with chloroform, as no indications of a stabilizing effect of chloroform on octahedral chloro complexes of either cobalt(II) or nickel(II) are observed in the other donor solvents like acetonitrile or dimethyl sulfoxide. In addition, it would be difficult to understand the above discussed different behaviors of the $CoCl_2(py)_4$ and $CoCl_2(py)_2$ complexes, if the coordinated chloride anions, and not the pyridines, were involved in the interaction with chloroform.

It seems that a consistent explanation of the present results is possible on the assumption that chloroform interacts via the $H\cdots\pi$ type bonds with the coordinated pyridine molecules, while the π-electron density on the latter is controlled by the $d \rightarrow \pi^*$ electron delocalization. Although symmetry considerations do not preclude proper d_π–p_π orbital overlap in tetrahedral coordination, conditions for d_π electron back-donation in the latter are likely to be worse than in the octahedral one.[23–25] This would explain the observed relative stabilization of the $CoCl_2(py)_4$ octahedral complex by the protic solvent chloroform, on the assumption that the $d \rightarrow \pi^*$ electron delocalization cooperates with the $\pi\cdots H$ interaction of the complex with the solvent. As already mentioned, chloroform additions to pyridine containing dissolved $CuCl_2$ were recently found to induce transformation of the $CuCl_2py_3$ square-pyramidal complex into the $CuCl_2(py)_4$ octahedral one. Since conditions for the $d \rightarrow \pi^*$ electron delocalization in an out-of-plane square-pyramidal complex certainly are worse than in an octahedral one, the latter effect likewise might be ascribed to the cooperative effect of $d \rightarrow \pi^*$ electron delocalization and the $\pi\cdots H$ type interaction of the complex with the protic solvent. On the basis of those observations, we seem to be justified in claiming that protic solvents like chloroform may induce stereochemical effects in transition-metal complexes involving heterocyclic aromatic amines as ligands.

Importance of the $d \rightarrow \pi^*$ electron delocalization in determining interaction of complexes of the above type with chloroform may also be inferred from a comparison of the heats of transfer of the $CoCl_2(py)_4$ complex with that of the "free" pyridine. The latter, calculated from the heat of mixing data of Becker et al.[19] in Figure 5 are indicated by the full line. We note, that directly comparable with the heat of transfer of the complex only is the heat of transfer of pyridine from its pure liquid to the pure chloroform, as it is only then that the standard states become comparable.[26] As is seen, the heat of transfer of four pyridine molecules only approaches that of the $CoCl_2(py)_4$ complex as pure chloroform is approached, despite the fact that the "free" pyridines act not only as π-type but primarily as the n-type bases.[27] It becomes clear that the pyridine molecules in the complex aquire additional π-electron density as a result of their interaction with the central metal atom. Further support for the above claimed dependence of the $H\cdots\pi$ type interaction between the complex and a protic solvent on the $d \rightarrow \pi^*$ electron delocalization is provided by the fact, visualized in Figure 4, that the stabilizing effect of chloroform on the MCl_2py_4 type complexes increases in the order Mn(II) < Co(II) < Ni(II), thus in the order of increasing number of d_π electrons of the central metal atom.

Registry No. $CoCl_2(py)_4$, 13985-87-0; $CoCl_2(py)_2$, 14024-92-1.

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Trans Effect in Octahedral Complexes. 4. Kinetic Trans Effect Induced by the S-Bonded Thiosulfato Ligand in Bis(ethylenediamine)cobalt(III) Complexes[1–3]

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The new complex *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ has been prepared by stoichiometric oxidation of *trans*-$[(en)_2Co(S_2O_3)_2]^-$ with I_3^-, $\Delta([(en)_2Co(S_2O_3)_2]^-)/\Delta(I_3^-) = 2.08 \pm 0.06$, and has been characterized by a variety of indirect techniques. This complex contains S-bonded thiosulfate situated trans to a reasonably labile water ligand and is therefore a suitable substrate for investigation of the sulfur-induced kinetic trans effect (KTE). The pK_a of the trans water ligand is 7.4 ± 0.1. The rate law governing anation by SCN^- or NO_2^- to yield the characterized complexes *trans*-$(en)_2Co(L)(S_2O_3)$ is rate = $k[(en)_2Co(OH_2)(S_2O_3)^+][L^-]$; at 26.4 °C, $\mu = 1.00$ M ($LiClO_4$), $k_{SCN} = 0.040$ (2) and $k_{NO_2} = 0.046$ (2) $M^{-1}\ s^{-1}$, $\Delta H^*_{SCN} = 14.5$ (5) and $\Delta H^*_{NO_2} = 13.8$ (5) kcal/mol, and $\Delta S^*_{SCN} = -17$ (2) and $\Delta S^*_{NO_2} = -19$ (2) eu. Through comparisons with literature data these results show (1) S-bonded $S_2O_3^{2-}$ is a relatively efficient trans-labilizing group, substitution trans to $S_2O_3^{2-}$ occurring ca. 2×10^4 times faster than substitution trans to NH_3, (2) the KTE induced by S-bonded SO_3^{2-} on H_2O is ca. 5×10^3 times larger than that induced by S-bonded $S_2O_3^{2-}$, and (3) the KTE series for ligands S-bonded to cobalt(III) is $SO_3^{2-} > RSO_2^- > S_2O_3^{2-}$ in exact correspondence with the structural trans effect (STE) series determined for these ligands. Thus, the lability of the ligand situated trans to sulfur (KTE) is highly correlated with the length of the trans Co–L bond (STE). In agreement with a simple theoretical model, log (KTE) is linearly related to STE for the three S-bonded ligands SO_3^{2-}, RSO_2^-, and $S_2O_3^{2-}$.

Introduction

Over the past few years we have been interested in elucidating the nature of trans effects in octahedral complexes, especially those induced by sulfur bonded to cobalt(III).[1–3,6–8] Coordinated sulfur atoms can exert both a kinetic trans effect (KTE), wherein the ligand situated trans to sulfur is labilized, and a structural trans effect (STE), wherein the ligand situated trans to sulfur has a lengthened Co–ligand bond. We have

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Table I. Characterization Data for (Thiosulfato)bis(ethylenediamine)cobalt(III) Complexes

A. Elemental Analyses

complex	% C		% H		% N		% Co		% S	
	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$Na[(en)_2Co(S_2O_3)_2]$	11.27	11.59	3.78	4.27	13.14	12.95	13.82	13.82	30.08	30.12
$(en)_2Co(SCN)(S_2O_3)$	17.19	17.35	4.58	4.41	20.06	19.92	16.91	16.10	27.51	27.33
$(en)_2Co(NO_2)(S_2O_3)\cdot H_2O$	13.52	13.46	5.07	4.97	19.72	19.83	16.62	16.42	18.02	17.94

