line with a nonzero intercept. The values of A and B from this plot were found to be 3.0×10^{-4} M^{-1} s^{-1} and 1.5×10^{-2} M^{-1} s^{-1}. Thus, the values of A and B obtained from different plots are in good agreement. With the latter values of A and B and of K_3 so obtained and with k_{uncat} from the uncatalyzed study, k_{cat} can be calculated by making use of eq 19. These values along with the experimental values are shown in Table II, and the agreement among them is more than satisfactory.

Rate law 20 was verified in one more way. It can be rearranged as (25), and thus a plot of left side of eq 25 vs. [$^{-}O_2CCH_3$] can

$$k_{\text{cat}}([\mathrm{H}^+] + K_3)(1 + K[^{-}\mathrm{O_2CCH_3}]) = A + B[^{-}\mathrm{O_2CCH_3}] \quad (25)$$

be made (Figure 2). A straight line with nonzero intercept resulted, yielding values of $A = 3.0 \times 10^{-4}$ M^{-1} s^{-1} and $B = 1.5 \times 10^{-2}$ M^{-1} s^{-1} at 40 °C, and $I = 1.0$ M. Thus, in all cases the values of A and B are similar, and rate law 19 holds for the Ag(I) catalyzed oxidation of hydrazine with peroxodiphosphate.

It appears that Ag(I) may have the catalytic role in all peroxodiphosphate reactions as in the case of peroxodisulfate reactions, but the two differ in their mechanisms. In the case of pds oxidations of most of the inorganic species like hydrazine,[5] cerium(III),[18] manganese(II),[5,19] water,[20] vanadyl ion,[21] thallium(I),[22] etc., the rates are similar, and the reaction between pds and Ag(I) is rate controlling. Thus a Ag(I)/Ag(II) cycle operates. The second-order rate constant was found to be ~0.45 M^{-1} s^{-1} at 35 °C and $I = 1.0$ M and was independent of acid concentration (0.1–2.0 M). In the case of pdp, the oxidations so far studied are those of water,[1] arsenic(III),[2] antimony(III),[2] and phosphite,[3] and all of them have different rates under similar conditions. Thus, the reducing substance has also a role in controlling the rate. Although, in the case of pdp, Ag(I) catalysis has been explained through complexation with pdp, the point of interest is whether Ag(0) or Ag(II)/Ag(III) is formed or not. A reaction of Ag(I) and N_2H_4 forming Ag(0) has been reported,[6] and Ag^{II} or Ag^{III} is also obtained from pdp–Ag(I) reaction.[1] There is absolutely no kinetic evidence for either of these two situations, though one may be tempted to suggest a mechanism involving Ag(0) or Ag(II)/Ag(III). In view of the two observations in connection with the formation of different oxidation states of silver, the question of details of mechanism seems still open and perhaps a fresh study of the direct reactions of Ag(II) and hydrazine and of Ag(I) and hydrazine may be helpful in shedding light on the mechanism of the catalyzed reaction.

Registry No. Ag, 7440-22-4; N_2H_4, 302-01-2; $K_4P_2O_8$, 15593-49-4.

Supplementary Material Available: Tables of rate constant data (1 page). Ordering information is given on any current masthead page.

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Complexes of Thiosulfate and Disulfanemonosulfonate with *cis*-Bis(ethylenediamine)cobalt(III)

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The preparation and characterization of the anionic thiosulfato complexes *cis*-$[(en)_2Co(SO_3)(S_2O_3)]^-$ and *cis*-$[(en)_2Co(S_2O_3)_2]^-$ and of the molecular complex *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$ are reported. The structures of the latter and of the salt $[(en)_2Co(S_2O_3)]^+ClO_4^-$, containing the chelating thiosulfato-*O,S* ligand, have been determined by single-crystal X-ray diffraction. Both compounds crystallize in the monoclinic class: the salt in space group $P2_1/c$ with 4 formula units in a unit cell of dimensions $a = 9.335$ (5) Å, $b = 9.423$ (4) Å, $c = 15.339$ (2) Å, and $\beta = 90.43$ (4)° and the molecular nitrito-*N* complex in space group $P2_1$ with 2 formula units in a unit cell of dimensions $a = 6.706$ (2) Å, $b = 13.223$ (3) Å, $c = 6.776$ (1) Å, and $\beta = 102.72$ (2)°. The molecular nitrito-*N* complex and the bis(thiosulfato) anion are each readily oxidized by aqueous I_2 to produce respectively *cis*-$[(en)_2Co(NO_2)(S_3O_3)]$ and the substitution-labile *trans*-$[(en)_2Co(H_2O)(S_3O_3)]^+$ ion, two notably photoreactive Co(III) complexes of the unstable ligand disulfanemonosulfonate, $S_3O_3^{2-}$.

