$(NH_3)_5CoNCCH_2^{\bullet}$ radical at about the same rate as with other organic radicals ($\sim 10^7$ M^{-1} s^{-1})[4], then the Cr(II) concentration of $\sim 10^{-2}$ M in the earlier study allows one to estimate an upper limit for the intramolecular electron transfer of $\sim 10^5$ s^{-1}. The suggestion that $Co(DMGH)_2$ reacts more slowly than Cr(II) with the radical is consistent with the observations of Elroi and Meyerstein[21] from a pulse radiolysis study. Their results with a cobalt(II) macrocycle imply that the rate constant for a radical with an electron-withdrawing substituent, such as $NCCH_2^{\bullet}$ would be $<10^7$ M^{-1} s^{-1}. Flash photolysis studies of Endicott and coworkers[22] give much larger rates near the diffusion-controlled limit. These differences can be rationalized if the flash photolysis is measuring a cage recombination process.

Experimental Section

Materials. Iodoacetonitrile and $((NH_3)_5CoNCCH_2I)(ClO_4)_3$ were prepared as described previously.[5] Dimethylglyoxime (Aldrich) and 4-morpholineethanesulfonic acid (MES) (Aldrich) were used as supplied.

Solutions of bis(dimethylglyoximato)cobalt were prepared by adding an appropriate volume of aqueous cobalt(II) perchlorate from a syringe to a solution of dimethylglyoxime in MES buffer. The pH was adjusted by addition of NaOH or $HClO_4$ before the addition of cobalt(II). All solutions were deoxygenated by bubbling argon that was passed through a chromium(II) scrubber, and they were protected from air by standard serum caps. Deoxygenated solutions of the substrates, iodoacetonitrile or $((NH_3)_5CoNCCH_2I)(ClO_4)_3$, were added by syringe to the $Co(DMGH)_2$ as soon as possible after preparation of the latter.

$(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)(ClO_4)_3$. This solid was prepared from an aqueous solution initially containing 4.4×10^{-3} M cobalt(II) perchlorate, 2.4×10^{-2} M dimethylglyoxime, and 2.0×10^{-3} M $((NH_3)_5CoNCCH_2I)(ClO_4)_3$ at pH 6.0 in 0.01 M MES at 40 °C. Reagents were mixed as described in the preceding paragraph, and the reaction was quenched after 3–4 min by exposure to air. The products were separated on Sephadex SP-C25 resin by elution with increasing concentrations of $HClO_4$ from 0.1 to 1.0 M. The desired product is contained in 1.0 M $HClO_4$ eluant, and cooling of this solution at 5 °C yielded the desired solid. The properties of this species are described elsewhere in the text.

Analytical Methods. Cobalt was determined in $(NH_3)_5CoNCCH_2Co(DMGH)_2(OH_2)^{3+}$ by heating the complex in alkaline solution for $\sim$2 h at $\sim$70 °C to remove the ammonia. Then the solution was acidified, hydrogen peroxide was added, and the solution was heated as before to remove the DMGH. The resultant solution was analyzed for cobalt(II), as described previously.[5,12]

Iodide was determined spectrophotometrically by the method of Nikolelis et al.[13] When the analyte solution was yellow, then iodide was oxidized to iodine and the iodine extracted into chloroform and determined spectrophotometrically (ϵ 917 M^{-1} cm^{-1} at 470 nm).

Kinetic Methods. Solutions for kinetic analysis were prepared by adding a solution of the substrate to a solution of $Co(DMGH)_2$, MES, and $NaClO_4$ in a 5-cm path length cell. The latter solution was preequilibrated at the appropriate temperature in a thermostated cell holder. All solutions were deoxygenated with argon. The measurements were done on a Hewlett-Packard 8451 diode array spectrophotometer and analyzed by nonlinear least squares to obtain the rate constant.

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Registry No. $Co(DMGH)_2$, 3252-99-1; $NCCH_2I$, 624-75-9; $(NH_3)_5CoNCCH_2I^{3+}$, 88157-85-1; $(NH_3)_5CoNCCH_2ICo(DMGH)_2(OH_2)(ClO_4)_3$, 119480-27-2.

Supplementary Material Available: Table SI, containing kinetic results for the reaction of $Co(DMGH)_2$ with $NCCH_2I$ (1 page). Ordering information is given on any current masthead page.

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Synthesis, Kinetics, and Stereochemistry of the Aquation of *cis*-[Chlorosulfitobis(ethylenediamine)cobalt(III)]

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The synthesis of *cis*-$[Co(en)_2(SO_3)Cl]$ by SO_3^{2-} substitution on aqueous *cis*- or *trans*-$[Co(en)_2Cl_2]^+$, *cis*- or *trans*-$[Co(en)_2(NCS)Cl]^+$, or *cis*-$[Co(en)_2ACl]^+$ ($A^- = N_3^-$, NO_2^-) is described. This unusual observation, preferential loss of A^- rather than Cl^-, is discussed and a redox mechanism proposed. The stereochemistries for the unusually rapid (and clean) SO_3^{2-} substitution on the dichloro complexes have been determined by ^{13}C NMR spectroscopy; remarkably, the same initial distribution of $[Co(en)_2(SO_3)Cl]$ isomers (>75% cis) is observed, but principally trans isomer results on standing. A high-yield synthesis of either isomer can be obtained by control of the reaction conditions; mechanisms are discussed. The kinetics (k_1) and steric course of spontaneous aquation of *cis*-$[Co(en)_2(SO_3)Cl]$ have been investigated, as well as the steric course of its Hg^{2+}-induced hydrolysis and the temperature dependence of the kinetics (k_2) of the subsequent *cis*- to *trans*-$[Co(en)_2(SO_3)OH_2]^+$ isomerization. The *cis*-$[Co(en)_2(SO_3)Cl]$ isomer gives 53 ± 3% *cis*- and 46 ± 3% *trans*-$[Co(en)_2(SO_3)OH_2]^+$ in spontaneous aquation but 62 ± 2% *cis*-$[Co(en)_2(SO_3)OH_2]^+$ in the induced reaction. These results are discussed with respect to recent related work. The following specific rates and activation parameters were determined: $k_1 = 5.0 \times 10^{-4}$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 86 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -20 \pm 9$ J mol^{-1} K^{-1}; $k_2 = 1.5 \times 10^{-3}$ s^{-1} at 25 °C, $\Delta H^{\ddagger} = 107 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 60 \pm 13$ J mol^{-1} K^{-1}. Trans activation by S-bonded sulfite is well documented, but we show that a cis SO_3^{2-} is quite unremarkable, kinetically and stereochemically.

Introduction

The sulfite ion can bond to cobalt(III) through either the sulfur or the oxygen center.[1,2] The oxygen-bonded isomers, for example, *cis*-$[Co(en)_2(OH_2)OSO_2]^+$ [3] or $(NH_3)_5CoOSO_2^+$,[4] are unstable and undergo an internal redox reaction ultimately yielding Co(II) quantitatively. However the oxygen-bonded isomers of polydentate aminecobalt(III) complexes are more resistant to reduction; for example, the $\alpha,\beta(R)$- and $\alpha,\beta(S)$-$Co(tetren)OSO_2^+$ species can be observed to isomerize slowly but completely to the more stable[2] S-bonded forms.[5]

The area of inorganic reaction mechanisms has been well served by the S-bonded sulfitotetraaminecobalt(III) complexes.[6-8]

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Studies of their substitution reactions have provided what were[7] for many years[6,8] believed to be the classic examples of limiting dissociative mechanisms. Most of these studies involved $CoL_4(SO_3)X$ complexes where SO_3^{2-} was trans to the leaving group X and, in that position, remarkably labilizing. Recently some cis isomers of this kind have been synthesized and their kinetics and stereochemistry of substitution examined.[7,9] Crucial to the determination of the steric course of hydrolysis of the *cis-* (and *trans-*) $[Co(en)_2(SO_3)X]$ species was the isolation of the putative *cis*-$[Co(en)_2(SO_3)OH_2]^+$ ion. The rate and equilibrium parameters for its isomerization to the trans isomer have been determined, as well as the steric course for the NO^+-assisted hydrolysis of *cis*-$[Co(en)_2(SO_3)N_3]$.[9] More recently we have sought *cis*-$[Co(en)_2(SO_3)X]$ complexes containing more labile X groups since to date there have been no studies of the stereochemistry of spontaneous aquation of *cis*-$[Co(en)_2(SO_3)X]$. It is noted that the hydrolysis of $[Co(en)_2(SO_3)X]$ needs to be fast if the initial stereochemistry is to be precisely determined because $[Co(en)_2(SO_3)OH_2]^+$ isomerization is fairly rapid.[9]

In this article we describe the synthesis of a prototype, *cis*-$[Co(en)_2(SO_3)Cl]$, and report the kinetics of its hydrolysis and the stereochemistry of its spontaneous and Hg^{2+}-induced aquation. We also describe some unusual observations of SO_3^{2-} as an apparent nucleophile toward cobalt(III). Although these studies were initiated independently, the results are here presented jointly for the purposes of discussion and analysis.

