these constants at 15, 25, and 35 °C are given in Table III.

The rate data for [total sulfite] dependence (as illustrated by Figure 5) were also analyzed according to eq 2, where now all

(23) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; 2nd ed.; Wiley: New York, NY, 1967; p 193 ff.
(24) The spectra given are for the phen compounds. Those for the bpy group are very similar.
(25) Balch, A. L.; Watkins, J. J.; Doonan, D. J. *Inorg. Chem.* **1979**, *18*, 1228.

Table V. Rate Parameters for the Formation of $[Co(bpy)_2(SO_3)_2]^-$ as a Function of [Sulfite][a]

| temp, °C	pH	k_1, s^{-1}	k_2/k_{-1}, M^{-1}
15	3.40	5.00	36
	4.60	5.00	47
	6.46	5.00	48
25	3.40	15.0	31
	4.60	14.0	32
	6.46	11.0	42
35	3.40	42.0	32
	4.60	40.0	45
	6.46	42.0	53

[a] I = 1.0 M (NaNO$_3$), [complex] = 1 × 10^{-3} M.

the terms in the expression must be utilized. The best values for k_1 were obtainable by extrapolating plots of the horizontal portion of k_{obsd}/f_2 vs. {[HSO$_3^-$] + [SO$_3^{2-}$]} to zero sulfite concentration. These are the values given in column 3 of Tables IV and V and are seen to be independent of pH, as they should be. The average values also agree very well with the k_1 values extracted from the bell-shaped curves (Table III). The values for k_2/k_{-1} were evaluated from the known k_1 values and the conventional inverse plots of f_2/k_{obsd} vs. {[HSO$_3^-$] + [SO$_3^{2-}$]}$^{-1}$ (from which may be derived the magnitudes of k_1k_2/k_{-1}). The k_2/k_{-1} values are subject to considerable error but range from 40 to 80 for the (phen)$_2$ and from 30 to 50 for the (bpy)$_2$ species. These data, together with the known values of the various equilibrium constants, were used to calculate the solid curves given in Figure 5 (according to eq 2) and are seen to provide an excellent fit. The values for k_2/k_{-1} are clearly much more consistent with the D than with the I$_d$ mechanism. For the latter they represent values of ion-pair association constants for $[Co(LL)_2(SO_3)(H_2O)]^+$ with either HSO$_3^-$ or SO$_3^{2-}$, for which a maximum magnitude of ~15 is to be expected.[26]

There are only a few experiments reported in the literature that provide comparable data for substitution by sulfite in an aqua sulfito complex to yield a bis(sulfito) complex. In the first of these,[27] for which no temperature variation studies were recorded, SO$_3^{2-}$ reportedly reacts with *trans*-[Co(en)$_2$(SO)$_3$(H$_2$O)]$^+$ with a rate constant at 25 °C of ~600 M^{-1} s^{-1}, to be compared with our values of 131 and 15 M^{-1} s^{-1} for the analogous *cis*-(phen)$_2$ and -(bpy)$_2$ complexes, respectively. Some similar data[7] for the complex [Co(tren)(SO$_3$)(H$_2$O)]$^+$ yields an analogous (though rather indirectly deduced) rate constant value of ~1 M^{-1} s^{-1} with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values of ~12 kcal mol^{-1} and ~-18 cal deg^{-1} mol^{-1}. It is seen from Table III that the much more negative entropy of activation is a prominent factor in the considerably reduced rate for the tren complex. There is also good evidence in the literature for a D mechanism for the reaction of [Co(NH$_3$)$_5$SO$_3$]$^+$ with sulfite to produce *trans*-[Co(NH$_3$)$_4$(SO$_3$)$_2$]$^-$: the rate constant is independent of the sulfite concentration and the volume of activation is +13.7 ± 0.7 cm^3 mol^{-1} ($\Delta H^{\ddagger}$ = 23.8 ± 1.0 kcal mol^{-1}; $\Delta S^{\ddagger}$ = +12.6 ± 3.3 cal deg^{-1} mol^{-1}).[28]