Introduction

Although thiosulfato complexes of bis(ethylenediamine)cobalt(III) with the trans configuration are well-known and have been extensively characterized,[3,4] those with the cis configuration have been less widely reported,[4-6] owing presumably to the trans-labilizing character of the thiosulfato group.[3] We report here an improved preparation and characterization of the previously reported[6] bis(thiosulfato) anion $[(en)_2Co(S_2O_3)_2]^-$ and the preparation and characterization of two new complexes in this *cis*-bis(ethylenediamine) Co(III) series, the (thiosulfato)(sulfito) complex *cis*-$[(en)_2Co(SO_3)(S_2O_3)]^-$ and the (thiosulfato)(nitrito-*N*) complex *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$. The single-crystal X-ray structural determinations of the latter and of the salt $[(en)_2Co(S_2O_3)]^+ClO_4^-$ [5] are reported and confirm the monodentate S-bonded thiosulfato ligand in the former and the chelated thiosulfato-*O,S* ligand in the latter.

The reactivity of the bis(thiosulfato) anion with aqueous I_2 to produce Co(III) complexes of the disulfanemonosulfonato ligand, $S_3O_3^{2-}$, has been reported.[7] Coordination to Co(III) confers some kinetic stability to this ligand that, as the free anion, rapidly reacts with H_2O.[8] This coordination stabilization led us to investigate the reactivity of aqueous I_2 with other thiosulfato complexes, and we have isolated and characterized a new complex in this series, *cis*-$[(en)_2Co(NO_2)(S_3O_3)]$. Both this complex and the previously reported *trans*-$[(en)_2Co(H_2O)(S_3O_3)]^+$ are photoreactive in the

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near-UV region. The quantum yield for the photolysis of each and the stoichiometry of the latter in dilute acid are reported.

Experimental Section

General Data. Sodium perchlorate, LiCl, and $LiClO_4 \cdot 3H_2O$ were obtained from G. F. Smith Chemical Co., made up as concentrated solutions for ion-exchange elutions, and filtered before use. Other common chemicals were of reagent grade and were used without further purification. Chromatographic separations were accomplished as previously described[3] by use of a Sephadex resins (SP-C-25, Na^+ form; QAE-Q-25, Cl^- form; G-10 to desalt). Elemental analyses of solid samples were performed by Galbraith Laboratories, Inc., Knoxville, TN. UV–visible spectra were recorded either on a Hitachi 110A or on a Beckman DBGT spectrophotometer in Milli-Q (Millipore) water, and are reported as λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1}). IR spectra were recorded on a Perkin-Elmer 337 or 599 spectrophotometer by use of KBr pellets and are reported in cm^{-1}. pH values were determined on a Corning 12 Research pH meter using a Sensorex semimicro combination glass reference electrode, calibrated against standard buffers. Photolyses were performed on magnetically stirred solutions at room temperature with a 4-W UV lamp from Ultraviolet Products, Inc. The lamp was operated in the long-wavelength mode (λ_{max} ca. 350 nm) and was calibrated by ferrioxalate actinometry.[9] Identification and assay of the S-containing photolysis product, $S_6O_6^{2-}$, was accomplished by the procedures described by Haff.[10]

^{13}C and ^1H NMR spectra were obtained on a JEOL FX90-Q spectrometer at 22.50 and 89.55 MHz, respectively, in D_2O. Chemical shifts are reported in ppm downfield from the methyl groups on TSP (2,2-dimethyl-2-silapentanoate, sodium salt), which was the internal reference. The ^{13}C NMR spectra were run in the proton-decoupled mode; 40000 scans were averaged for the ^{13}C NMR spectra, 1000 for the ^1H NMR spectra.