B. Visible-UV Spectrophotometric Parameters[a]

complex	λ_{max} (ϵ)			
trans-$[(en)_2Co(S_2O_3)_2]^-$	600 sh (611)	545 (85.5)	333 (27 700)	216 (11 900)
trans-$[(en)_2Co(OH_2)(S_2O_3)]^+$	531 (65)	390, sh (250)	289 (9970)	216 (12 600)
trans-$(en)_2Co(OH)(S_2O_3)$	531 (80.7)		283 (14 500)	214 (13 000)
trans-$(en)_2Co(SCN)(S_2O_3)$	529 (116)		282 (11 800)	216 (18 400)
trans-$(en)_2Co(NO_2)(S_2O_3)$	485 (136)	344 (4800)	292 (18 500)	205 (16 800)

C. IR Spectral Parameters[b]

complex	ν (intens)
Na[*trans*-$(en)_2Co(S_2O_3)_2$]	3260 (vs), 3210 (s), 3140 (s), 1600 (m), 1570 (m), 1320 (w), 1280 (m), 1230 (m), 1190 (vs), 1170–1150 (vs), 1115 (s), 1055 (s), 1050 (vs), 995 (vs), 890 (w), 790 (w), 635–625 (vs), 580 (w), 575 (w), 540 (m), 525 (m), 505 (m)
trans-$(en)_2Co(SCN)(S_2O_3)$	3280–3110 (s), 2100 (s), 1640 (sh), 1590 (s), 1300 (m), 1290 (m), 1230 (m), 1180 (s), 1140 (s), 1053 (s), 1000 (s), 890 (w), 830 (w), 797 (m), 645 (s), 585 (w), 535 (w), 525 (w), 505 (w)
trans-$(en)_2Co(NO_2)(S_2O_3)$	3290–3110 (vs), 2110 (w), 1605 (m), 1580 (w), 1420 (w), 1335 (m), 1280 (m), 1200 (s), 1130 (s), 1053 (s), 990 (s), 890 (w), 812 (m), 750 (w), 635 (s), 580 (w), 555 (w), 535 (w), 515 (m), 505 (w)

[a] λ in nm; ϵ in M^{-1} cm^{-1}; sh = shoulder. [b] In Nujol mulls; ν values in cm^{-1}; v = very, s = strong, m = medium, w = weak.

recently shown[3] that for the two strongly trans-labilizing ligands SO_3^{2-} and RSO_2^- the magnitude of the sulfur-induced KTE is correlated with the magnitude of the concomitant STE. This correlation is not readily extended because of the limited range and precision of observable S-induced STE's and because of the scarcity of accurate structural data on relevant complexes. However, the crystal structure of $[(NH_3)_5Co(SSO_3)]Cl\cdot H_2O$ has recently been described[9] and the STE induced by S-bonded thiosulfate determined to be only 0.019 (8) Å, much smaller than the 0.056 (6) and 0.089 (3) Å STE's induced by S-bonded RSO_2^- and SO_3^{2-}, respectively.[3] It is therefore of interest to determine if the previously noted STE–KTE correlation holds and the KTE induced by S-bonded thiosulfate is also significantly less than the KTE induced by RSO_2^- and SO_3^{2-}. Since one of us[10] has had an interest in the chemistry of (thiosulfato)bis(ethylenediamine)cobalt(III) complexes, we decided to evaluate the extent of the thiosulfate induced KTE within this system.

The anion *trans*-$[(en)_2Co(S_2O_3)_2]^-$ has been known since Ray and Maulik[11] isolated it as the sodium salt in 1933, but very little is known of the chemistry of it or of its derivatives. The visible–UV spectrum[12,13] and a partial IR spectrum[13] have been reported, and the thiosulfate assigned as having the S-bonded configuration. Babaeva et al.[14] reported "almost no reaction" of SO_3^{2-} or NO_2^- with *trans*-$[(en)_2Co(S_2O_3)_2]^-$ in aqueous solution at room temperature but that heating with SO_3^{2-} yielded *trans*-$[(en)_2Co(SO_3)_2]^-$. They also reported preparation of a nitro derivative, formulated as $(en)_2Co(NO_2)(S_2O_3)$, but their elemental analyses are inconsistent with this formulation and no supporting evidence was provided. To our knowledge, no redox studies of *trans*-$[(en)_2Co(S_2O_3)_2]^-$ have been reported. We describe herein studies on the chemistry and reactivity of *trans*-$[(en)_2Co(S_2O_3)_2]^-$, and one of its derivatives *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, designed to delineate the extent to which S-bonded thiosulfate labilizes the ligand situated trans to it.

Experimental Section

General Data. Common laboratory chemicals were of reagent grade. Kinetic experiments employed triply distilled water[15] and doubly vacuum distilled perchloric acid (70–72%, G. F. Smith). Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate.[16] Sephadex ion-exchange resins, obtained from Pharmacia Fine Chemicals, were prepared and stored as recommended by the manufacturer. Elemental analyses of solid samples were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., or MHW Laboratories, Phoenix, Ariz. Visible–UV spectra were recorded on either a Cary 14 or a Beckman DB-GT spectrophotometer; IR spectra were recorded on a Perkin-Elmer 337 instrument using Nujol mulls. pH values were determined by using a Beckman Research pH instrument equipped with a Sensorex semimicro combination glass-reference pH electrode which had been calibrated against standard (MCB) buffers. Kinetic data were obtained on a Cary 118B spectrophotometer equipped with a thermostated sample compartment that maintained temperatures to ±0.1 °C, the temperature being known with an accuracy of ±0.3 °C. Computer calculations were performed on an AMDAHL 470/V6 located at the University of Cincinnati.

Sodium *trans*-Bis(thiosulfato)bis(ethylenediamine)cobaltate(III) Na[*trans*-$(en)_2Co(S_2O_3)_2$]. This material was prepared by a modification of Ray's procedure.[11] Ten grams of $CoCl_2\cdot 6H_2O$ and 20 g of $Na_2S_2O_3\cdot 5H_2O$ in 20 mL of H_2O were mixed with 4.8 g of ethylenediamine in 50 mL of 0.80 M acetic acid at or below 10 °C. After vigorous aeration in an ice bath for 2 h, the resulting crude solid product was separated by filtration and dried in air. This crude material was purified as follows: to a saturated aqueous solution (ca. 0.03 g/mL), one-tenth the volume of a saturated aqueous NaCl solution was added and the mixture cooled at 0 °C for 30 min to yield a green crystalline precipitate (yield ca. 45%). Analytical and spectral data are given in Table I. The visible–UV spectrum is consistent with that previously reported[12-14] for the trans isomer. Repeated attempts at characterization of this complex by single-crystal X-ray

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structural analysis were frustrated by its apparent instability under X-ray irradiation. However, it was determined that the crystals are of the monoclinic class ($a = 10.27$ Å, $b = 8.37$ Å, $c = 8.24$ Å, $\beta = 94.8°$) with a cell volume of 707.2 Å^3 and a measured density of 1.95 g/cm^3. With the assumption that $Z = 2$ molecules/cell, these parameters lead to a molecular weight of 415, in acceptable agreement with the calculated value of 426.