Kinetics of Formation of [Co(LL)$_2$(SO$_3$)(OH)]. It has been noted above that beyond pH ~7 the rate of formation of the bis(sulfito) complex from diaqua complex and free sulfite becomes very slow. The preparative work showed that at pH ~9 the only product in similar experiments is [Co(LL)$_2$(SO$_3$)(OH)]. Some clarification of this switchover in the nature of the reaction was sought by stopped-flow experiments at 25 °C and pH 6.7 and 8.0 with the [Co(phen)$_2$(H$_2$O)$_2$]$^{3+}$/free sulfite reactant mixture. As seen in Figure 7, curve A, the run at pH 6.7 produces the standard type of curve for bis(sulfito) complex formation from mono-(sulfite), as discussed in detail above. The initial rapid increase is complete within 1 ms and so does not show in the figure since the experimental procedure utilized a 1-ms time delay in the run.[29]
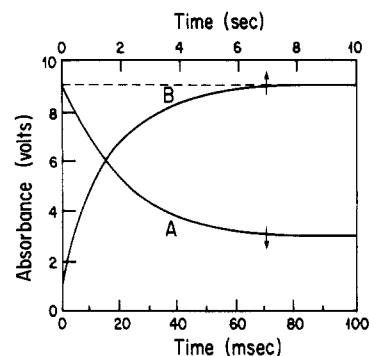
Figure 7. Stopped-flow traces for the formation of (phen)$_2$ complexes ([complex] = 1 × 10^{-3} M; [sulfite] = 0.05 M): (A) [Co(phen)$_2$(SO$_3$)$_2$]$^-$ (pH 6.7); (B) [Co(phen)$_2$(SO$_3$)(OH)] (pH 8.0).
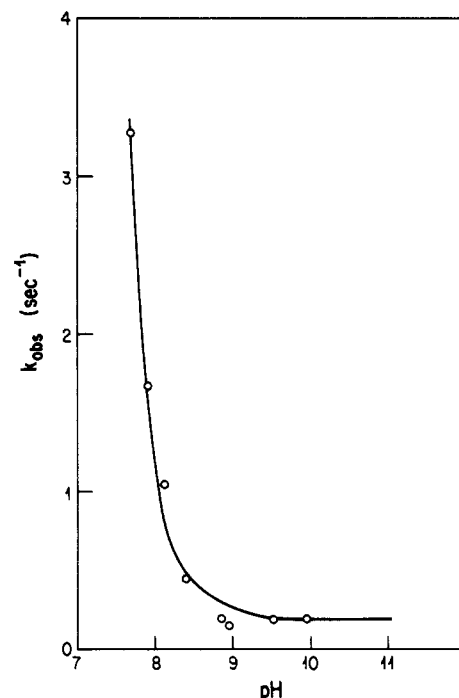
Figure 8. Plot of k_{obsd} vs. pH for the formation of [Co(phen)$_2$(SO$_3$)(OH)] at 25 °C ([complex] = 1.0 × 10^{-3}, [sulfite] = 0.05 M).

The indicated value of k_{obsd} is ~35 s^{-1}, in agreement with that interpolated from the appropriate calculated bell-shaped curve (Figure 3). At pH 8, the switchover is complete—the initial absorbance now corresponds to that of [Co(phen)$_2$(OH)$_2$]$^+$ (see curve B) and the final absorbance to that of [Co(phen)$_2$(SO$_3$)(OH)]. This is the starting complex (along with a small fraction of its partially but highly reactive protonated congener [Co(phen)$_2$(SO$_3$)(H$_2$O)]$^+$) in the pH 6.7 experiment, accounting for the equality of the absorbances indicated by the dotted line. The rate constant for mono(sulfito) complex formation deduced from curve B is k_{obsd} = 0.8 s^{-1} as compared to a probable value of several thousand[29] at pH 6.7. A number of other experiments were now carried out of the same type as shown in Figure 7, Curve B, covering the range of 7.5 ≤ pH ≤ 10.0, with typical results as shown in Figure 8. In the higher pH range, k_{obsd} approaches a constant and rather low value as expected[30] for the slow residual reaction between a dihydroxo cobalt(III) complex and a doubly negative anion. However, k_{obsd} exhibits a very steep rise in the lower pH range, suggesting increasing domination of the process by a rapid addition reaction to the parent diaqua complex (which in this pH range exists predominantly in the fully deprotonated equilibrium form [Co(LL)$_2$(OH)$_2$]$^+$).