Sodium *cis*-Bis(thiosulfato)bis(ethylenediamine)cobaltate(III) Trihydrate, Na(*cis*-[(en)$_2$Co(S$_2$O$_3$)$_2$])·3H$_2$O. The purple complex is a byproduct of the Ray synthesis[3,11] for *trans*-$[(en)_2Co(S_2O_3)_2]^-$ but is more expeditiously prepared by the action of $Na_2S_2O_3$ on solutions of *cis*-$[(en)_2CoCl_2]Cl$.[6] In our procedure 3.8 g of $Na_2S_2O_3 \cdot 5H_2O$ in 15 mL of H_2O is added to 2.2 of *cis*-$[(en)_2CoCl_2]Cl$[12] in 35 mL of H_2O, and the mixture is heated gently at 38–40 °C for 18–20 min, until the initially purple solution becomes a chocolate–coffee brown. The warm mixture is immediately quenched to 20 °C and filtered. The filtrate is diluted to 100 mL with H_2O and separated on a preparative scale (35 × 4 cm, i.d.) anion-exchange column by elution with 0.25 M NaCl. The purple *cis*-$[(en)_2Co(S_2O_3)_2]^-$, band immediately follows the green-black, *trans*-$[(en)_2Co(S_2O_3)_2]^-$, band and is concentrated by flash evaporation to ca. 30 mL. Desalting is accomplished by elution of the band from a G-10 column, and the purple effluent is reconcentrated by flash evaporation to the first appearance of a persistent purple solid. An equal volume of ethanol is added dropwise, and the mixture is cooled in an ice bath; the product is collected by filtration and air-dried. Yield: 0.45 g (12%). Anal. Calcd for $Na[(C_2N_2H_8)_2Co(S_2O_3)_2] \cdot 3H_2O$: C, 10.00; H, 4.62; N, 11.66; S, 26.69; Co, 12.27. Found: C, 10.56; H, 4.58; N, 11.43; S, 26.36, Co 12.17. IR spectrum (KBr): thiosulfato, 1205, 1145, 1110, 990, 635. UV-vis spectrum: 545 (168), 289 (15800), 206 (17600).

***trans*-(Disulfanemonosulfonato)chlorobis(ethylenediamine)cobalt(III), *trans*-[(en)$_2$CoCl(S$_3$O$_3$)].** The stoichiometry of this synthesis was reported in a preliminary communication;[7] we include here the details of the procedure and the characterization. Owing to the photosensitivity of the complex in the near-UV region, all operations were conducted in the dark or in subdued lighting from a shaded 75-W tungsten lamp. Typically 20 mL of 0.02 M NaI_3 is added with stirring to a solution of 0.20 g of Na(*cis*-$[(en)_2Co(S_2O_3)_2]$)·$3H_2O$ in 15 mL of H_2O. After 20 min, the acid is back-titrated with NaOH to pH 6.5 and the yellow-brown product is isolated by elution from a cation-exchange column (Li^+ form) with 0.15 M LiCl. The effluent from the column is concentrated to ca. 1 mL by flash evaporation; during the concentration, a green solid settles out. This solid is collected by filtration, rinsed with cold H_2O, and air-dried. Yield: 0.12 g (75%). Anal. Calcd for $[(C_2N_2H_8)_2CoCl(S_3O_3)]$: C, 13.39; H, 4.50; N, 15.62; S, 26.81; Co, 16.43; Cl, 9.88. Found: C, 13.22; H, 4.69; N, 15.24; S, 25.58; Co, 16.60; Cl, 10.16. IR spectrum (KBr): disulfanemonosulfonato, 1220, 1180, 1100, 1010, 615. UV–vis spectrum (in solution): 600 sh (73), 520 (97), 367 (9000), 212 (14000). Photoacoustic spectrum (solid): λ_{max} 550, 350 nm; λ_{min} 500 nm.