Preparation of Solutions Containing the *trans*-(Thiosulfato)aquobis(ethylenediamine)cobalt(III) Cation, *trans*-[(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$. Oxidation of a slight excess of *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ by aqueous I$_3^-$ leads almost exclusively to a brown cation, formulated as *trans*-[(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$, which is readily isolated by ion-exchange chromatography. In a typical preparation, 0.9 mmol of Na[*trans*-(en)$_2$Co(S$_2$O$_3$)$_2$] in ca. 20 mL of H$_2$O were oxidized with 0.4 mmol of I$_3^-$ in ca. 20 mL of H$_2$O (total iodide ca. 0.06 M (pH ~5) HClO$_4$). The reaction mixture is loaded onto a Sephadex SP-25 cation-exchange column (Li$^+$ form, 2.0-cm i.d. × 24.0 cm) and the predominant brown band eluted with aqueous LiClO$_4$ (0.07–0.25 M (pH ~5) HClO$_4$). A trace of more highly charged, yellow, cationic product, which apparently decomposes as it is eluted from the column, does not interfere with the preparation. Attempts to isolate solid salts were unsuccessful; these attempts led to solid materials of different colors, suggesting that the added anion (ClO$_4^-$, I$^-$, Cl$^-$) was coordinated to the cobalt center. Visible–UV spectrophotometric parameters of *trans*-[(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ are given in Table I; evidence supporting the indicated formulation of this cation is presented and discussed in the following section.

***trans*-(Thiosulfato)(thiocyanato)bis(ethylenediamine)cobalt(III) and *trans*-(Thiosulfato)nitrobis(ethylenediamine)cobalt(III), *trans*-(en)$_2$Co(X)(S$_2$O$_3$) with X = SCN$^-$ and NO$_2^-$.** Addition of a fivefold molar excess of NaSCN (or NaNO$_2$) as a 0.1 M aqueous solution to a 0.02 M aqueous solution of *trans*-[(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ rapidly (ca. 30 min at room temperature) yielded the neutral complex *trans*-(en)$_2$Co(SCN)(S$_2$O$_3$) (or *trans*-(en)$_2$Co(NO$_2$)(S$_2$O$_3$)). The neutral product was purified and isolated by application of the following procedure, hereafter designated as procedure IEX. The reaction solution was passed successively through columns of Sephadex SP-25 (Li$^+$ form) and Sephadex QAE-25 (Cl$^-$ form) to convert ionic impurities to LiCl and finally through a column of Sephadex G-10 to remove LiCl; the desalted solution was flash evaporated to a small volume, and the product complex was precipitated with methanol or ethanol, separated by filtration, and then dried in air. Analytical and spectral data are given in Table I. These neutral complexes were also prepared by two other substitution routes. (1) A fivefold molar excess of NaSCN (or NaNO$_2$) as a 0.3 M aqueous solution was added to a 0.03 M solution of Na[*trans*-(en)$_2$Co(S$_2$O$_3$)$_2$] and the reaction mixture allowed to stand at room temperature for 12–24 h. The product complex was isolated by procedure IEX. (2) A 1.0-g sample of *trans*-[(en)$_2$CoCl$_2$]Cl and 1 equiv of NaSCN were gently warmed in 20 mL of H$_2$O at 45 °C until the NaSCN dissolved, whereupon an equivalent amount of Na$_2$S$_2$O$_3$·5H$_2$O was added and the mixture heated at 45°C for an additional hour. Application of procedure IEX led to ca. 30% yield of *trans*-(en)$_2$Co(SCN)(S$_2$O$_3$). The nitro derivative was obtained similarly, except that the reaction mixture was allowed to stand 12–24 h at room temperature and the desired neutral product isolated in about 25% yield from the supernatant over an uncharacterized, sparingly soluble, orange solid.

Kinetic Measurements and Calculations. All kinetic experiments were conducted in aqueous perchlorate solutions maintained at constant ionic strength 1.00 ± 0.01 M with LiClO$_4$ unless otherwise indicated. In SCN$^-$ anation reactions, pH was controlled either by a tris(hydroxymethyl)aminomethane–HClO$_4$ (Tris–HClO$_4$) buffer or by excess HClO$_4$; in NO$_2^-$ anation reactions, pH was controlled with a 2-(*N*-morpholino)ethanesulfonic acid (MES) buffer. Stock solutions of [(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ were eluted from Sephadex SP-25 columns with 0.25 M LiClO$_4$ (vide supra) immediately prior to a series of experiments, then made up to 1.0 M ClO$_4^-$, and allowed to equilibrate for 20–30 min before use. Kinetics were monitored (a) generally at the visible absorption maximum of the product complex (see Table I), (b) with initial concentrations of [(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ in the range (0.7–3.1) × 10^{-3} M, (c) with pseudo-first-order concentration excesses of ligand and proton source maintained over cobalt(III), and (d) for at least 4 half-lives. No measurable dependence of observed rates on initial concentration of [(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$, total concentration of buffer, or the wavelength of monitoring radiation was observed. A minimum of 20 OD$_t$–t data points were obtained for each kinetic experiment. The previously described[17] LASL nonlinear least-squares program was employed to determine the values of k_{obsd}, OD$_0$ and OD$_\infty$ which best fit the OD$_t$–t data within the first-order rate expression

$$\mathrm{OD}_t = \mathrm{OD}_\infty - (\mathrm{OD}_\infty - \mathrm{OD}_0)e^{-k_{\text{obsd}}t} \tag{1}$$

This analysis also yielded values of $\sigma_{k_{\text{obsd}}}$, the standard deviation associated with each individual value of k_{obsd}. In SCN$^-$ anation reactions the infinite-time readings, OD$_\infty$, were stable, but in the NO$_2^-$ reactions the optical density slowly increased after completion of the anation reaction and therefore only the first 90% of the reaction was used to calculate k_{obsd}. Typically, after 10 half-lives the observed OD$_t$ at 484 nm was 2–3% larger than the OD$_\infty$ calculated by eq 1 from the OD$_t$–t data of the first 90% of the reaction. Activation parameters were calculated within the Eyring formalism[18] by using nonlinear least-squares procedures.[17] In all calculations, individual values of k_{obsd} were weighted as $(1/\sigma_{k_{\text{obsd}}})^2$. Unless otherwise noted, all reported errors are standard deviations.