Results and Discussion

Synthesis and Characterization. The synthesis of sulfitocobalt(III) complexes by direct substitution of aqueous sulfite on halocobalt(III) complexes in solution is not new, but there are several unusual features of this reaction, each of which is dealt with in turn.

The red-brown charge-neutral *cis*-$[Co(en)_2(SO_3)Cl]$ complex is new and is prepared in situ by the addition of concentrated aqueous sodium sulfite to a solution of any of the following: *cis*- or *trans*-$[Co(en)_2Cl_2]Cl$, *cis*- or *trans*-$[Co(en)_2(NCS)Cl]Cl$, *cis*-$[Co(en)_2(NO_2)Cl]Cl$, or *cis*-$[Co(en)_2(N_3)Cl]Cl$. The substitution of SO_3^{2-} on *cis*- or *trans*-$[Co(en)_2Cl_2]^+$ proceeds smoothly and *un*usually rapidly (seconds) at ambient temperature. No attempt was made to exclude ambient lighting; the rate appears to be reproducible, and the yield of *cis*-$[Co(en)_2(SO_3)Cl]$ is good.

The pure solid cis complex is salmon pink while, under reflected fluorescent light and depending upon particle size, the trans isomer is chocolate brown to brown-pink. Thus, although impure specimens of either isomer containing yellow bis(sulfito) complex appear very similar, the pure isomers are visually quite distinct and can be distinguished by their visible and ultraviolet spectra. Furthermore, their isomeric purity is clear from their ^{13}C NMR spectra. The cis isomer shows a characteristic four-line spectrum, while the trans form shows a single line in a different position that is an average signal since, on the NMR time scale, exchange with the trans aqua species and free Cl^- is rapid. The isomers are also distinguished by their behavior on ion-exchange resins: in contrast to the trans isomer which aquates so rapidly that it is retained quantitatively on cation-exchange resins as $[Co(en)_2(SO_3)OH_2]^+$, the charge-neutral cis isomer is retained by neither cation not anion resins. Isolated by removal of cations using cation-exchange chromatography, the cis isomer slowly aquates over a period of hours at ambient temperature with the liberation of 1.0 ± 0.1 equiv of Cl^-, ultimately to give the reported equilibrium mixture of $[Co(en)_2(SO_3)OH_2]^+$. Thus the stoichiometry of the cis isomer is clearly $[Co(en)_2(SO_3)Cl]$.

Controlled aquation of *cis*-$[Co(en)_2(SO_3)Cl]$ followed by rechromatographing on a cation-exchange resin yields $[Co(en)_2(SO_3)OH_2]^+$ in a nonequilibrium, isomeric mixture displaying the properties (isosbestic points, isomerization rate, equilibrium spectrum) reported previously.[9] Strong charge-transfer absorption was observed for this mixture (276 nm (ϵ = 15 500)) as well as for the $[Co(en)_2(SO_3)Cl]$ starting complex (ca. 289 nm), characteristic[10] of sulfito-*S* ligation in all these complexes.

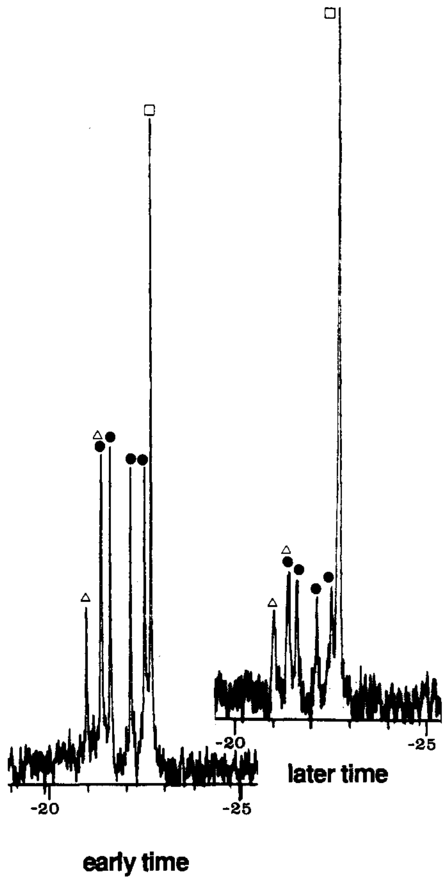

Figure 1. ^{13}C NMR spectra for the products of the reaction between *cis*-$[Co(en)_2Cl_2]^+$ and 1 equiv of Na_2SO_3 in H_2O: (△) unreacted *cis*-$[Co(en)_2Cl_2]^+$; (●) *cis*-$[Co(en)_2SO_3)Cl]$; (□) *trans*-$[Co(en)_2(SO_3)Cl]$/*trans*-$[Co(en)_2(SO_3)OH_2]^+$.

Initially, we followed the SO_3^{2-} substitution of *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ in D_2O using proton-decoupled ^{13}C NMR spectroscopy. The results revealed more peaks than could be immediately accounted for, owing to H/D exchange occurring at the NH_2 sites in SO_3^{2-} solution (pH ca. 9). For each D atom substituted at NH_2, the α-carbon is shifted upfield ca. 0.1 ppm; all of the resulting isotopomers are resolved at 75 MHz. Data sets (Figures 1 and 2) were obtained by using H_2O rather than D_2O as the reaction medium with an acid quench to prevent subsequent H/D exchange when the deuterium lock (D_2O) was introduced. Under these conditions, any residual SO_3^{2-} is converted to innocuous HSO_3^-, and the pH is sufficiently low to prevent O-bonded sulfito complex formation from any aqua species present. With this strategy, the peak multiplicity disappeared and the products were clearly identified.

Surprisingly the product distribution, commencing with either the *cis*- (Figure 1) or the *trans*-dichloro complex (Figure 2) was the same: largely *cis*-$[Co(en)_2(SO_3)Cl]$. During the 5 min required for accumulation of a reasonable spectrum, some trans isomer necessarily arises through subsequent hydrolysis/isomerization; the first observed cis/trans distributions, starting with either isomer (75–80% cis), represent the ***minimum*** cis content. The later time spectra (ca. 45 min at 22 °C) reveal considerably more trans isomer (Figures 1 and 2).

Finally, the recent claim[9] that the Cl^- anation of $[Co(en)_2(SO_3)OH_2]^+$ under equilibrium conditions is not negligible can be supported. Chromatographic elution of the aquasulfito species by 0.25 M NaCl is substantially easier than by 0.25 M $NaClO_4$. The enhanced mobility in Cl^- media is consistent with in situ formation of neutral sulfitochloro species; a similar phenomenon has been noted[11] for the *trans*-$[Co(en)_2(S_2O_3)OH_2]^+$ ion.