Sodium *cis*-(thiosulfato)(sulfito)bis(ethylenediamine)cobaltate(III) Pentahydrate, Na(*cis*-[(en)$_2$Co(SO$_3$)(S$_2$O$_3$)])·5H$_2$O. The red-orange complex anion is a common byproduct in the synthesis of *cis*- or *trans*-$[(en)_2Co(S_2O_3)_2]^-$ but is more efficiently prepared by the direct action of Na_2SO_3 on saturated aqueous solutions of Na(*trans*-$[(en)_2Co(S_2O_3)_2]$). Typically 0.14 g of Na_2SO_3 is added with stirring to a solution of 0.42 g of Na(*trans*-$[(en)_2Co(S_2O_3)_2]$) in 20 mL of H_2O. The solution quickly becomes red-orange but is stirred at 35 °C for 1 h to improve yields. The product is isolated by elution with 0.07 M NaCl from a preparative scale (12 × 4 cm, i.d.) anion-exchange column. The red-orange band, which elutes in front of the unreacted *trans*-$[(en)_2Co(S_2O_3)_2]^-$, is collected and concentrated by flash evaporation to ca. 10 mL and is desalted by elution from a G-10 column with H_2O. The red-orange band is reconcentrated to ca. 2 mL, and 5–10 mL of ethanol is carefully layered on top of the aqueous sample in a small, stoppered vial. The two layers are allowed to mix at −10 °C for a week or more. The red-orange, microcrystalline powder is collected by filtration and dried in a stream of dry N_2. Anal. Calcd for $Na[(C_2N_2H_8)_2Co(SO_3)(S_2O_3)] \cdot 5H_2O$: C, 9.92; H, 5.41; N, 11.57; Co, 12.17; S, 19.86. Found: C, 10.01; H, 5.45; N, 11.45; Co, 11.56; S, 19.46. IR spectrum-(KBr): sulfito, 965, 628; thiosulfato, 1150, 1125, 1005, 645. UV-vis spectrum: 530 sh (98) 465 (148), 285 sh (17800), 272 (18800). ^{13}C NMR, CH_2: 48.10, 47.39, 46.58, 46.42. ^1H NMR, CH_2, asymmetric multiplet: 3.24, 3.14, 3.00, 2.91, 2.74.

The ammonium salt is prepared similarly except that elution from the anion column is accomplished with 0.07 M NH_4Cl and crystallization is effected with methanol layered on the aqueous sample. In this case, two crystalline forms, orange needles and dark orange blocks, are obtained. Physical separation of the two forms was not pursued.

***cis*-(Thiosulfato)(nitrito-*N*)bis(ethylenediamine)cobalt(III), *cis*-[(en)$_2$Co(NO$_2$)(S$_2$O$_3$)].** The red-orange complex is sparingly soluble in water, but readily forms supersaturated solutions and can be obtained in low yields from the direct, room-temperature anation with nitrite of an equilibrium mixture of *cis*/*trans*-$[(en)_2Co(H_2O)(S_2O_3)]^+$.[3,4] In a more efficient procedure, 0.31 g of *cis*-$[(en)_2Co(NO_2)Cl]Cl$[13] in 15 mL of H_2O is allowed to aquate overnight in the dark. Anation of the resulting *cis*-$[(en)_2Co(H_2O)(NO_2)]^{2+}$ is accomplished by the addition of 0.26 g of $Na_2S_2O_3 \cdot 5H_2O$ with stirring followed by gently heating the solution to 40–45 °C for 3 h in the dark. The neutral, red-orange product is separated from the cationic species, and a trace of the neutral, isomeric *trans*-$[(en)_2Co(NO_2)(S_2O_3)]$,[3] by elution with H_2O from a cation column. The product crystallizes as small blocks from the solution on standing at 5 °C overnight. Anal. Calcd for $[(C_2N_2H_8)_2Co(NO_2)(S_2O_3)]$: C, 14.24; H, 4.78; N, 20.77; Co, 17.47; S, 19.01. Found: C, 14.17; H, 4.92; N, 20.59; Co, 17.10; S, 19.23. IR spectrum (KBr): nitrito-*N*,1410, 1335, 820; thiosulfato, 1175, 1140, 1005, 635. UV-vis spectrum: 530 sh (98), 484 (122), 292 (13100), 241 (14200), 204 (14900).

***cis*-(Disulfanemonosulfonato)(nitrito-*N*)bis(ethylenediamine)cobalt(III) Hydrate, *cis*-[(en)$_2$Co(NO$_2$)(S$_3$O$_3$)]·H$_2$O.** A freshly prepared, supersaturated solution of *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$ is assayed at 484 nm (above). Aqueous NaI_3 ca. 0.05 *M* is added dropwise with stirring in a mole ratio, NaI_3/complex, of 0.50. The mixture is allowed to react in the dark for 0.5 h and is filtered. The filtrate is separated in subdued lighting by elution with H_2O from a cation column, and a neutral, honey brown band is collected and concentrated by flash evaporation to ca. 10 mL. The concentrate is eluted with H_2O from a second cation column to separate the neutral compound from the salts and is reconcentrated by flash evaporation to the first appearance of a permanent solid. When the mixture is allowed to stand overnight at 5 °C, orange-brown crystals precipitate and are collected by filtration and air-dried. Anal. Calcd for $[(C_2N_2H_8)_2Co(NO_2)(S_3O_3)] \cdot H_2O$: C, 12.40; H, 4.68; N, 18.08; Co, 15.21; S, 24.83. Found: C, 12.19; H, 4.66; N, 17.77; Co, 14.90; S, 25.89. IR spectrum(KBr): nitrito-*N*, 1410, 1400, 1340, 827; disulfanemonosulfonato, 1225, 1205, 1165, 1125, 1015, 635. UV-vis spectrum: 550 sh (146), 500 sh (232), 366 (9300), 237 (18350).