Results and Discussion

Preparation and Characterization of (Thiosulfato)bis(ethylenediamine)cobalt(III) Complexes. The only (thiosulfato)bis(ethylenediamine)cobalt(III) complexes readily accessible from fundamental starting materials are the cis and trans isomers of [(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$.[10–14] Since the reactions of *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ with nucleophiles are slow and lead to multiple products[14] (vide supra), we decided to probe the trans-labilizing influence of S-bonded thiosulfate by investigating the reactions of a more labile complex. Such a complex was prepared by a clean, convenient route during our studies on the oxidation of coordinated thiosulfate. We formulate this complex as *trans*-[(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ and in this work report on the kinetics of the displacement of the labilized trans water by added nucleophiles. Clearly the proposed formulation of *trans*-[(en)$_2$Co(OH$_2$)(S$_2$O$_3$)]$^+$ is crucial to this study, but the lability of this complex has prevented direct confirmation of this formulation through the classical means of isolating and characterizing solid salts. However, several independent lines of indirect evidence strongly support this formulation, and this evidence is detailed below:

(1) Oxidation of *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ by I$_3^-$ in aqueous media rapidly leads to a brown species which has the same ion-exchange characteristics as known complexes of 1+ formal charge. We temporarily designate this monocationic species as B$^+$.

(2) When the preparative reaction is conducted quantitatively, with *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ in excess, spectrophotometric analysis of the excess *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ ($\lambda = 545$ nm, $\epsilon_{545} = 85.5$ M^{-1} cm^{-1}) after removal of the cationic product by ion exchange shows that the consumption ratio Δ([(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$)/Δ(I$_3^-$) is 2.08 ± 0.06. Thus the reaction stoichiometry is analogous to the I$_3^-$ oxidation of noncoordinated thiosulfate in eq 2 and may be represented as eq 3.

$$\mathrm{I_3^-} + 2\mathrm{S_2O_3^{2-}} \rightarrow 3\mathrm{I^-} + \mathrm{S_4O_6^{2-}} \tag{2}$$

$$\mathrm{I_3^-} + 2\,trans\text{-}(\mathrm{en})_2\mathrm{Co(S_2O_3)_2^-} \rightarrow 3\mathrm{I^-} + \mathrm{S_4O_6^{2-}} + 2\mathrm{B^+} \tag{3}$$

(3) B$^+$ reacts rapidly with a slight excess of thiosulfate to regenerate *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ (eq 4), establishing that

$$\mathrm{B^+} + \mathrm{S_2O_3^{2-}} \rightarrow trans\text{-}(\mathrm{en})_2\mathrm{Co(S_2O_3)_2^-} \tag{4}$$

B$^+$ differs from *trans*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ only by the presence of an easily replaceable ligand.

(4) B$^+$ also reacts rapidly (vide infra) with SCN$^-$ or NO$_2^-$ to yield the neutral derivatives *trans*-(en)$_2$Co(SCN)(S$_2$O$_3$) or *trans*-(en)$_2$Co(NO$_2$)(S$_2$O$_3$) (eq 5 and 6). These derivatives

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$$B^+ + SCN^- \rightarrow trans\text{-}(en)_2Co(SCN)(S_2O_3) \qquad (5)$$

$$B^+ + NO_2^- \rightarrow trans\text{-}(en)_2Co(NO_2)(S_2O_3) \qquad (6)$$

have been isolated as pure solids and characterized by elemental analyses, visible–UV, and IR spectrophotometry (Table I). The questions of geometrical and ligand isomerism in these materials are treated below.

(5) B^+ undergoes a rapid, reversible equilibrium with base to form a red-purple, neutral complex (eq 7). Quantitative

$$B^+ + OH^- = B + H_2O \qquad (7)$$

additions of base yield the ratio $\Delta(OH^-)/\Delta(B^+) = 0.94 \pm 0.03$, and analysis of the spectrophotometric changes associated with this neutralization yields the estimate $pK_a = 7.4 \pm 0.1$ for the acid dissociation constant of B^+. This shows that B^+ is a weak, monoprotic acid, consistent with B^+ containing a single coordinated water. B is therefore formulated as *trans*-$(en)_2Co(OH)(S_2O_3)$, and visible–UV spectrophotometric parameters for this complex are given in Table I.

(6) All the complexes listed in Table I, including B^+, exhibit an intense absorption band in the 282–292-nm region of the UV spectrum. This band is diagnostic for the Co(III)–S bond[19,20] and has been assigned as a ligand-to-metal charge transfer (LTMCT) arising from coordination of sulfur to a potentially oxidizing center.[20] This LTMCT band has been observed in cobalt(III) complexes containing S-bonded thiolato,[20] thioether,[8] disulfide,[21] sulfenato,[7] sulfinato,[22] sulfito,[3] thiocyanato,[23] and thiosulfato[9] ligands. Its presence in the spectrum of B^+ establishes that B^+ contains thiosulfate S-bonded to the cobalt(III) center.

(7) Attempts to isolate solid salts of B^+ lead to neutral materials which behave as though the added anion (ClO_4^-, Cl^-, I^-, etc.) is incorporated into the cobalt(III) coordination sphere. For example, precipitation of the "chloride salt" from a concentrated, aqueous LiCl solution with (with ethanol and diethyl ether) leads to a green material for which elemental analyses indicate the mole ratios C/H/N/S/Cl/Co = 3.8/21.4/3.9/1.8/1.4/1.00 and a weight per mole of Co of 389 (theoretical for $[(en)_2Co(OH_2)(S_2O_3)]Cl\cdot1.7H_2O\cdot0.4LiCl$ is C/H/N/S/Cl/Co = 4/21.4/4/2/1.4/1, M_r = 392). Dissolution of this green material in water induces a rapid ($t_{1/2} \simeq 30$ min) conversion to B^+. Similar behavior is observed for the red "perchlorate salt", and even addition of B^+ to concentrated aqueous ClO_4^- solutions (1–3 M) apparently induces formation (in ca. 30 min) of an equilibrium amount of this red species. This general behavior of B^+ with added anions strongly suggests that B^+ contains a labile cordination site.

The evidence accumulated above strongly suggests that *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ is indeed the most reasonable chemical formulation for B^+ and that the trans water ligand in this complex is relatively labile. The complex *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ is therefore an appropriate substrate for investigation of the trans-labilizing ability of S-bonded thiosulfate.

Isomerism. Potential questions of geometrical and ligand isomerism pervade this study. All the bis(ethylenediamine)cobalt(III) complexes discussed can have cis and trans isomers, and the ligands $S_2O_3^{2-}$, SCN^-, and NO_2^- can generate linkage isomers. However, sufficient evidence exists to decide most of these questions.