(26) Reference 23, p 34 ff.
(27) Farrell, S. M.; Murray, R. S. *J. Chem. Soc., Dalton Trans.* **1977**, 322.
(28) Spitzer, U.; van Eldik, R. *Inorg. Chem.* **1982**, *21*, 4008.
(29) This indicates that the rate constant for this process must be considerably greater than 1000 s^{-1} at this pH.

(30) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 3684. These authors found that the rate constant for CO$_3^{2-}$ substitution in dihydroxo (β,β',β''-triaminotriethylamine)cobalt(III) is ~10^{-4} M^{-1} s^{-1}.

Table VI. Rate Parameters for the Formation of [Co(phen)$_2$(SO$_3$)(OH)] as a Function of pH^a

temp, °C	k_0', M^{-1} s^{-1}	k_1', M^{-1} s^{-1}	k_2', M^{-1} s^{-1}	k_2',^{b} M^{-1} s^{-1}
15	6.8 × 10^8	75.0	0.5	0.7 ± 0.1
25	7.2 × 10^8	82.0	4.3	4.1 ± 0.3
35	2.0 × 10^9	120	7.0	7.0 ± 0.3
ΔH^*, kcal mol^{-1}	8.8 ± 5.1	3.5 ± 1.6	23.0 ± 8.0	20.0 ± 6.0
ΔS^*, cal deg^{-1} mol^{-1}	12.2 ± 17.1	−37.8 ± 5.2	20.0 ± 27.0	10.0 ± 20.0

^{a} I = 1.0 M (NaNO$_3$); [complex] = 1.0 × 10^{-3} M; [sulfite] = 0.05 M. ^{b} Values of k_2' derived from the k_{obsd} vs. [sulfite] data at high pH, i.e., the slopes of the curves given in Figure 9.

Table VII. Rate Parameters for the Formation of [Co(bpy)$_2$(SO$_3$)(OH)] as a Function of pH^a

temp, °C	k_0', M^{-1} s^{-1}	k_1', M^{-1} s^{-1}	k_2', M^{-1} s^{-1}	k_2',^{b} M^{-1} s^{-1}
15	1.6 × 10^9	50.0	0.5	0.45 ± 0.05
25	5.0 × 10^9	90.0	0.65	0.63 ± 0.03
35	8.5 × 10^9	130	1.7	1.7 ± 0.1
ΔH^*, kcal mol^{-1}	14.2 ± 2.8	7.8 ± 1.0	10.1 ± 3.8	11.1 ± 3.6
ΔS^*, cal deg^{-1} mol^{-1}	33. ± 9.5	−23.4 ± 3.2	−24.9 ± 12.6	−21.9 ± 12.0

^{a} I = 1.0 M (NaNO$_3$); [complex] = 1.0 × 10^{-3} M; [sulfite] = 0.05 M. ^{b} Values of k_2' derived from the k_{obsd} vs. [sulfite] data at high pH, i.e., the slopes of curves for the bpy system of the same type as in Figure 9.

Scheme II. Mechanism of Formation of [Co(LL)$_2$(SO$_3$)(OH)]

Figure 9. Plots of k_{obsd} vs. [SO$_3^{2-}$] for the formation of [Co(phen)$_2$-(SO$_3$)(OH)] at pH 10.01: (O) 15 °C; (△) 25 °C; (□) 35 °C.