X-ray Characterizations

In general (Table I), precession photographs were taken with the use of Cu Kα radiation and the crystal densities were measured by neutral buoyancy in $CHCl_3$–$CHBr_3$. The diffractometer was a Syntex $P\bar{1}$, equipped with a Mo X-ray tube ($\lambda_{K\alpha}$ = 0.71073 Å) and a graphite monochromator in the incident beam. Crystal quality was checked with three axial rotation photographs, and mosaic-scan measurements and

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Table I. Crystallographic Data for Thiosulfato Complexes

formula	$[(en)_2Co(NO_2)(S_2O_3)]$	$[(en)_2Co(S_2O_3)]^+ClO_4^-$
fw	337.27	390.41
cryst class	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$
T, °C	20 ± 2	20 ± 2
a, Å	6.706 (2)	9.335 (5)
b, Å	13.223 (3)	9.423 (4)
c, Å	6.776 (1)	15.339 (2)
β, deg	102.72 (2)	90.43 (4)
V, Å^3	586.1 (2)	1349.2 (9)
Z	2	4
d(calcd), g/cm^3	1.91	1.92
cryst size, mm	0.013 × 0.075 × 0.21	0.045 × 0.13 × 0.45
radiation	Mo Kα	Mo Kα
μ, cm^{-1}	18.08	18.05
scan	θ–2θ	θ–2θ
scan speed, deg/min	2–8	1–8
scan range, deg	±0.8	±1.2
2θ limit, deg; hkl measd	61; $h,k,\pm l$	47; $h,k,\pm l$
no. of std reflcns	4	4
no. of indep data	1802	1893
no. of data with $\lvert F_o\rvert > 3\sigma(F)$	1061	1550
no. of params	153	172
R_1	0.047	0.087
R_2	0.055	0.061
max Δ/esd, last cycle	0.011	0.033

intensities were measured at 20 ± 2 °C. Four standard reflections were monitored every 36 reflections to check for crystal stability and to account for long-term drift.

cis-$[(en)_2Co(NO_2)(S_2O_3)]$. A small brick red plate of mean dimensions 0.013 × 0.075 × 0.21 mm was mounted on a glass fiber, and precession photographs of the $0kl$, $hk0$, $1kl$, and hkl layers were taken. Systematic absences were observed for $0k0$, k = odd; these absences indicated a space group $P2_1$, for a monoclinic cell. The crystal was mounted on the diffractometer and cell constants were determined by least-squares refinement using 2θ values for 15 pairs of reactions, measured at $+2\theta$ and -2θ values. The drift correction ranged randomly from 0.986 to 1.023. The calculated linear absorption coefficient was 18.08 cm^{-1}. Empirical absorption corrections based on repeated measurements of reflection intensity as the crystal was stepped around the diffraction vector were applied;[14] transmission coefficients ranged from 0.881 to 0.981.

With a spherical quadrant, $2\theta < 61°$, 2231 reflections were measured; from these, 1862 independent reflections were obtained by averaging.[15] Of the latter, 1061 had $I > 3\sigma(I)$, where p, the ignorance factor used to calculate $\sigma(I)$, was set equal to 0.01.