All complexes discussed in this work are assigned the trans configuration primarily on the basis of the preparative chemistry employed for their syntheses. For example, *trans*-$(en)_2Co(SCN)(S_2O_3)$ and *trans*-$(en)_2Co(NO_2)(S_2O_3)$ can be prepared from either *trans*-$[(en)_2Co(S_2O_3)_2]^-$ or *trans*-$[(en)_2CoCl_2]^+$ under mild conditions. More extensive heating of the latter preparation results in the appearance of a second neutral complex, exhibiting a visible–UV spectrum similar to that of the predominant trans product, which is eluted more slowly than the trans isomer from Sephadex SP-25 and QAE-25 ion-exchange columns. This second complex is presumably the cis isomer which has a higher affinity for the ion-exchange matrix because of the greater dipole moment associated with this configuration. In addition, the IR spectra of *trans*-$(en)_2Co(SCN)(S_2O_3)$ and *trans*-$(en)_2Co(NO_2)(S_2O_3)$ are consistent with the assigned trans geometry:[24,25] for both complexes only single weak bands appear in the CH_2 rocking region 870–900 cm^{-1} and in the NH_2 region 780–820 cm^{-1}; the thiocyanate derivative shows a single sharp band at 1590 cm^{-1} and the nitrite derivative shows only two sharp bands in this region.

Observation of the diagnostic LTMCT band in the UV spectra of the complexes listed in Table I suffices to establish that they all contain at least one Co(III)–S bond. For *trans*-$(en)_2Co(NO_2)(S_2O_3)$ and *trans*-$(en)_2Co(OH)(S_2O_3)$ this establishes that $S_2O_3^{2-}$ is S-bonded, but for *trans*-$[(en)_2Co(S_2O_3)_2]^-$ leaves the possibility that one $S_2O_3^{2-}$ is S-bonded and one is O-bonded. Similarly, *trans*-$(en)_2Co(NO_2)(S_2O_3)$ must contain S-bonded thiosulfate, but *trans*-$(en)_2Co(SCN)(S_2O_3)$ could contain the O-bonded isomer (however, the mild preparative conditions make this possibility very unlikely).

The kinetics of the NO_2^- + *trans*-$[(en)_2Co(H_2O)(S_2O_3)]^+$ ligation reaction show that the initial product (λ_{max} = 492 nm, isosbestic points with *trans*-$[(en)_2Co(H_2O)(S_2O_3)]^+$ at 557 and 445 nm maintained through 95% reaction) is metastable and converts slowly to the final product (λ_{max} = 485 nm, isosbestic points with the metastable product at 507 and 433 nm). Thus, the initial metastable product is taken to be the O-bonded nitrito isomer *trans*-$(en)_2Co(ONO)(S_2O_3)$ which then isomerizes to the final, isolated, N-bonded nitro product *trans*-$(en)_2Co(NO_2)(S_2O_3)$ with a half-life of ca. 40 min at 25 °C. For comparison, under similar conditions the isomerization of $[(NH_3)_5CoONO]^{2+}$ (λ_{max} = 486 nm) to $[(NH_3)_5CoNO_2]^{2+}$ (λ_{max} = 460 nm) occurs with a half-life of ca. 120 min. In both systems the N-bonded isomer has a λ_{max} at higher energy than the O-bonded isomer, consistent with N-bonded NO_2^- providing a greater ligand field than O-bonded ONO^-. Also, the high value of ν_{as} for NO_2 in the final *trans*-$(en)_2Co(NO_2)(S_2O_3)$ product (1420, 1335 cm^{-1}) is consistent with the N-bonded assignment.

No firm conclusion can be reached about whether SCN^- in *trans*-$(en)_2Co(SCN)(S_2O_3)$ is N- or S-bonded, although the observed C–S stretch at 797 cm^{-1} implies N-bonding.[26] This conclusion would be consistent with the N-bonded SCN^- observed crystallographically in the analogous complex *trans*-$(en)_2Co(SCN)(SO_3)$.[27] Experiments designed to establish this point are currently in progress.

Anation Kinetics. The successful fit of the observed OD_t–t data to the first-order rate equation (eq 1) and the independence of k_{obsd} on the initial concentration of cobalt(III) establish that the rate law for anation is first order in *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$. The pH dependence of the SCN^- anation reaction (Table II) shows that the aquo form

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Table II. Observed First-Order Rate Paramters, k_{obsd}, Describing the pH, Temperature, and $[SCN^-]$ Dependence of the Anation of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ by SCN^-

pH 1.50 ± 0.04[a]		pH 7.45 ± 0.04[a]		pH 7.74 ± 0.04[a]		pH 1.50 ± 0.04[e]		pH 1.50 ± 0.04[f]	
$10^2 \times [SCN^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^3 \times [SCN^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^2 \times [SCN^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^3 \times [SCN^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^2 \times [SCN^-]$, M	$10^3 k_{obsd}$, s^{-1}
2.51	1.17 ± 0.01	2.51	0.77 ± 0.01	7.54	1.20 ± 0.02[b]	7.52	1.13 ± 0.07	2.51	2.74 ± 0.04
7.52	3.20 ± 0.04[b]	7.52	2.12 ± 0.06[c]	22.6	3.11 ± 0.13	15.07	3.02 ± 0.05	5.01	4.69 ± 0.10[d]
12.5	5.15 ± 0.09	12.5	3.56 ± 0.14[d]	37.6	5.16 ± 0.13	22.6	4.43 ± 0.10	7.52	7.36 ± 0.10
17.5	6.72 ± 0.11	20.0	5.32 ± 0.13	52.7	6.58 ± 0.16	30.1	5.53 ± 0.15	10.02	9.94 ± 0.15
20.0	8.95 ± 0.15					45.2	8.13 ± 0.38		

[a] $t = 26.4$ °C. [b] Average of three determinations. [c] Average of eight determinations. [d] Average of two determinations. [e] $t = 16.4$ °C. [f] $t = 36.4$ °C.