The curve of Figure 8 can be adequately fitted by making the following assumptions: (1) SO$_2$, while present in almost negligible concentration, is the dominant sulfito reactant in the pH <8 range. Since it can react by addition to the aqua hydroxo or dihydroxo forms of the complex, it is very much more reactive than HSO$_3^-$ and SO$_3^{2-}$, which must react by substitution. (2) The addition reaction of SO$_2$ has the same rate for either of the hydroxo forms of the complex but concurrent rearrangement from the expected O-bonded sulfito product to the S-bonded form must take place. (3) By contrast, the ionic species HSO$_3^-$ and SO$_3^{2-}$ are, within the limits of experimental error, equally reactive substituents with each of the hydroxo complexes, but their common rate is considerably greater for the aqua hydroxo than for the dihydroxo species.[31]

These various ideas are incorporated in the mechanism outlined in Scheme II. The corresponding rate law is

rate = $k_0'\{$[Co(LL)$_2$(H$_2$O)(OH)]$^{2+}$ + [Co(LL)$_2$(OH)$_2$]$^+\}$ × [SO$_2$] + k_1'[Co(LL)$_2$(H$_2$O)(OH)]$^{2+}$\{[HSO$_3^-$] + [SO$_3^{2-}$]\} + k_2'[Co(LL)$_2$(OH)$_2$]$^+$\{[HSO$_3^-$] + [SO$_3^{2-}$]\}

or

k_{obsd} = [$k_0'\alpha_0'(\alpha_1 + \alpha_2)$ + $k_1'\alpha_1(\alpha_1' + \alpha_2')$ + $k_2'\alpha_2(\alpha_1' + \alpha_2')$][total sulfite] (3)

In eq 3, α_0, α_1, and α_2 are the fractions of the three acid–base forms of the diaqua complex, and α_0', α_1', and α_2' are the corresponding fractions of the various free sulfite forms and may be calculated from the known values of the equilibrium constants

K_3 and K_4 and K_1 and K_2, respectively. The k's are the rate constants as defined in Scheme II. The data of the type for Figure 8 have been evaluated by means of a nonlinear least-squares program according to eq 3, yielding the magnitudes of k_0', k_1', and k_2' given in Tables VI and VII.

Confirmatory evidence for the above treatment is provided by the study of the variation of k_{obsd} with [total sulfite] at high pH, as exemplified by Figure 9. These plots are seen to be strictly linear with a zero intercept so that the reaction is clearly first order in [total sulfite] over the whole range. The constant limiting value at high pH of k_{obsd} seen in Figure 8 indicates that the contributions to eq 3 from the $k_0'\alpha_0'$ and $k_1'\alpha_1$ terms are negligible. Thus, since ($\alpha_1' + \alpha_2'$) = 1, eq 3 becomes

$$k_{obsd} = k_2'[\text{total sulfite}] \quad (4)$$

Data of the type for Figure 9 can now be subjected to linear least-squares analysis to yield a second set of k_2' values, with the results recorded in the last columns of Tables VI and VII. It is apparent that good agreement is obtained. Another noteworthy feature of these tabulations is that the ratios k_1'/k_2' at 25 °C, though subject to rather large errors, average out at a value somewhere between 50 and 100 for both (LL)$_2$ complexes, in keeping with the expectation already pointed out.[31] The magnitude of k_0', the SO$_2$-uptake rate constant, approaches the collision frequency limit, as has been observed in previous comparable SO$_2$-uptake studies.[2,6] The new factor here is the instantaneous rearrangement to S-bonded sulfito complexes concurrent with the uptake process. Temperature dependence parameters for the various reactions of interest are also included in the tables. The

(31) Such behavior is to be expected. For example, the lability of ligand water (as exhibited by its exchange rate[32] with labeled solvent water) is at 25 °C approximately 30 times greater for cis-[Co(en)$_2$(H$_2$O)-(OH)]$^{2+}$ than it is for cis-[Co(en)$_2$(OH)$_2$]$^+$.