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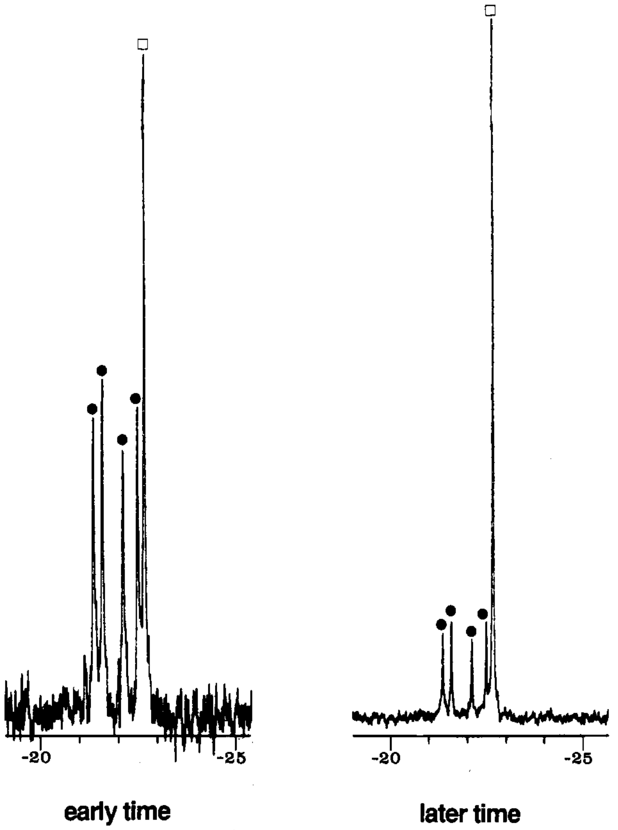
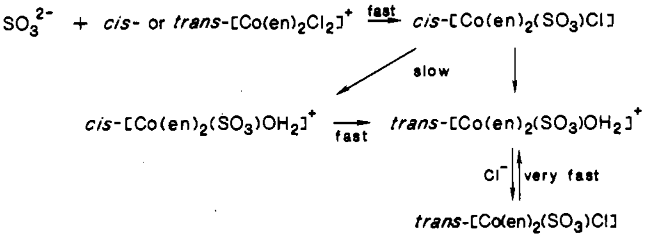


Figure 2. ^{13}C NMR spectra for the products of the reaction between *trans*-[Co(en)$_2$Cl$_2$]$^+$ and 1 equiv of Na$_2$SO$_3$ in H$_2$O: (●) *cis*-[Co(en)$_2$(SO$_3$)Cl]; (□) *trans*-[Co(en)$_2$(SO$_3$)Cl]/*trans*-[Co(en)$_2$(SO$_3$)OH$_2$]$^+$.

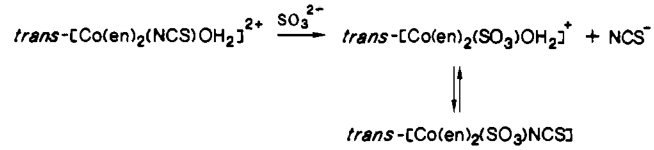
An overall reaction scheme consistent with these observations, the preparative chemistry (see Experimental Section), and the kinetic and stereochemical studies described below is as follows:



Note that, depending on the concentrations, the reaction can proceed from start to finish in ca. 1 h at 20 °C in moderately concentrated solution without crystallization of the very insoluble intermediate *cis*-[Co(en)$_2$(SO$_3$)Cl], whose solutions easily supersaturate.

The material that Baldwin prepared[12] from *cis*-[Co(en)$_2$(NCS)Cl]$^+$ and SO$_3^{2-}$ and believed to be the same as the trans isomer[9] that is obtained by other routes was probably largely the *cis*-[Co(en)$_2$(SO$_3$)Cl] complex; thus, we find *cis*-[Co(en)$_2$(NCS)Cl]$^+$ and SO$_3^{2-}$ give the cis isomer (see below). Baldwin's material was characterized by its IR spectrum alone. We also note that Baldwin reported that the same [Co(en)$_2$(SO$_3$)Cl] species was obtained from *cis*- or *trans*-[Co(en)$_2$Cl$_2$]Cl and SO$_3^{2-}$, although the synthesis using cis reactant was not described in her Experimental Section. Our results below show that the stereochemical outcome is independent of the starting geometry but depends critically on the conditions: concentrations, reaction time, and temperature. It is impossible to infer precisely what product Baldwin[12] obtained because these conditions were not completely specified and the characterization was incomplete.

We conclude that the initial stereochemistries previously reported for SO$_3^{2-}$ substitution may have been only apparent, especially where near-boiling conditions were used;[12,13] under such conditions the observed isomer ratios would approach the equilibrium rather than the kinetic distribution. Further, the yields of isolated product may not reflect the solution composition if, as in the case of the [Co(en)$_2$(SO$_3$)A] complexes, one isomer, e.g. the cis, is much less soluble than the other and the isomers equilibrate on a time scale that is short with respect to crystallization. Baldwin prepared *trans*-[Co(en)$_2$(SO$_3$)NCS] by heating *trans*-[Co(en)$_2$(SO$_3$)H$_2$O]$^+$ with SO$_3^{2-}$ in aqueous solution.[12] In view of our findings described below, it appears likely that this reaction proceeds by loss of NCS$^-$ first:



Anation of cobalt(III) complexes in aqueous solution usually occurs in a two-step hydrolysis/anation mechanism:[14,15]

$$\mathrm{Co(en)_2AX} \xrightarrow{\mathrm{H_2O}} \mathrm{Co(en)_2A(OH_2)} + \mathrm{X} \xrightarrow{\mathrm{Y}} \mathrm{Co(en)_2AY} + \mathrm{H_2O}$$

Although not negligible, direct one-step anation in competition with the hydrolysis of tetraamine and pentaaminecobalt(III) complexes is known to be small for a wide range of nucleophiles.[14] Thus the rate of formation of [Co(en)$_2$AY] by the usual two-step mechanism can be no faster than the hydrolysis rate of the [Co(en)$_2$AX] complex. The observed SO$_3^{2-}$ substitution reactions are far faster than would be anticipated for the two-step mechanism. For example, the reaction for both *cis*- and *trans*-[Co(en)$_2$Cl$_2$]$^+$ is considerably faster than the normal hydrolysis reactions, even for dilute equimolar solutions (0.01 M) of complex and SO$_3^{2-}$, and the product is still the chlorosulfito species. Even the SO$_3^{2-}$ substitution reactions of *cis*-[Co(en)$_2$X$_2$]$^+$ (X = N$_3^-$,[9,13] NO$_2^-$, NCS$^-$, and others[16]), although intrinsically slower than those for the dichloro complexes, are faster than the corresponding hydrolysis reactions.

We note that both *cis*- and *trans*-[Co(en)$_2$Br$_2$]$^+$ undergo reaction with SO$_3^{2-}$ much like the corresponding dichloro complexes. A red-brown charge-neutral complex with kinetic and spectral properties similar to the *cis*-chlorosulfito complex and believed to be *cis*-[Co(en)$_2$SO$_3$Br] has been isolated, although in very low yield.

The fact that, in addition to the *cis*- and *trans*-dihalo cations, both *cis*-[Co(en)$_2$ACl]$^+$ (A = NO$_2^-$, N$_3^-$, NCS$^-$) and *trans*-[Co(en)$_2$(NCS)Cl]$^+$ give *cis*-[Co(en)$_2$(SO$_3$)Cl] on reaction with SO$_3^{2-}$ rather than *cis*-[Co(en)$_2$(SO$_3$)A] is quite remarkable. For H$_2$O as the entering group, loss of Cl$^-$ from [Co(en)$_2$ACl] is several orders of magnitude faster than loss of A$^-$,[17] whereas with SO$_3^{2-}$ as the entering group we find the converse to be true; loss of Cl$^-$ is at least 10-fold faster than loss of A$^-$.

The common product distribution for the [Co(en)$_2$Cl$_2$]$^+$/SO$_3^{2-}$ reactions, coupled with their rapidity, is unusual in Co(III) chemistry; together, these strongly suggest that the mechanism is not an associative reaction between SO$_3^{2-}$ and cobalt(III) complexes.