Table III. Observed First-Order Rate Parameters, k_{obsd}, Describing the Temperature and $[NO_2^-]$ Dependence of the Anation of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ by NO_2^- [a]

$t = 16.4$ °C		$t = 26.4$ °C		$t = 36.4$ °C	
$10^2[NO_2^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^2[NO_2^-]$, M	$10^3 k_{obsd}$, s^{-1}	$10^2[NO_2^-]$, M	$10^3 k_{obsd}$, s^{-1}
5.00	0.86 ± 0.02	2.50	1.24 ± 0.02	2.50	2.63 ± 0.04
10.00	1.92 ± 0.04	5.0	2.63 ± 0.06[b]	5.00	5.00 ± 0.10
15.00	3.05 ± 0.07	10.0	4.30 ± 0.04	7.50	7.25 ± 0.49[c]
20.00	4.43 ± 0.10	15.0	7.63 ± 0.06	10.0	10.10 ± 0.10
		20.0	9.67 ± 0.08	12.5	13.9 ± 0.4[c]
		25.0	11.1 ± 0.09		

[a] pH 6.03 ± 0.04. [b] Average of four determinations. [c] Average of two determinations.

of the starting material is more reactive than the hydroxo form, consistent with the usual behavior of H_2O and OH^- as leaving groups. The SCN^- reactions were conducted primarily at pH 1.5 where all the starting material is in the aquo form. The NO_2^- anation reactions were conducted at pH 6.0 which is sufficiently acidic to ensure that more than 90% of the starting material is in the aquo form but also sufficiently basic to preclude significant nitrous acid formation. It is interesting to note that the MES buffer used to control pH in the NO_2^- anation reaction is one of the few buffer systems encountered that does *not* react with *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$. For example, acetate buffer (pH ca. 5) reacts rapidly to yield a neutral, red-purple species (presumably *trans*-$(en)_2Co(OOCCH_3)(S_2O_3)$) which rapidly reconverts to *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ when the pH is lowered to 3, and Tris buffer (pH 7.7) causes a slow conversion to several products including *trans*-$[(en)_2Co(S_2O_3)_2]^-$.

For both the SCN^- and NO_2^- reactions, k_{obsd} is directly proportional to ligand concentration over the concentration ranges investigated (see Tables II and III). Thus the rate law governing the reaction

$$\textit{trans}\text{-}(en)_2Co(OH_2)(S_2O_3)^+ + L^- \rightarrow \textit{trans}\text{-}(en)_2Co(L)(S_2O_3) + H_2O \qquad (8)$$

is under these conditions

$$d[(en)_2Co(L^-)(S_2O_3)]/dt = k[(en)_2Co(OH_2)(S_2O_3)^+][L^-] \qquad (9a)$$

$$k_{obsd} = k[L^-] \qquad (9b)$$

Table IV. Observed First-Order Rate Parameters, k_{obsd}, Describing the $[L^-]$ and $[SO_4^{2-}]$ Dependence of the Sulfate-Inhibited Anation of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ by NO_2^- and SCN^- [a]

$[NO_2^-]$, M	$[SO_4^{2-}]$, M	$10^3 k_{obsd}$, s^{-1}
0.0989	0.000	5.86 ± 0.06
0.0989	0.060	2.37 ± 0.02
0.0989	0.090	1.71 ± 0.02
0.0989	0.120	1.41 ± 0.01
0.1978	0.000	10.17 ± 0.08
0.1978	0.036	6.10 ± 0.06
0.1978	0.060	4.66 ± 0.03
0.1978	0.100	3.29 ± 0.03
0.0659	0.000	3.53 ± 0.02
0.0659	0.0264	2.38 ± 0.02
0.0659	0.0536	1.80 ± 0.02
0.0659	0.0800	1.33 ± 0.02
$[SCN^-]$, M	$[SO_4^{2-}]$, M	$10^3 k_{obsd}$, s^{-1}
0.0441	0.000[b]	1.93 ± 0.03
0.0441	0.040[b]	1.36 ± 0.08
0.0441	0.060	0.89 ± 0.01
0.0441	0.090	0.69 ± 0.01
0.0441	0.120[b]	0.48 ± 0.01
0.0882	0.000	3.94 ± 0.09
0.0882	0.040	2.59 ± 0.09
0.0882	0.060	2.00 ± 0.05
0.0882	0.081	1.62 ± 0.03
0.0882	0.105	1.28 ± 0.01
0.0265	0.000	1.31 ± 0.03
0.0265	0.015	0.89 ± 0.03
0.0265	0.030	0.75 ± 0.03
0.0265	0.060	0.53 ± 0.01
0.0265	0.096[c]	0.335 ± 0.005
0.0265	0.120[c]	0.230 ± 0.004

[a] Conditions: $t = 26.4$ °C; pH 5.9–6.3; $\mu = 1.00$ M ($LiClO_4$). [b] Average of two determinations. [c] Average of three determinations.

This linear dependence of k_{obsd} on [L] is somewhat unusual, the more complex dependence

$$k_{obsd} = \frac{a + bc[L^-]}{1 + c[L^-]} \qquad (10)$$

being expected, and observed, for analogous anation reactions at trans-labilized cobalt(III) centers.[1-3,28] Presumably under the reaction conditions employed, $c[L^-] \ll 1$ and $a \ll bc[L^-]$, causing eq 10 to reduce to the observed eq 9b. The rate law expressed by eq 10 can result from either a limiting S_N1 mechanism or a prior association mechanism.[1-3] To test whether or not prior association, i.e., outer-sphere complexation between the cobalt cation and the entering anion, plays a role in the NO_2^- and SCN^- anations of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, the rates of these reactions were determined as a function of sulfate concentration (see Table IV). Under the conditions employed, sulfate does not form detectable

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Table V. Selected Rate and Activation Parameters Describing Anation of *trans*-$[(en)_2Co(OH_2)(SO_3)]^+$ [a,b]

anation reaction	k, $M^{-1}\ s^{-1}$	ΔH^*, kcal/mol	ΔS^*, eu	ref
trans-$[(en)_2Co(OH_2)(S_2O_3)]^+ + SCN^-$	0.040 ± 0.002	14.5 ± 0.5	−17 ± 2	*c*
trans-$[(en)_2Co(OH_2)(S_2O_3)]^+ + NO_2^-$	0.046 ± 0.002	13.8 ± 0.5	−19 ± 2	*c*
trans-$[(en)_2Co(OH_2)(SO_3)]^+ + SCN^-$	275 ± 4	10.9 ± 1.2	−11 ± 4	28
trans-$[(en)_2Co(OH_2)(SO_3)]^+ + NO_2^-$	206 ± 6			28

[a] Net reaction is displacement of coordinated water by entering anion. [b] Conditions: for *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ reactions, $t = 26.4$ °C and $\mu = 1.00$ M ($LiClO_4$); for *trans*-$[(en)_2Co(OH_2)(SO_3)]^+$ reactions, $t = 25$ °C and $\mu = 1.00$ M ($NaClO_4$). [c] This work.