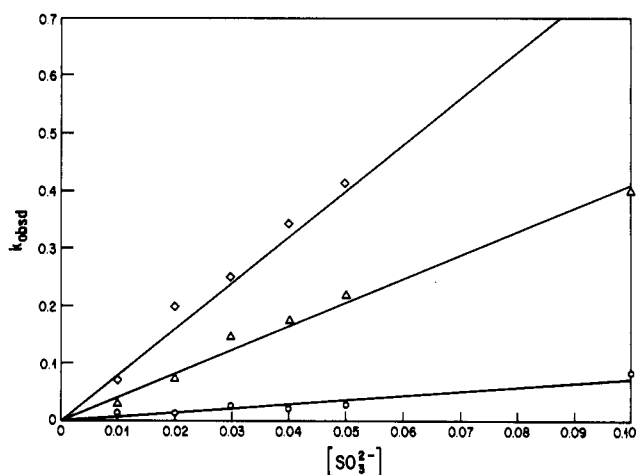(32) Kruse, W.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280.

Table VIII. Rate Parameters for Intramolecular Reduction of [Co(LL)$_2$(SO$_3$H)(SO$_3$)] and [Co(phen)$_2$(SO$_3$H)(OH$_2$)]$^{2+}$ Complexes

complex ion	temp, °C	10^4k_r, s^{-1}	10^3K, M^{-1}	pK
[Co(phen)$_2$(SO$_3$H)(SO$_3$)]	45	1.18 ± 0.05	19.9 ± 1.5	1.7
	55	2.62 ± 0.30		
	65	12.9 ± 1.4		
$\Delta H^* = 25.0 \pm 2.3$ kcal mol^{-1}				
$\Delta S^* = 1.1 \pm 7.0$ cal deg^{-1} mol^{-1}				
[Co(bpy)$_2$(SO$_3$H)(SO$_3$)]	45	0.833 ± 0.071		
	55	3.55 ± 0.12		
	65	16.9 ± 1.1		
$\Delta H^* = 31.7 \pm 0.5$ kcal mol^{-1}				
$\Delta S^* = 21.9 \pm 1.6$ cal deg^{-1} mol^{-1}				
[Co(phen)$_2$(SO$_3$H)(OH$_2$)]$^{2+}$	45	1.68 ± 0.03	5.28 ± 0.32	2.3
	55	4.70 ± 0.38		
	65	25.0 ± 2.6		
$\Delta H^* = 28.3 \pm 1.9$ kcal mol^{-1}				
$\Delta S^* = 12.3 \pm 5.8$ cal deg^{-1} mol^{-1}				

values are subject to large errors, but one useful comparison is possible. At pH >7.5, a large fraction of the diaqua reactants of our study are in the form [Co(LL)$_2$(OH)$_2$]$^+$, so a comparison is possible with [Co(tren)(OH)$_2$]$^+$ of our previous study.[6] For the latter the uptake rate data at 25 °C is $k = 2.4 \times 10^9$ M^{-1} s^{-1}, $\Delta H^* = 11.5 \pm 0.3$ kcal mol^{-1}, and $\Delta S^* = 23 \pm 3$ cal deg^{-1} mol^{-1}. These are seen to compare reasonably well with the k_0' data of Tables VI and VII, suggesting that O-bonded sulfito complex formation is indeed the first step in these reactions, in spite of our inability to observe anything but S-bonded product in any of our experiments. Unfortunately, there are no data in the literature that enable similar comparisons for k_1' and k_2' other than the ratio analogy already discussed.