Given that SO$_3^{2-}$ is a reducing agent and that cobalt(II) complexes are labile, we suspect that SO$_3^{2-}$ substitution occurs by some form of redox process. However there is no accumulation of appreciable Co(II) at any time; synthetically there is material balance for cobalt(III), and significantly, no contact shifts were observed in the NMR spectra for reacting cobalt(III)/SO$_3^{2-}$ solutions.

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Table I. Kinetic Data for the Aquation of *cis*-$[Co(en)_2(SO_3)Cl]$ and Isomerization of $[Co(en)_2(SO_3)OH_2]^+$ in 0.01 M $HClO_4$ at 25 °C

			five-param fit[c,d]	
wavelength, nm	three-param fit[a,d] 10^4k_1, s^{-1}	four-param fit[b,d] 10^4k_1, s^{-1}	10^4k_1, s^{-1}	10^3k_2, s^{-1}
380[f]	3.98 ± 0.27 (5)	4.70 ± 0.16 (5)	4.78 ± 0.11 (3)	1.42 ± 0.11
	4.06 ± 0.03 (2)	5.04 ± 0.04 (2)	5.15 ± 0.02 (2)	1.42 ± 0.02 (2)
470[f]	3.97 ± 0.11 (5)	4.66 ± 0.15 (5)	4.76 ± 0.16 (3)	1.43 ± 0.08 (3)
	4.52 ± 0.09	5.04 ± 0.05		
530[f]	4.27 ± 0.08 (5)	4.56 ± 0.08 (5)		
	4.48 ± 0.06	4.87 ± 0.04		
weighted av	4.14 ± 0.13	4.86 ± 0.11[e]	5.12 ± 0.11	1.42 ± 0.07

[a] D and t data fitted to $D = P(1)\exp(-[P(2)]t + P(3)$, where $P(2) = k_1$. [b] D and t data fitted to $D = P(1)\exp(-[P(2)]t) + P(3)\exp(-0.00156t) + P(4)$, where $P(2) = k_1$. [c] D and t data fitted to $D = P(1)\exp(-[P(2)]t + P(3)\exp(-[P(4)]t) + P(5)$, where $P(2) = k_1$ and $P(4) = k_2$. [d] Mean and mean deviations; the number of determinations is given in parentheses. [e] Best value for k_1. [f] Top line, Cary 118C results; lower line, Cary 210 results.

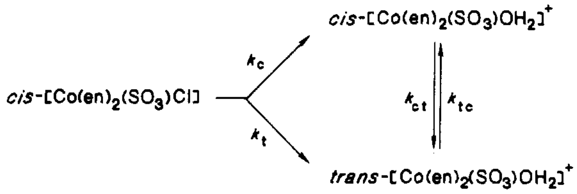
Lowering the pH (below 10) slowed the reactions dramatically. It was shown in control experiments that the reduction in rate was not simply removal of the base-catalyzed hydrolysis[18] contribution to the rate, since at pH 10 in the absence of SO_3^{2-} the rates were quite slow (minutes). The rate reduction is accommodated by the conversion of SO_3^{2-} to HSO_3^- below pH 10, since we could show independently that HSO_3^- was quite unreactive toward the Co(III) complexes.

When the reactants, complex plus SO_3^{2-}, are combined in edta (Na_3Hedta/Na_4edta), self-buffered to pH 10 to keep the S(IV) as SO_3^{2-} and to scavenge Co(II), the rate is greatly reduced. Further, Co(II) added as the hydrated perchlorate salt catalyzes the substitutions of SO_3^{2-} on *cis*- and *trans*-$[Co(en)_2(NCS)Cl]^+$, reactions that are otherwise relatively slow at ambient temperature. We interpret this as clear evidence that the reaction is a redox process involving Co(II). Indeed, we find that even the rapid $[Co(en)_2Cl_2]^+/SO_3^{2-}$ reactions are accelerated by added $Co^{II}Cl_2$; this acceleration indicates some rate dependence on [Co(II)]. We remain unsure whether the SO_3^{2-} reactions are catalyzed in general by adventitious Co(II) rather than by Co(II) produced in situ from a $Co(III)/SO_3^{2-}$ reaction. Finally, it is intriguing that the Co(II) seems to catalyze only the SO_3^{2-} substitution process; it does not, for example, catalyze the hydrolysis of *cis*-$[Co(en)_2(SO_3)Cl]$ or cis to trans isomerization of $[Co(en)_2(SO_3)OH_2]^+$.

One possible mechanism is inner-sphere electron transfer with a bridging Cl^- that is incorporated in the sulfitocobalt(III) product; until such time as the rate law is determined and other more searching experiments performed, it is premature to suggest a detailed mechanism for this unusual substitution reaction.

Spontaneous Aquation. Reacting solutions of *cis*-$[Co(en)_2(SO_3)Cl]$ in dilute $HClO_4$ were scanned in the range 600–350 nm; these spectra revealed two sharp isosbestic points at early reaction times. The 496-nm point (ϵ = 105.5) remained sharp throughout the reaction, while the initial 432.5-nm point (ϵ = 102.5) shifted, indicative of subsequent reaction. However neither isosbestic point defines the initial steric course of substitution because each is close to one of those observed[9] for the subsequent cis/trans isomerization of $[Co(en)_2(SO_3)OH_2]^+$ (the 496-nm point is almost coincident; cf. 499 nm).[19] It is pertinent to comment here that the ^{13}C NMR spectrum of $[Co(en)_2(SO_3)Cl]$ reveals peaks attributable to both *cis*- and *trans*-$[Co(en)_2(SO_3)OH_2]^+$ as the hydrolysis proceeds. This result indicates that the subsequent cis to trans isomerization reaction is not overwhelmingly more rapid than the hydrolysis of the *cis*-chlorosulfito species. This fact was confirmed by the separation of $[Co(en)_2(SO_3)OH_2]^+$, containing considerable cis isomer, from partially reacted $[Co(en)_2(SO_3)Cl]$ with ion-exchange chromatography.

The kinetics were monitored spectrophotometrically at 380, 470, and 530 nm and independently at 399 and 465 nm. At these wavelengths, the spectra of *cis*- and *trans*-$[Co(en)_2(SO_3)OH_2]^+$ differ appreciably, especially[9] at 380 and at 399 nm. The absorbance/time data (25 °C) followed a single exponential function with fair precision, and the first-order rate constants k_1 so obtained agreed at different wavelengths (Table I). This number, the hydrolysis rate constant for the *cis*-$[Co(en)_2(SO_3)Cl]$ species, is approximately one-third of that (k_2) for the isomerization of *cis*- and *trans*-$[Co(en)_2(SO_3)OH_2]^+$ (1.56×10^{-3} s^{-1}). Thus the subsequent isomerization of the initial cis-rich *cis-/trans*-$[Co(en)_2(SO_3)OH_2]^+$ mixture is *not* so much faster than the primary hydrolysis that it goes undetected; at early times the residuals of the fit of the absorbance/time data to single exponential behavior reveal small but systematic departures, especially at 380 and 399 nm. The D/t data were reanalyzed by using the two-exponential function appropriate to the consecutive first-order reaction scheme



The data were fitted by a weighted nonlinear regression to the function

$$D = \Delta D_1 \exp(-k_1t) + \Delta D_2 \exp(-k_2t) + D_\infty$$

where ΔD_1, ΔD_2, D_∞, k_1, and k_2 are parameters ($k_1 = k_c + k_t$, $k_2 = k_{ct} + k_{tc}$). The results obtained (Table I) reveal that the (true) k_1 value is a little larger than that obtained by using the simpler single-exponential fit, and the k_2 value agrees reasonably well (380, 530 nm) with that determined independently. This agreement indicates that the fit is not "overparametrized". Further, the standard deviations of the rate parameters are smaller than the corresponding ones for the single-exponential (three-parameter) fit.