amounts of an inner-sphere complex with *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, but because of its 2− formal charge, sulfate is expected to form a more stable outer-sphere complex than NO_2^- or SCN^-[29,30] and therefore decrease the net rate of *trans*-$(en)_2Co(L)(S_2O_3)$ formation. Within the prior association mechanism the appropriate equations are

$$M\text{-}OH_2^+ + SO_4^{2-} = M\text{-}OH_2,SO_4^- \quad K_{os,S} \tag{11a}$$

$$M\text{-}OH_2^+ + L^- = M\text{-}OH_2,L \quad K_{os,L} \tag{11b}$$

$$M\text{-}OH_2,L \rightarrow M\text{-}L + H_2O \quad k_L \tag{11c}$$

where $M\text{-}OH_2^+$ represents *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$. This scheme leads to the rate expression

$$k_{obsd} = \frac{k_L K_{os,L}[L^-]}{1 + K_{os,L}[L^-] + K_{os,S}[SO_4^{2-}]} \tag{12}$$

The data of Table IV describing NO_2^- anation are sufficiently precise to allow nonlinear least-squares analysis within eq 12 (the data describing SCN^- anation are not sufficiently precise to allow simultaneous three-parameter optimization[34]); the resulting optimized parameters are $k_{NO_2} = 0.17 \pm 0.16\ s^{-1}$, $K_{os,S} = 22.6 \pm 1.2\ M^{-1}$, and $K_{os,NO_2} = 0.34 \pm 0.34\ M^{-1}$. The product $k_{NO_2}K_{os,NO_2} = 0.06 \pm 0.08\ M^{-1}\ s^{-1}$ is in agreement with the value $k = 0.046 \pm 0.002\ M^{-1}\ s^{-1}$ (Table V) obtained by linear least-squares analysis of the k_{obsd} and $[NO_2^-]$ data of Table III. While neither k_{NO_2} nor K_{os,NO_2} is well-defined by the experimental data, the overall results of the calculation support the prior association mechanism. The calculated values of K_{os,NO_2} and $K_{os,S}$ are in good agreement with theoretical[29,30] and observed[31,32] values of outer-sphere association constants for 1+/1− and 1+/2− complexes. For example, K_{os} for the outer-sphere complexes of SO_4^{2-}, CO_3^{2-}, and $S_2O_3^{2-}$ with $[(NH_3)_5CoSO_4]^+$ have been determined[31] to be 15, 17, and 22 M^{-1}, respectively (25 °C; $\mu = 0.5$ M $NaClO_4$) in excellent agreement with $K_{os,S}$ for *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+,SO_4^{2-}$. Also, K_{os} for *trans*-$[(en)_2Co(SCN)_2]^+,SCN^-$ has been found to be 0.3 M^{-1} (25 °C, μ = 3 M $NaClO_4$) in excellent agreement with K_{os,NO_2} calculated for *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+,NO_2^-$. We therefore believe that the prior exchange mechanism, with dissociative interchange of leaving and entering ligands, provides an appropriate framework for discussion of our results and also allows facile comparison with the results of Yandell and Tomlins on the analogous *trans*-$[(en)_2Co(OH_2)(SO_3)]^+$ system.[28] However, the possibility of the limiting S_N1 mechanism being operative in these systems cannot be conclusively discounted.[1-3]

Kinetic Trans Effect (KTE). Analysis of the k_{obsd}–$[L^-]$ data of Tables II and III within eq 9b and the Eyring formalism leads to the rate and activation parameters listed in Table V for the anation of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$. Comparable parameters, obtained by Yandell and Tomlins,[28] for the anation of *trans*-$[(en)_2Co(OH_2)(SO_3)]^+$ are also given in Table V. Within the prior association mechanism, the tabulated rate parameters are composite parameters; i.e., $k = k_L K_{os,L}$. Theoretical treatment of outer-sphere complex formation,[30] based on the Fuoss equations,[29] shows that at constant ionic strength the value of K_{os} and of the related thermodynamic parameters $\Delta H_{os}°$ and $\Delta S_{os}°$ are primarily dependent on the formal charges of the interacting species. Since all the entries of Table V involve interaction between 1+ and 1− species at μ = 1.0 M, common values of K_{os}, $\Delta H_{os}°$ and $\Delta S_{os}°$ apply; from the analysis of Hyde and Sykes[30] these values can be estimated as $K_{os} = 0.3\ M^{-1}$, $\Delta H_{os}° = 0.5$ kcal/mol, and $\Delta S_{os}° = +1$ eu. Thus k_L, the specific-rate-governing first-order interchange of H_2O and L^- within the outer-sphere complex (eq 11c), is about $10^{-1}\ s^{-1}$ when S-bonded $S_2O_3^{2-}$ is the trans-labilizing group and about $10^3\ s^{-1}$ when S-bonded SO_3^{2-} is the trans-labilizing group. Because of the small values of $\Delta H_{os}°$ and $\Delta S_{os}°$, enthalpies and entropies governing this first-order interchange process will have essentially the same numerical values as the composite enthalpies and entropies given in Table V.

From Table V it is clear that both S-bonded SO_3^{2-} and S-bonded $S_2O_3^{2-}$ cause a significant labilization of the trans situated water ligand. For example, second-order rate constants for anation of $[(NH_3)_5CoOH_2]^{3+}$ by a variety of monoanionic ligands lie in the range (1.3–2.5) × $10^{-6}\ M^{-1}\ s^{-1}$ (25 °C, μ = 0.5 M).[33] This provides a convenient reference point for the rate of nonlabilized displacement of water; replacement of NH_3 by S-bonded $S_2O_3^{2-}$ causes approximately a 20 000-fold increase in the rate of substitution at the trans site.

Given that a common K_{os} value applies to all the entries of Table V, the data of this table also allow a direct comparison of the trans-labilizing abilities of S-bonded SO_3^{2-} and S-bonded $S_2O_3^{2-}$. For SCN^- as the entering ligand, the KTE induced by S-bonded SO_3^{2-} on H_2O is 6800 ± 400 times larger than the KTE induced by S-bonded $S_2O_3^{2-}$; this effect originates both in the smaller ΔH^* for the sulfito reaction ($\Delta H^*(S_2O_3) - \Delta H^*(SO_3) = 3.6 \pm 1.3$ kcal/mol) and in the less negative ΔS^* of the sulfito region ($\Delta S^*(S_2O_3) - \Delta S^*(SO_3) = -6 \pm 5$ eu). For NO_2^- as the entering ligand, $KTE(SO_3)/KTE(S_2O_3) = 4500 \pm 300$, showing that as expected the effect is not strongly dependent on the entering group.