Internal Redox Decomposition of [Co(LL)$_2$(SO$_3$)$_2$]$^-$ and [Co(phen)$_2$(SO$_3$)(OH)] Complexes. In preliminary experiments, it was shown that both the (phen)$_2$ and (bpy)$_2$ bis(sulfito) complexes are stable to internal redox in neutral aqueous solution. The same is true of the (phen)$_2$ aqua sulfito species,[33] though, as already discussed, it reacts rapidly with free sulfite. Internal redox becomes readily observable only at elevated temperatures and acidities, such as 45 °C and [H$^+$] = 1.0 M. At still higher acidities, acid-catalyzed hydrolysis begins to compete with redox decomposition so that at 4 M acid the sulfito complexes all revert completely to the corresponding diaqua congener. The stoichiometry of the redox reaction, determined in the lower acidity range after long standing in solution, was carried out as previously described.[4] The data show that there is complete conversion of cobalt(III) to cobalt(II) and that the Co(II):SO$_4$$^{2-}$ ratio in the products is 2:1, as expected. Several preliminary kinetic experiments illustrated that the observed rate constants are independent of [complex ion], [free amine], and added [cobalt(II) salt].

Detailed kinetic studies were performed at 45 °C in the range 0.0–1.0 M acid with the two (phen)$_2$ complexes, and the results for both systems are summarized in Figure 10. It is seen that k_{obsd} increases from the zero value in absence of acid to an essentially constant value at ≥0.4 M. The high acid concentration required to achieve the limiting value suggests that the species that undergo redox are relatively strong acids and must be fully protonated. This undoubtedly involves the equilibrium

$$[Co(phen)_2(SO_3H)(SO_3)] \underset{K_7}{\overset{}{\rightleftharpoons}} H^+ + [Co(phen)_2(SO_3)_2]^- \quad (5)$$

for the bis(sulfito) and eq 1 for the aqua mono(sulfito) analogue. This type of mechanism can be expressed by rate equations of the form

$$k_{obsd} = k_r[H^+]/(K + [H^+]) \quad (6)$$
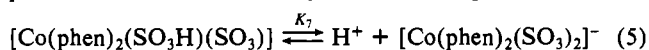
where k_r is the limiting high-acid redox rate constant and K is K_7 for the bis(sulfito) and K_5 for the mono(sulfito) complex. Plots of $1/k_{obsd}$ vs. $1/[H^+]$ should yield straight lines of slope K/k_r and intercept $1/k_r$. Such plots are indeed linear, and least-squares
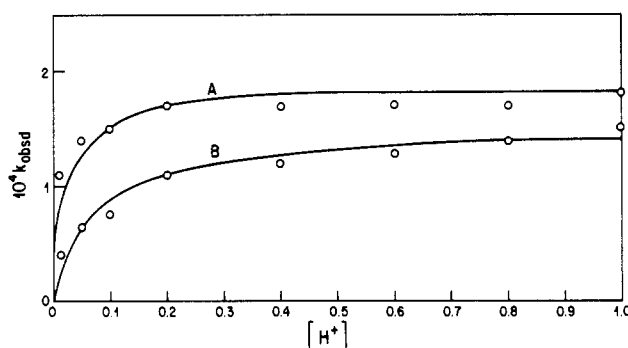

Figure 10. Plots of k_{obsd} vs. [H$^+$] for internal redox reactions of (phen)$_2$ sulfito complexes at 45 °C: (A) [Co(phen)$_2$(SO$_3$)(OH)]; (B) [Co(phen)$_2$(SO$_3$)$_2$]$^-$.

analysis yields the values of k_r, K, and pK presented in Table VIII. The additional k_r data in the tabulation were derived by evaluating the average limiting values of k_{obsd} in experiments run at various temperatures and with several acid concentrations in the range 0.4 M ≤ [H$^+$] ≤ 1.0 M. This enables the temperature parameter estimates for the various k_r's, also given in Table VIII.