The results of the weighted nonlinear regression were interpreted by the function

$$D = [(D_0 - D_\infty) + k_1(D_B - D_\infty)/(k_2 - k_1)]\exp(-k_1t) - [k_1(D_B - D_\infty)/(k_2 - k_1)]\exp(-k_2t) + D_\infty$$

appropriate for the scheme above (D_B, the absorbance of the first-formed *cis-/trans*-$[Co(en)_2(SO_3)OH_2]^+$ mixture, was computed from the optimized values for ΔD_2, k_1, k_2, and D_∞, since $\Delta D_2 = -k_1(D_B - D_\infty)/(k_2 - k_1)$).[20-23] For the purpose of computing the steric course of aquation, more reliable values of the parameters involved, including ΔD_2, were obtained by using a reduced four-parameter fit to the original D and t data, by constraining k_2 to its known value (1.56×10^{-3} s^{-1}).

The results of multiple determinations of D_B (and hence ϵ_B) indicated the 380-nm data to be the best; this was expected because the largest spectral difference for *cis*- and *trans*-$[Co(en)_2(SO_3)OH_2]^+$ occurs at this wavelength. The results obtained from the 470- and 530-nm data (Table II) were regarded as confir-

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[18] Tobe, M. L. In *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed. Academic Press: London, 1983; Vol. 2, pp 1–94.

[19] The kinetics of hydrolysis of the $[Co(en)_2(SO_3)Cl]$ complex could not be followed at 499 nm or indeed at any of the wavelengths corresponding to isosbestics in the $[Co(en)_2(SO_3)OH_2]^+$ isomerization because the absorbance changes were too small.

[20] Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.

[21] Jackson, W. G.; Begbie, C. M. *Inorg. Chim. Acta* **1982**, *61*, 167.

[22] Begbi, C. M.; Jackson, W. G. *Inorg. Chim. Acta* **1982**, *60*, 115.

[23] Jackson, W. G. *Inorg. Chim. Acta* **1981**, *47*, 159.

Table II. Steric Course of Spontaneous and $\mathrm{Hg^{2+}}$-Induced Hydrolysis of *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ at 25 °C in 0.01 M $\mathrm{HClO_4}$

wavelength, nm	ϵ_B,[a] $\mathrm{M^{-1}\,cm^{-1}}$	% cis product[b]	ϵ_B(obsd)[c], $\mathrm{M^{-1}\,cm^{-1}}$	% cis product[b]
380[d]	163.2 ± 5.0	53 ± 2	184.8 ± 5.0	62 ± 2
470[d]	143.4 ± 3.0	55.5 ± 8.5	140.1 ± 1.5	65 ± 4.5
530[d]	40.5 ± 2.5	38.5 ± 9.5	46.4 ± 1.0	60 ± 4
weighted av		53 ± 3		62 ± 2

[a] ϵ value obtaineed from $P(3)$ in the four-parameter fit to the kinetics (refer to Table I); $P(3) = -k_1(\epsilon_B - \epsilon_C)/(k_2 - k_1)$, where A_0 = [total complex], ϵ_B refers to the initial (kinetic) *cis-/trans*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ isomer distribution, and ϵ_C refers to the final (equilibrium) distribution. The relevant k_1 and k_2 values recorded in column 3 of Table I were used together with the following ϵ_C values: 380 (ϵ = 43.0), 470 (ϵ = 162.0), 530 nm (ϵ = 31.1). [b] *cis*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$, calculated from the relation $\epsilon_B{}^\lambda = f\epsilon^\lambda(\mathrm{cis}) + (1 - f)\epsilon^\lambda(\mathrm{trans})$, where f is the fraction cis product, and ϵ^λ(cis) and ϵ_λ(trans) are the molar absorptivity coefficients for the pure cis and trans isomers at wavelength λ; the following ϵ values were used: 380 (ϵ(cis) = 276.3, ϵ(trans) = 35.6), 470 (ϵ(cis) = 127.8, ϵ(trans) = 162.9), 530 nm (ϵ(cis) = 57.2, ϵ(trans) = 30.1). [c] Directly observed values. [d] Mean results from the Cary 118C and Cary 210 instruments.

Table III. Kinetic Data for the Aquation[d] of *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ and Isomerization[e] of $[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ in 0.25 M $\mathrm{NaClO_4}$ at Several Temperatures[a]

wavelength, nm	temp, °C	10^4k_1,[d] $\mathrm{s^{-1}}$	10^4k_2[e], $\mathrm{s^{-1}}$	10^4k_3,[e] $\mathrm{s^{-1}}$
465	15	1.31	5.1	
399		1.55[b]	3.04[b]	3.8[b]
465	20	2.59	13.6	
399		2.83[b]	7.4[b]	7.74
465	25	5.26, 5.19[c]	16.7, 18.6[c]	
399		5.39	15.9	15.6
465	30	8.4	105	
399		9.16	31.8	30.4

[a] No added acid (pH = 6.4), except where noted otherwise. [b] Mean of duplicate determinations. [c] pH = 2.2. [d] $\Delta H^* = 86 \pm 3$ kJ $\mathrm{mol^{-1}}$; $\Delta S^* = -20 \pm 9$ J $\mathrm{mol^{-1}\,K^{-1}}$. [e] The 465-nm data were ignored in the fit to the Eyring equation: $\Delta H^* = 107 \pm 3$ kJ $\mathrm{mol^{-1}}$; $\Delta S^* = 60 \pm 13$ J $\mathrm{mol^{-1}\,K^{-1}}$.

matory and were not weighted in the final result.

The final spectrum (ϵ_{465}(max) = 161) was the same as that reported for the 97%/3% *trans-/cis*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ equilibrium isomer mixture.[9]

The temperature dependence of the kinetic parameters for the aquation of *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ and subsequent isomerization of the aquasulfito complex studied at 465 and 399 nm is given in Table III. The results are essentially independent of pH (2.2–6.4) and of added NaCl (0.1 M). With the five parameters and *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ as reactant, absorbance/time data were adequately fit by nonlinear regression ($\sigma \le 0.001$), yielding specific rates for hydrolysis (k_1) and subsequent isomerization (k_2). Absorbance/time data for the isomerization of the chromatographically isolated $[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ were adequately fit ($\sigma \le 0.001$) with a three-parameter function, $D = D_\infty + (D_0 - D_\infty)\exp(-k_3t)$. Values for k_1, k_2, and k_3 at 15, 20, 25, and 30 °C are recorded in Table III.

The agreement between k_1 values obtained from 399 and 465 nm data is acceptable, but the agreement between the corresponding k_2 values is poor. The absorbance changes at 465 nm for the isomerization were small, however, and the 399-nm k_2 value agrees reasonably with the independently determined value k_3 (Table III) as well as with the 25 °C value (1.56×10^{-3} $\mathrm{s^{-1}}$) reported[9] earlier.

Activation parameters were obtained from weighted nonlinear least-squares analyses of the kinetic data using the Eyring equation; data sets combined with equal weights were used as follows: $k_1(465)$ and $k_1(399)$ for the hydrolysis reaction; $k_2(399)$ and $k_3(399)$ for the isomerization reaction. Weights ($1/\sigma^2$) assumed the same ±5% error in the rate constants for all wavelengths and temperatures. For the hydrolysis reaction, $\Delta H^* = 86 \pm 3$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^* = -20 \pm 9$ J $\mathrm{mol^{-1}\,K^{-1}}$ and for the isomerization reaction, $\Delta H^* = 107 \pm 3$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^* = 60 \pm 13$ J $\mathrm{mol^{-1}\,K^{-1}}$.

Mercuric Ion Induced Aquation. A solution of the isolated, crystalline $[\mathrm{Co(en)_2(SO_3)Cl}]$ complex reacted completely within seconds, using somewhat more than the required $^1/_2$ equiv of $\mathrm{Hg^{2+}}$ in dilute $\mathrm{HClO_4}$ at 25 °C ([Co] = 0.005–0.01 M, $[\mathrm{Hg^{2+}}]$ = 0.010 M). The product spectrum was repetitively scanned (600–370 nm) and extrapolated to zero time to obtain the true spectrum of the first-formed *cis-/trans*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ mixture. This was analyzed at three wavelengths (380, 470, and 530 nm), with use of the reported molar extinction coefficient data (Table II), to provide three independent determinations of the isomeric composition. The results recorded in Table II are in reasonable agreement; as before, the 380-nm result is the most reliable.