A Patterson vector map was computed, and the positions of the cobalt and the two sulfur atoms were determined. In succeeding electron density maps, the five nitrogen, five oxygen, and four carbon atoms were located. Further refinement was accomplished with anisotropic thermal parameters and calculated H atom positions (C–H = 0.98 Å; N–H = 0.90 Å), and the chirality of the complex was confirmed by reflection through the x,z plane. Final convergence was achieved with R_1 = 0.047 and R_2 = 0.055.[16] A final difference map was essentially featureless, with the largest peak of density less than 0.73 e Å^{-3}. Neutral-atom scattering curves as given by Cromer[17] were used for Co, S, O, N, and C. H atom curves were as given by Stewart.[18] Corrections for anomalous dispersion were made by using $\Delta f'$ and $\Delta f''$ values of 0.299 and 0.973 for Co, 0.110 and 0.124 for S, 0.008 and 0.006 for O, 0.004 and 0.004 for N, and 0.002 and 0.002 for C.[19] The values of $|F_o|$ and F_c are found in Table A.[20]

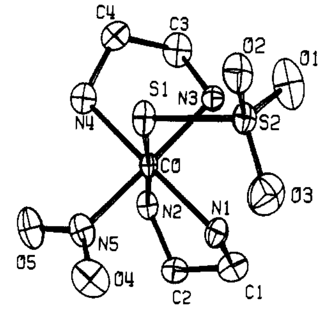

Figure 1. Perspective ORTEP drawing of *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$. Hydrogen atoms are omitted for clarity.

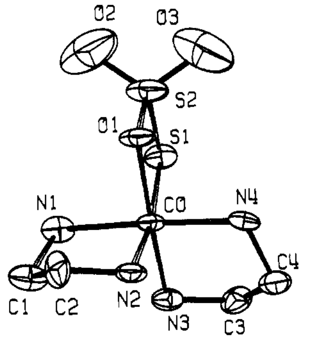

Figure 2. Perspective ORTEP drawing of the cation $[(en)_2Co(S_2O_3)]^+$. Hydrogen atoms are omitted for clarity.

$[(en)_2Co(S_2O_3)]^+ClO_4^-$. The salt was obtained as a red, microcrystalline powder[5] and was recrystallized from an ice-cold saturated aqueous solution by the addition of ice-cold, saturated $NaClO_4$. The red crystalline product was isolated by filtration, rinsed with a minimum of ice-cold H_2O, and air-dried.

A small cherry red plate of mean dimensions 0.045 × 0.13 × 0.45 mm was mounted on a glass fiber, and precession photographs of the $0kl$, $hk0$, $1kl$, and hkl layers were taken. The systematic absences $h0l$, l = odd, and $0k0$, k = odd, indicated a space group $P2_1/c$ for a monoclinic cell. Cell constants were determined by least-squares refinement using $\pm 2\theta$ values measured on the diffractometer for 15 pairs of reflections. The drift correction ranged randomly from 0.933 to 1.053. The calculated linear absorption coefficient was 18.05 cm^{-1}. Absorption corrections were applied empirically, and transmission coefficients ranged from 0.789 to 0.976. Within a quadrant, $2\theta < 47°$, 2421 reflections were measured; from these, 1893 independent reflections were obtained by averaging. Of the latter 1550 had $I > 3(I)$, where p, the ignorance factor, was set equal to 0.01.

A Patterson vector map was computed, and the positions of the cobalt, the two sulfur, and the chlorine atoms were determined. In succeeding electron density maps, the four nitrogen, seven oxygen, and four carbon atoms were located. Refinement was continued with anisotropic thermal parameters and calculated H atom positions. Final convergence was achieved with R_1 = 0.087 and R_2 = 0.061. A final difference map was essentially featureless, with the largest electron density peaks, 1.12 and 0.97 e Å^{-3}, coinciding with the positions of N(4) (Figure 2) and O(5) in ClO_4^-. For N(4) and O(5) some of the bands are somewhat longer than expected, and the positive residual density may indicate some misplacement or partial disorder. The results listed are from the converged calculation; these atom positions are of little interest to the overall structure and were not further investigated. Neutral atom scattering curves as given by Cromer[17] were used for Co, Cl, S, O, N, and C. Those for H atoms were as given by Stewart.[18] Corrections for anomalous dispersion were made by using the $\Delta f'$ and $\Delta f''$ values indicated above and 0.132 and 0.159 for Cl.[19] The values of $|F_o|$ and F_c are listed in Table E.

cis-$[(en)_2Co(NO_2)(S_3O_3)]\cdot H_2O$. A small red-brown crystal was mounted on a glass fiber and precession photographs of the $h0l$, $h1l$, $hk0$, and hkl layers were taken. The systematic absences $0k0$, k = odd, and $h0l$, $h + l$ = odd, were consistent with a $P2_1/n$ space group with a monoclinic cell. The crystal quality was checked on the diffractometer, and cell constants were determined by a least-squares calculation using $+2\theta$ values from 15 reflections. The values obtained were a = 6.515 (3)

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(20) Supplementary material; this includes all tables designated by alphabetic characters.