The pK_5 value of 2.3 and the pK_7 value of 1.7, both obtained at 45 °C, are to be compared with the 25 °C values of 3.2 and 2.6, respectively, already mentioned. While the data obtained near 25 °C for aqueous SO$_2$ suggest an *increase* in pK_1 with temperature, the opposite is usually observed, as exemplified by pK_3 and pK_4 (Table I). In fact, for [Co(phen)$_2$(H$_2$O)$_2$]$^{3+}$, a temperature increase from 15 to 35 °C decreases pK_3 by ~0.6 unit, paralleling the changes we have deduced for pK_5 and pK_7 for a similar temperature change. The unusual behavior of aqueous SO$_2$ may well be a result of the apparent nonexistence of molecular H$_2$SO$_3$, requiring much greater solvation/desolvation rearrangements for the release of a proton, apparently sufficient to reverse completely the sign of $\Delta H°$ for the acid dissociation process. The magnitudes of k_r for all three redox reactions are within a factor of 2 of one another at all three temperatures. There are some differences in the distribution of ΔG^* between ΔH^* and ΔS^* but not sufficiently beyond the error limits to warrant detailed comparison. It is noteworthy, however, that these k_r values do not differ greatly from those found for the corresponding rate constant for the intramolecular reduction of the S-bonded *cis*-[Pt(NH$_3$)$_4$(SO$_3$)$_2$] complex,[34] which also reacted in the protonated form *cis*-[Pt(NH$_3$)$_4$(SO$_3$H)(SO$_3$)]$^+$. However, the rate constants for similar redox reactions for the O-bonded species[4,2,7] [Co(NH$_3$)$_5$OSO$_2$]$^+$, [Co(en)$_2$(OSO$_2$)(OH$_2$)]$^+$, and [Co(tren)(OSO$_2$)(OH$_2$)]$^{2+}$ are much more rapid and are not greatly dependent on the acidity in the range 3 < pH < 7 in which the studies were made. As has been noted previously,[4] metal–oxygen bonding is apparently substantially more conductive to electron

(33) As mentioned earlier, it was impossible to prepare pure [Co(bpy)$_2$-(SO$_3$)(OH)] due to solubility problems.

(34) Koshy, K. C.; Harris, G. M. *Inorg. Chem.* **1983**, *22*, 2947.

transfer between the sulfite moiety and the reducible metal than is metal–sulfur bonding. This is probably to be expected in view of the greater electronegativity of the O^{2-} species as compared to the S^{IV} species.

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Mechanistic Information from the Micellar Effect on the Base Hydrolysis of (αβS)-(3-Nitrosalicylato)(tetraethylenepentamine)cobalt(III) Ion

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The kinetics of base hydrolysis of the (αβS)-(tetren)(3NO₂-salicylato)Co(III) ion has been investigated in the presence and absence of cationic (CTAB) and anionic (SDS) surfactants at 30.0 ± 0.1 °C. The phenoxide form of the complex undergoes aquation in the micellar pseudophase of the surfactants much faster than in the aqueous pseudophase, the effect being much more pronounced for SDS. This supports the internal conjugate base mechanism, the reactive amine conjugate base being generated by the intramolecular proton-transfer equilibrium [(tetren)CoO₂CC₆H₃(3NO₂)O]⁺ ⇌ [(tetrenN-H)CoO₂CC₆H₃(3NO₂)OH]⁺. The CTAB micelle, however, retards the second-order base hydrolysis of the micelle-bound phenoxide species. The dipositive phenol form of the complex binds strongly to the anionic micelle of SDS, but this does not lead to detectable enhancement of its rate of aquation.

Introduction

A recent study by A.C.D.[1] elucidated that the base hydrolysis of the phenoxide species of (αβS)-(salicylato)(tetren)Co(III) involved two pathways, namely, the pseudo-first-order OH⁻-independent aquation and the second-order OH⁻-catalyzed base hydrolysis. The rate and activation parameters for the OH⁻-independent path, in comparison to the relevant data for the corresponding species of *cis*-(salicylato)(NH₃)(en)₂Co(III) and α-*cis*-(NH₃)(salicylato)(trien)Co(III) and related systems (see Table II of ref 1), provided evidence in favor of the internal conjugate base mechanism (ICB) involving the intramolecular phenoxide-assisted generation of the reactive amine conjugate base.[2] A detailed understanding of the ICB mechanism in cobalt(III) and other related systems is at present a rather difficult task due to the lack of data on sufficient number of representative systems.