The product spectra displayed sharp isosbestic points at 443 (ϵ = 130.0), 498 (ϵ = 99.5), and 588 nm (ϵ = 9.0), characteristic of *cis-/trans*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ isomerization and very similar to those reported previously (444 (ϵ = 127.9), 499 (ϵ = 101.0), 588 nm (ϵ = 8.9)).[24] From D and t data read at 380 nm, good fits to a single exponential function were obtained, and the specific rate 1.5×10^{-3} $\mathrm{s^{-1}}$ was determined, also in good agreement with that obtained previously.[9] The final spectrum (ϵ_{465}(max) = 161) was also the same as that reported[9] for the 97%/3% *trans-/cis*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ equilibrium isomer mixture.

Kinetics. Despite a vast literature on sulfitocobalt(III) kinetics,[2,6,7] the $[\mathrm{Co(en)_2(SO_3)Cl}]$ complex is the first for which there are data on the kinetics and stereochemistry of spontaneous aquation of a cis isomer.[25] The specific hydrolysis rates for the *trans*- ($>10^3$ $\mathrm{s^{-1}}$)[7] and *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ (5.0×10^{-4} $\mathrm{s^{-1}}$) species show $k(\mathrm{trans})/k(\mathrm{cis}) > 2 \times 10^6$, comparable to that for the corresponding $[\mathrm{Co(en)_2(SO_3)N_3}]$ species, $k(\mathrm{trans})/k(\mathrm{cis}) = 5.0 \times 10^6$,[9,25] and with that deduced[9] for the $[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ ions, $k(\mathrm{trans})/k(\mathrm{cis}) = 7 \times 10^6$; these ratios emphasize the strong trans labilization afforded by the S-bonded $\mathrm{SO_3{}^{2-}}$ ion.

Aquation of the neutral *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ species (51×10^{-5} $\mathrm{s^{-1}}$, 25 °C) is somewhat, but not greatly, faster than aquation of the cis isomers of $[\mathrm{Co(en)_2(N_3)Cl}]^+$ (24×10^{-5}), $[\mathrm{Co(en)_2Cl_2}]^+$ (24×10^{-5}), or $[\mathrm{Co(en)_2(NCS)Cl}]^+$ (1.1×10^{-5}). Thus, not surprisingly, the activation enthalpies are not very different for $[\mathrm{Co(en)_2ACl}]^+$: A = $\mathrm{SO_3{}^{2-}}$, $\Delta H^* = 86 \pm 3$ kJ $\mathrm{mol^{-1}}$; A = $\mathrm{NCS^-}$, $\Delta H^* = 87$; A = $\mathrm{Cl^-}$, $\Delta H^* = 92$.[26] Clearly there is no striking *cis*-$\mathrm{SO_3}$ effect.

The activation parameters for the $[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ isomerization, $\Delta H^* = 107 \pm 3$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^* = 60 \pm 13$ J $\mathrm{mol^{-1}\,K^{-1}}$, are each significantly larger than those for the corresponding reaction of the $[\mathrm{Co(en)_2(S_2O_3)OH_2}]^+$ species: 92.0 ± 0.08 kJ $\mathrm{mol^{-1}}$ and −0.8 ± 3.8 J $\mathrm{mol^{-1}\,K^{-1}}$, respectively. The corresponding rates for hydrolysis of *trans*-$[\mathrm{Co(en)_2(SO_3)Cl}]$[7] and *trans*-$[\mathrm{Co(en)_2(S_2O_3)Cl}]$,[11] for example, are also very different and there is as yet no clear explanation for these differences.

Stereochemistry of Hydrolysis. There has been an interest in defining the steric course of aquation of $[\mathrm{Co(en)_2AX}]$ with sufficient accuracy to comment on any leaving group dependence.[14,20-23] For the $[\mathrm{Co(en)_2(SO_3)X}]$ systems, it was confirmed recently that the *trans*-$[\mathrm{Co(en)_2(SO_3)X}]$ complexes were retentive,[9] and it was shown that the $\mathrm{NO^+}$-induced hydrolysis of the *cis*-$[\mathrm{Co(en)_2(SO_3)N_3}]$ complex gave 57 ± 2% *cis*- and 43 ± 2% *trans*-$[\mathrm{Co(en)(SO_3)OH_2}]^+$. In the present work, the *cis*-$[\mathrm{Co(en)_2(SO_3)Cl}]$ complex yields 53 ± 3% *cis*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ in spontaneous aquation and 62 ± 2% *cis*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ in the $\mathrm{Hg^{2+}}$-induced aquation. The accuracy of these data is such that it can be said that the first and third reaction do not give

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(24) The isosbestic point previously reported[9] as occurring at 283.5 nm should have read 275.5 nm; 283.5 nm is the UV maximum in the *cis*-$[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ spectrum.

(25) The value of k_s reported[9] for the *cis*-$[\mathrm{Co(en)_2(SO_3)N_3}]$ complex is inaccurate both because of the neglect of $[\mathrm{Co(en)_2(SO_3)OH_2}]^+$ isomerization and because the reaction is acid-catalyzed and the reported value is an extrapolation, as discussed in ref 9. We have since directly measured k_s (ca. 1.5×10^{-7} $\mathrm{s^{-1}}$) in $\mathrm{H_2O}$; it is much slower than previously believed. The steric course of aquation remains unknown.

(26) Pratt, J. M.; Thorp, R. G. In *Advances in Inorganic Chemistry and Radiochemistry*; Harper and Row: New York, 1983; Vol. 12, p 407.

a common stereochemistry, albeit they are similar.[27] The result is consistent with previous findings;[14,20,28] clearly the leaving group has only the smallest influence in the transition state, and consequently, the hydrolysis mechanism is dissociative. It is interesting to note that again we appear to have an example of induced aquation reactions that yields similar but nonidentical product distributions. Another example is the Hg^{2+}- (or $HgBr^+$-) induced hydrolysis of *cis*-[Co(en)$_2$Br$_2$]$^+$ (61.5% cis) compared with the NO^+-induced hydrolysis of *cis*-[Co(en)$_2$BrN$_3$]$^+$ (72.5% cis),[14,20] and there are others.[28]

Experimental Section

Chemicals were AnalaR grade or the equivalent. Infrared spectra were recorded on a Nicolet 5DXC FT-IR instrument on KBr pellets. Electronic spectra were measured on a Cary 210, a Cary 118C, or a Varian DMS 90 instrument, thermostated to 25.0 ± 0.1 °C by a water circulation bath. Kinetic data were collected either as described previously[9,19–23] or as absorbance/time pairs (>900/run) that were sampled digitally at fixed time intervals (2–10 s) from the DMS output interfaced to an Apple II/e computer through an Adalab I/O card (IMI Inc., State College, PA). These data were analyzed by nonlinear regression with use either of the program Kincal[11] adapted to run on a 1-Mbyte Apple Macintosh computer or the program Bimed BMD-P3R operating on a Honeywell CP6 computer. All reactions were sufficiently slow to follow in situ in a cell thermostated within the spectrophotomer. Published[9] molar extinction coefficients for *cis*- and *trans*-[Co(en)$_2$(SO$_3$)OH$_2$]$^+$ were used in the calculation of the isomeric ratios for the hydrolysis reactions. Carbon-13 NMR spectra were obtained with a Varian XL-300 instrument in H_2O/D_2O solutions with dioxane as the internal reference; shifts are reported as positive downfield from this signal.

***trans*-[Co(en)$_2$Cl$_2$]Cl.** A cis-free and essentially Co(II)-free sample of *trans*-[Co(en)$_2$Cl$_2$]Cl was prepared as follows. Crude trans isomer[29] was crystallized from a warm aqueous solution by the careful addition of 1 M $HClO_4$. The collected solid was washed with water until the washings were pale green. The material was then washed with ethanol and ether, dried at the pump, and converted back to the chloride salt by dissolution in Me_2SO (45 g/450 mL) and treatment with a fifth volume of Me_2SO saturated with LiCl. The Cl^- salt was collected as its Me_2SO solvate, and washed with Me_2SO, acetone, and ether. Finally it was recrystallized from a minimum volume of water by addition of an equal volume of methanol and the careful dilution with acetone.