In the previous article of this series we showed that in the pentaamminecobalt(III) system, the KTE induced by S-bonded SO_3^{2-} on NH_3 is 160 ± 7 times that induced by S-bonded RSO_2^- ($R = C_6H_5$; while this analysis was conducted within the S_N1 limiting mechanism, the same result obtains from analysis within the prior association mechanism). Thus, by comparing the effects of SO_3^{2-} and RSO_2^- on the rate of NH_3 loss in the $[(NH_3)_5CoX]^{n+}$ system with the effects of SO_3^{2-} and $S_2O_3^{2-}$ on the rate of H_2O loss in the *trans*-$[(en)_2Co(OH_2)(X)]^+$ system, it is seen that the KTE series for ligands S-bonded to cobalt(III) is $SO_3^{2-} > RSO_2^- > S_2O_3^{2-}$. This KTE series is in exact correspondence to the STE series

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(34) Weighted linear least-squares analysis of the data of Table IV according to the expression $1/k_{obsd} = A + B[SO_4^{2-}]/[L^-] + C/[L^-]$ yields the following parameters: for NO_2^- $A = 7 \pm 6$ M s, $B = 401 \pm 12$ M s, and $C = 17.7 \pm 0.7\ M^2$ s; for SCN^- $A = -90 \pm 70$ M s, $B = 570 \pm 32$ M s, and $C = 25 \pm 4\ M^2$ s.

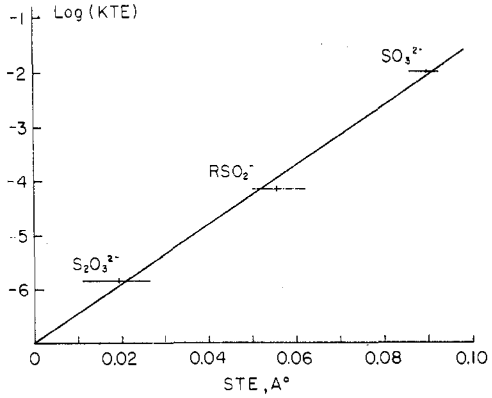

Figure 1. Plot of log (KTE) vs. STE (Å) for the S-bonded ligands SO_3^{2-}, RSO_2^-, and $S_2O_3^{2-}$.

noted earlier, supporting the hypothesis[3] that in these systems the sulfur induced structural and kinetic trans effects are highly correlated. This correlation is to be expected on the basis that a longer metal–ligand bond is a weaker bond which should be more readily cleaved no matter what the detailed mechanism of the cleavage.

Quantitative evaluation of the STE–KTE correlation is difficult because of the imprecision inherent in the STE measurements, the fact that because of different reactivities the KTE's have been determined within different systems (NH_3 vs. OH_2 as leaving groups), and the lack of basic understanding as to the electronic origins of trans effects. Despite these inherent difficulties, we have presented[3] a nascent model for the quantitative analysis of STE–KTE interrelationships. This model assumes (1) a simple harmonic oscillator description of the trans Co–L bond and (2) that the different ΔH^* values governing the KTE arise from the different energies necessary to stretch the trans Co–L bonds from their ground-state distances to some common transition-state distance. We have predicted[3] from this model that differences in activation enthalpies will depend linearly upon differences in ground-state trans Co–L bond lengths (i.e., STE's)

$$(\Delta H^*_a - \Delta H^*_b) \propto (R_a - R_b) \tag{13}$$

If, for the three S-bonded ligands considered in this paper, relative ΔH^* values can be approximated by relative ΔG^* values, then eq 13 predicts that log k, or log (KTE), should be linearly dependent on STE:

$$\log(\mathrm{KTE}) \propto \mathrm{STE} \tag{14}$$

Specific rates (25 °C, $\mu = 1.00$ M) for SO_3^{2-} and RSO_2^- labilized Co–NH_3 bond cleavage (SCN^- entering group) have been given previously[3] as 0.0103 ± 0.0003 and $(6.6 \pm 0.2) \times 10^{-5}$ s^{-1}, respectively. The rate of $S_2O_3^{2-}$ labilized Co–NH_3 bond cleavage (SCN^- entering group) can be estimated from the rates of $S_2O_3^{2-}$ labilized Co–OH_2 bond cleavage (Table V) and the rates of SO_3^{2-} labilized Co–NH_3 and Co–OH_2 (Table V) bond cleavage: i.e.

$$k_{S_2O_3\text{-}NH_3} = k_{S_2O_3\text{-}OH_2}K_{os}\left(\frac{k_{SO_3\text{-}NH_3}}{k_{SO_3\text{-}OH_2}K_{os}}\right) = (0.040 \pm 0.002)(0.0103 \pm 0.0003)/(275 \pm 4) = (1.5 \pm 0.1) \times 10^{-6}\ s^{-1} \tag{15}$$

Figure 1 shows a plot of the logarithm of the specific rate governing labilized Co–NH_3 bond cleavage (SCN^- entering group) vs. STE for the three S-bonded ligands SO_3^{2-}, RSO_2^-, and $S_2O_3^{2-}$. The linear relationship predicted by eq 14 is seen to hold within the experimental uncertainties, although the observed slope (55 $Å^{-1}$) is only about one-fourth that predicted by the model (220 $Å^{-1}$).[3,35]

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Registry No. Na[*trans*-$(en)_2Co(S_2O_3)_2$], 73746-90-4; *trans*-[$(en)_2Co(OH_2)(S_2O_3)$]$^+$, 62656-34-2; *trans*-$(en)_2Co(SCN)(S_2O_3)$, 73746-91-5; *trans*-$(en)_2Co(NO_2)(S_2O_3)$, 73746-92-6; *trans*-[$(en)_2CoCl_2$]Cl, 14040-33-6; *trans*-[$(en)_2Co(S_2O_3)_2$]$^-$, 62529-95-7; *trans*-$(en)_2Co(OH)(S_2O_3)$, 73746-93-7; SCN^-, 302-04-5; NO_2^-, 14797-65-0.

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(35) The theoretical slope of the line in Figure 1 may be derived from the treatment given in ref 3: R_a and R_b are the trans Co–N distances in the ground states of complexes a and b; R is the average of R_a and R_b; R^* is the trans Co–N distance in the transition state; all distances are in Å; enthalpies and free energies are in kcal/mol. From ref 3, $\Delta H^*_a - \Delta H^*_b = k'[(R^* - R_a)^2 - (R^* - R_b)^2] = -2k'(R_a - R_b)(R^* - R)$, where from ref 3 $k' = 122.4$ (kcal/mol)/(Å/bond)^2, $R^* = 3.2$ Å and $R = 2.03$ Å. Thus $\Delta H^*_a - \Delta H^*_b = -301(R_a - R_b) \simeq \Delta F^*_a - \Delta F^*_b = -RT[\ln(k_a/k_b)]$ and $\log(k_a/k_b) = -301(R_a - R_b)/(2.303)(0.002)(298) = 220(R_a - R_b)$. Therefore log k increases linearly with R, the calculated slope being 220 $Å^{-1}$.