This paper presents a study of the base hydrolysis of (αβS)-(3NO₂-salicylato)(tetren)Co(III) in buffered aqueous media in the presence and absence of cationic and anionic surfactants. The purpose was to generate the phenoxide species of the substrate in an aqueous medium and then partition it to the micellar pseudophase of the surfactants so that its reactivity in this phase can be assessed to support the ICB mechanism cited above. A preliminary report on the effect of CTAB on the base hydrolysis of *cis*-(5-nitrosalicylato)(ammine)bis(ethylenediamine)cobalt(III)[3] indicated that this dipolar substrate (phenoxide form) exchanged into the micellar pseudophase of CTAB in which it underwent base hydrolysis at a rate slightly faster than in the aqueous phase. However, the binding of this substrate with the CTAB micelle was observed to be weak, and the corresponding rate effect was also small. We chose the (3NO₂-salicylato)(tetren)Co(III) complex in the present work with the hope of observing enhanced micellar binding of this substrate and hence higher rate effects of the micelles.

Experimental Section

Tetraethylenepentamine was used as obtained from BDH. The bromide analysis of CTAB indicated that the sample has a purity of

99.8%. Sodium dodecyl sulfate (SDS) (Fluka, AG) was purified by repeated crystallization from ethanol and checked for purity by cmc determination (cmc = 0.008 M).[4] All other chemicals were of AR grade. Sodium perchlorate used for ionic strength adjustment was prepared by neutralizing HClO₄ with NaOH solution.

(αβS)-(3-Nitrosalicylato)(tetraethylenepentamine)cobalt(III) perchlorate was prepared from (αβ)-chloro(tetraethylenepentamine)cobalt(III) perchlorate as described earlier for the preparation of the corresponding salicylato complex.[1] Anal. Calcd for [Co(C₈N₅H₂₃)-(CO₂C₆H₃)(NO₂)OH](ClO₄)₂: Co, 9.36; N, 13.35. Found: Co, 9.3; N, 13.2. The spectral parameters of the complex measured by a Varian-Cary UV–visible recording spectrophotometer, Model 634S, are as follows [λ_max, nm (ε, M⁻¹ cm⁻¹)]: 492 (181), 310 (9512), and 228 (29368) in 0.01 M HClO₄ medium. These may be compared with corresponding data for the (αβS)-(salicylato)(tetren)Co(III) ion [λ_max, nm (ε, M⁻¹ cm⁻¹): 491 (170) and 298 (4318)][1] and for *cis*-(ammine)(3-nitrosalicylato)bis(ethylenediamine)cobalt(III) ion [λ_max, nm (ε, M⁻¹ cm⁻¹)]: 500 (109) and 312 (6689)].[5]

The pH measurements were made with an Elico digital pH meter, Model LI 120; the reference electrode was filled with saturated NaCl instead of KCl in order to avoid precipitation of KClO₄ and KDS during pH measurements.

The kinetics of hydrolysis of the cobalt(III) substrate was investigated at 30.0 ± 0.1 °C in the pH range 7.32 ≤ pH ≤ 10.1. The reaction was initiated by injecting 0.15 mL of stock solution of the complex into the preequilibrated reaction mixture (3 mL) taken in a 10-mm quartz cell placed in the thermostated cell compartment of the spectrophotometer. The mixing time was <15 s. The rate of decrease of absorbance (measured against solvent blank) at 400 or 450 nm was monitored manually or by a Varian 9176 strip chart recorder. Runs were made under pseudo-first-order conditions with [complex]_T = (0.29–3.20) × 10⁻⁴ M.

Results and Discussion

The complex ion is remarkably stable to aquation but it undergoes base hydrolysis quite rapidly. In mild alkaline medium, it dissociates to the highly absorbing phenoxide species, [Co(tetren)(O₂CC₆H₃(3NO₂)O]⁺, which exhibits λ_max at 400 nm with ε = 8054 M⁻¹ cm⁻¹ (see Figure 1).

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