***cis*-[Co(en)$_2$(SO$_3$)Cl]·1.5H$_2$O.** The crystalline *cis*-chlorosulfito compound can be prepared as follows from a variety of starting chloro complexes under a variety of conditions.

(i) An aqueous solution (50 mL) of Na_2SO_3 (5.04 g, 1.05 equiv) was added slowly (over 0.5 min) with stirring to a solution of *cis*-[Co(en)$_2$Cl$_2$]Cl (11.4 g, 0.04 mol)[29] in water (250 mL) at ambient temperature. The initially blue violet solution quickly became burnt orange; after 5 min, this was transferred to an ice bath and methanol (300 mL) was added carefully after filtration. Pink-orange crystals precipitated readily; after 10 min, these were collected by filtration. The product was submitted to a preliminary purification step by extraction on the filter with ice-cold water until the initially deep yellow extracts paled to a salmon pink. The extracts were retained (see below), while the residue was washed with methanol and ether and dried in air. The now pink solid was purified by recrystallization from water (500 mL) by the addition of an equal volume of methanol; in time, small shiny salmon pink plates of product crystallized from this stirred solution. Yield: 2.75 g, 22%. Freshly prepared *cis*-[Co(en)$_2$(SO$_3$)Cl]·1.5H$_2$O analyzed satisfactorily; it appeared to lose some of the lattice water on prolonged storage in air. ^{13}C NMR spectrum (D_2O): δ −21.56, −21.80, −22.36, −22.74 ppm. The retained aqueous extracts were treated with a one-fifth volume of $HClO_4$ (70%). Cooling for an extended period yielded the *trans*-[Co(en)$_2$(SO$_3$)OH$_2$]ClO$_4$·H$_2$O complex, which was identified by its ^{13}C NMR spectrum (−22.75 ppm in D_2O).

(ii) A sample of *cis*-[Co(en)$_2$(NO$_2$)Cl]ClO$_4$ (3.60 g, 0.01 mol)[30] was suspended in water (75 mL; ca. 20 °C) and to this was added with stirring Na_2SO_3 (1.26 g, 0.01 mol). Stirring was continued for 10 min at which time the solution had become burnt orange. It was filtered to remove some unreacted *cis*-[Co(en)$_2$(NO$_2$)Cl]ClO$_4$, which may be recycled; the filtrate was diluted with methanol (400 mL) to give a precipitate of crude *cis*-[Co(en)$_2$(SO$_3$)Cl]. The material was purified as described above, including the preliminary ice–water washing to remove the more soluble impurities. Yield: 0.28 g, 9% (a much higher yield is possible if recovered reactant is recycled). The same compound was prepared with the alternative starting materials *cis*-[Co(en)$_2$(N$_3$)Cl]ClO$_4$[20] or *cis*- or *trans*-[Co(en)$_2$(NCS)Cl]ClO$_4$.[31]

(iii) Solid samples of *cis*-[Co(en)$_2$(SO$_3$)Cl] were prepared directly by mixing ice-cold, saturated aqueous solutions containing 1 mmol of any of the following, *cis*- or *trans*-[Co(en)$_2$Cl$_2$]Cl,[32] *cis*-[Co(en)$_2$(NCS)Cl]Cl,[33] *cis*-[Co(en)$_2$(NO$_2$)Cl]Cl,[34] or *cis*-[Co(en)$_2$(N$_3$)Cl]Cl,[35] with 0.126 g (1.0 mmol) Na_2SO_3 in 1 mL of ice-cold H_2O and stirring vigorously. The pink-orange solid was filtered, washed with a minimum of ice-cold water until it was salmon pink and then with methanol and ether, and air-dried. IR (sulfito-*S*): 633, 970, 1098, 1120 cm^{-1}.

***cis*-[Co(en)$_2$(SO$_3$)Cl]·1.5H$_2$O from *trans*-[Co(en)$_2$Cl$_2$]Cl.** *trans*-[Co(en)$_2$Cl$_2$]Cl (14.3 g, 0.05 mol) in 40 mL of water was treated with Na_2SO_3 (6.3 g, 0.05 mol) in 60 mL of water while being well stirred. At ambient temperature the reaction proceeded rapidly (seconds) from green to orange-brown. After 1.0 min, it was quenched by the rapid addition of 500 mL of methanol. The fine orange-brown precipitate was filtered and washed with two bed volumes of methanol, to remove any residual *trans*-[Co(en)$_2$Cl$_2$]Cl, and ether and dried at the pump. The residue was extracted on the filter with ice-cold water (1 × 150 mL and 3 × 50 mL), then washed with methanol and ether, and air-dried; some yellow-brown trans isomer was removed, and the aqueous washings were retained. The residue (7.6 g, 47%) was essentially pure cis isomer, which could be recrystallized from water/methanol as described above. The aqueous washings were treated with 50 mL of $HClO_4$ (70%); after they were cooled at 0 °C for 1 h, the resultant *trans*-[Co(en)$_2$(SO$_3$)OH$_2$]ClO$_4$·H$_2$O (2.6 g, 13%) was collected, washed, and dried as above.

A solution of the purified [Co(en)$_2$(SO$_3$)Cl] complex passed through either anion- (Dowex AG1-X8, Cl^- form) or cation-exchange resin (SP-C25 Sephadex, Na^+ form) and left only a small stain on the Sephadex. This behavior is consistent with the material being charge neutral, containing no anionic bis(sulfito) impurity, and hydrolyzing only slightly to a cationic product in the time required for the cation exchange chromatography.

***trans*-[Co(en)$_2$(SO$_3$)Cl] from *trans*-[Co(en)$_2$Cl$_2$]Cl.** *trans*-[Co(en)$_2$Cl$_2$]Cl (31.4 g, 0.11 mol) in water (150 mL) was treated with Na_2SO_3 (13.87 g, 0.11 mol) in water (100 mL); the reaction proceeded rapidly (seconds) from green to orange-brown. The mixture was allowed to stand in the dark for 2 h or alternatively warmed to 60 °C for 5 min and then carefully diluted with methanol to a final volume of 750 mL. After the mixture was cooled overnight, the brown crystals were collected, washed with methanol and ether, and air dried (20.0 g). The product was recrystallized by dissolution in a minimum of warm water; after filtration, an equal volume of HCl (36%) was added, followed carefully by methanol. Alternatively, an aqueous solution may be slowly evaporated. The recovery is good in either case.

***trans*-[Co(en)$_2$(SO$_3$)OH$_2$]ClO$_4$·H$_2$O from *trans*-[Co(en)$_2$Cl$_2$]Cl.** This preparation followed that described above except that the first methanol addition step was omitted and $HClO_4$ (70%, 50 mL) was added instead. After the mixture was cooled and stirred at 0 °C for 1 h, the olive brown crystals were collected, washed with ethanol and ether, and air dried. The material was recrystallized from a saturated aqueous solution by using a one-fifth volume of $HClO_4$ (70%) as precipitant; recovery exceeds 90%.

***trans*-[Co(en)$_2$(SO$_3$)Cl] from *trans*-[Co(en)$_2$(SO$_3$)OH$_2$]ClO$_4$·H$_2$O.** The aqua complex (5.0 g) was slurried with HCl (36%, 70 mL); the olive crystals transformed very rapidly to yield brown crystals. These redissolved on addition of H_2O (30 mL) and stirring. The mixture was filtered and methanol (400 mL) added slowly; orange-brown crystals deposited on standing.

***trans*-[Co(en)$_2$(SO$_3$)Cl] or *trans*-[Co(en)$_2$(SO$_3$)OH$_2$]ClO$_4$·H$_2$O from *cis*-[Co(en)$_2$(SO$_3$)Cl]·1.5H$_2$O.** *cis*-[Co(en)$_2$(SO$_3$)Cl]·1.5H$_2$O (7.6 g) was suspended in H_2O (100 mL) and the mixture taken quickly nearly to boiling in a microwave oven. The pink solution rapidly became brown; this was filtered and cooled. Addition of methanol afforded the *trans*-[Co(en)$_2$(SO$_3$)Cl] complex (6.5 g, 93%); alternatively, the addition of

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(27) It is worth emphasizing that the isomer product ratio is optimally defined at 1.0, i.e. at 50% of each isomer, and at these ratios the leaving group dependence is most easily ascertained. Put another way, product proportions of 99.9% and 99.0% for one of the two isomeric products differ much more than, for example, 51% and 50%.

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$HClO_4$ (70%, 15 mL) yielded *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4{\cdot}H_2O$ (9.16 g, 98%).

NMR Experiments. The SO_3^{2-} substitution reactions on *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ were followed in situ by ^{13}C NMR spectroscopy as follows: A sample of the complex (0.143 g, 5×10^{-4} mol), dissolved (trans) or suspended (cis) in H_2O (1.0 mL), was treated with Na_2SO_3 (0.069 g, 1.1 equiv) in H_2O (1.0 mL) with use of calibrated syringes. After 2.0 min of reaction, the mixture was treated with 1.0 mL of D_2O containing dioxane and $HClO_4$ (150 μL, 11.7 M; Gilson pipet) to provide a deuterium lock while H–D exchange at the amine centers was prevented. Spectra were accumulated immediately thereafter. Similar experiments were performed without the acid quench with use of D_2O rather than H_2O and also with use of a 1 M Na_2SO_3 solution (2.0 mL) and 0.1 g of complex (SO_3^{2-}:Co = ca. 4:1) rather than stoichiometric amounts.

Some unreacted $[Co(en)_2Cl_2]^+$ was observed in the ^{13}C NMR spectrum commencing with the cis isomer and, correspondingly, some *trans*-bis(sulfito) complex, whose signal coincides with that of the *trans*-chlorsulfito signal. When the reaction was begun with the trans isomer, no unreacted *trans*-$[Co(en)_2Cl_2]^+$ (−21.55 ppm in D_2O) was found because the ClO_4^- was sufficient to precipitate it quantitatively.

Spontaneous Aquation and Isomerization. Either the crystallized *cis*-$[Co(en)_2(SO_3)Cl]$ was used directly or *cis*-$[Co(en)_2(SO_3)Cl]$ was generated in situ as follows. Solid Na_2SO_3 (1 mmol) was stirred into an ice-cold solution (ca. 3 mL) containing 1.0 mmol of any of the chloro salts listed above; usually the *cis*- or *trans*-dichloro species was used. The solutions became deep burnt-orange in 10–20 s. After 60 s, the solution was loaded on a short (6 × 2 cm) Sephadex cation-exchange column at 5 °C. The charge-neutral chlorosulfito species washed off with ice-cold water and was cleanly separated from some anionic *cis*-bis(sulfito) complex, which elutes more rapidly than the charge-neutral species [λ, nm (ε, $M^{-1}\,cm^{-1}$)]: 505 (105), 450 (110), 289 (ca. 16 000). Molar absorptivities are based on total cobalt concentrations determined by the Kitson[36] method.

The $[Co(en)_2(SO_3)OH_2]^+$ isomerization reaction, free from interference from the generating *cis*-$[Co(en)_2(SO_3)Cl]$ hydrolysis, was studied as follows. The neutral *cis*-$[Co(en)_2(SO_3)Cl]$ species isolated by ion exchange as above was allowed to aquate for 20 min at 20 °C and then cooled rapidly to 5 °C and was sorbed on and eluted from Sephadex as before. Washing with water removed residual reactant, and 0.25 M $NaClO_4$ eluted the desired yellow-orange $[Co(en)_2(SO_3)OH_2]^+$ band; its cis and trans isomers were not separated. Isosbestic points for the subsequent spectral changes were observed at 274 (ε = 15 400), 442 (ε = 116), 500 (ε = 90), and 587 nm (ε = 9.0); for the final equilibrium mixture, absorption maxima were at 465 (ε = 160) and 272 nm (ε = 15 600).

Hg^{2+}-Induced Hydrolysis. The *cis*-$[Co(en)_2(SO_3)Cl]{\cdot}1.5H_2O$ complex (ca. 50 mg) was dissolved directly in prefiltered 0.01 M $Hg(ClO_4)_2$/0.01 M $HClO_4$ (25.00 mL). For a semiquantitative confirmation of the stereochemistry by ^{13}C NMR spectroscopy, the complex suspended in D_2O was treated dropwise with $Hg(CH_3CO_2)_2$ in 2 M CF_3SO_3H to complete dissolution and the spectrum was immediately recorded.

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Multinuclear Magnetic Resonance Studies of the Reactions of Bidentate Ligands with $Pt(S_2CNEt_2)_2$. Comparisons with the Reactions of $Pt(S_2P\{OEt\}_2)_2$

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The interactions in dichloromethane solution of $Pt(S_2CNEt_2)_2$ with a number of potentially bidentate ligands have been studied by multinuclear (^{31}P, ^{77}Se, ^{195}Pt) magnetic resonance techniques. The ligands used (L-L′) were $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2PCH_2PPh_2$ (dpm), $Ph_2PCH_2P(E)Ph_2$ (E = S, Se to give dpmS, dpmSe), and $Ph_2AsCH_2CH_2P(E)Ph_2$ (apeS, apeSe). In 1:1 proportions the ligands dpe, ape, and dpm all eventually give $[(\eta^2\text{-L-L}')Pt(\eta^2\text{-}S_2CNEt_2)]^+$. With dpe, the reaction is fast and no intermediate is observed; with ape, $(\eta^1\text{-ape})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ is observable and kinetic and thermodynamic data for its conversion to the final product were obtained. The overall reaction with dpm is very slow and involves both $(\eta^1\text{-dpm})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ and the dimer *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$. In 1:2 proportions $[(\eta^1\text{-L-L}')_2Pt(\eta^2\text{-}S_2CNEt_2)]^+$ (L-L′ = ape, dpm) are formed but there is no further reaction in the dpe system. The relative instability of chelated ape and dpm is confirmed by reaction of $[(\eta^2\text{-L-L}')Pt(\eta^2\text{-}S_2CNEt_2)]^+$ with PPh_3 to give $[(\eta^1\text{-L-L}')(PPh_3)Pt(\eta^2\text{-}S_2SNEt_2)]^+$. The reaction between $Pt(S_2CNEt_2)_2$ and dpmSe in 1:1 proportions is extremely complicated and is determined by the reactivity of the P═Se bond. The initial products include $(\eta^1\text{-L-L}')Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ (L-L′ = dpmSe, dpm) and $dpmSe_2$. The reaction proceeds slowly to give *cis,cis*-$[Pt_2(S_2CNEt_2)_2(\mu\text{-dpm})_2]^{2+}$ and $[(\eta^2\text{-dpm})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ that then react with the generated $dpmSe_2$ to reinsert Se into a Pt–P bond to give $[(\eta^2\text{-dpmSe})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ as the final product. In contrast, dpmS reacts cleanly to give $(\eta^1\text{-dpmS})Pt(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ and then $[(\eta^2\text{-dpmS})Pt(\eta^2\text{-}S_2CNEt_2)]^+$ due to the lower lability of the P═S bond. No further reaction occurs with either ligand in 1:2 proportions. The ligands apeE do not react with $Pt(S_2CNEt_2)_2$ in dichloromethane solution.

Introduction

There have been extensive studies by Stephenson[1–5] and Fackler[6,7] and their co-workers on the interactions of monodentate group 15 ligands with platinum(II) bis(dithiolate) compounds $Pt(S\text{-}S)_2$ (S-S = $[S_2CNR_2]^-$, $[S_2COR]^-$, $[S_2P(OR)_2]^-$, $[S_2PR_2]^-$). In general, 1 mol of tertiary phosphine or phosphite reacts to generate the species $(PR_3)Pt(\eta^1\text{-S-S})(\eta^2\text{-S-S})$ and reaction of a second 1 mol of ligand causes displacement of the monodentate dithiolate to give $[(PR_3)_2Pt(\eta^2\text{-S-S})]^+$. These reactions have been

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