Table II. Fractional Atomic Positional Parameters[a,b] for *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$

atom	*x*	*y*	*z*
Co	0.2003 (2)	0	0.1275 (2)
S(1)	0.1040 (4)	0.0524 (3)	−0.2005 (3)
S(2)	−0.2087 (4)	0.0485 (3)	−0.2922 (4)
N(1)	−0.0171 (12)	−0.1003 (8)	0.1087 (13)
N(2)	0.2987 (12)	−0.0520 (8)	0.4094 (11)
N(3)	0.0378 (13)	0.1091 (7)	0.2214 (13)
N(4)	0.4196 (13)	0.1026 (8)	0.1589 (12)
N(5)	0.3677 (14)	−0.1022 (8)	0.0469 (13)
O(1)	−0.2930 (14)	0.1071 (10)	−0.1474 (13)
O(2)	−0.2454 (11)	0.0972 (7)	−0.4885 (11)
O(3)	−0.2765 (14)	−0.0560 (9)	−0.3052 (15)
O(4)	0.2947 (15)	−0.1731 (8)	−0.0655 (13)
O(5)	0.5534 (13)	−0.0984 (9)	0.1167 (15)
C(1)	−0.0101 (18)	−0.1486 (9)	0.3078 (16)
C(2)	0.2087 (17)	−0.1544 (9)	0.4210 (15)
C(3)	0.1824 (18)	0.1916 (11)	0.3133 (16)
C(4)	0.3349 (18)	0.2027 (10)	0.1873 (16)

[a] The estimated error in the last digit(s) is shown in parentheses. This form is used throughout. [b] The atom numbering is as shown in Figure 1.

Table III. Selected Bond Lengths (Å) for *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$

Co–N(1)	1.954 (10)	Co–N(4)	1.977 (10)
Co–N(2)	2.000 (7)	Co–N(5)	1.911 (11)
Co–N(3)	1.995 (11)	Co–S(1)	2.281 (3)
S(1)–S(2)	2.053 (3)	S(2)–O(2)	1.449 (8)
S(2)–O(1)	1.458 (11)	S(2)–O(3)	1.452 (12)
N(1)–C(1)	1.484 (15)	N(3)–C(3)	1.500 (16)
C(1)–C(2)	1.501 (15)	C(3)–C(4)	1.477 (18)
C(2)–N(2)	1.491 (15)	C(4)–N(4)	1.469 (17)
N(5)–O(4)	1.239 (14)	N(5)–O(5)	1.232 (12)

Table IV. Selected Bond Angles (deg) for *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$

	Metal Coordination Sphere		
N(1)–Co–N(2)	85.1 (4)	N(2)–Co–N(5)	86.5 (4)
N(1)–Co–N(3)	93.4 (4)	N(3)–Co–N(4)	85.1 (4)
N(1)–Co–N(5)	88.7 (4)	N(3)–Co–S(1)	91.9 (3)
N(1)–Co–S(1)	95.5 (3)	N(4)–Co–N(5)	92.6 (4)
N(2)–Co–N(3)	91.9 (4)	N(4)–Co–S(1)	86.6 (2)
N(2)–Co–N(4)	93.0 (4)	N(5)–Co–S(1)	89.7 (3)
	Ligands		
Co–N(1)–C(1)	111.0 (6)	Co–N(3)–C(3)	108.0 (7)
N(1)–C(1)–C(2)	108.6 (1.0)	N(3)–C(3)–C(4)	107.4 (1.0)
C(1)–C(2)–N(2)	106.8 (9)	C(3)–C(4)–N(4)	108.9 (1.1)
C(2)–N(2)–Co	108.0 (7)	C(4)–N(4)–Co	109.4 (7)
Co–N(5)–O(4)	122.3 (8)	O(4)–N(5)–O(5)	119.7 (1.1)
Co–N(5)–O(5)	118.0 (9)	Co–S(1)–S(2)	109.8 (1)
S(1)–S(2)–O(1)	107.7 (4)	S(1)–S(2)–O(2)	102.9 (4)
S(1)–S(2)–O(3)	109.1 (4)	O(1)–S(2)–O(2)	111.6 (6)
O(1)–S(2)–O(3)	112.6 (7)	O(2)–S(1)–O(3)	112.3 (6)

Table V. Fractional Atomic Positional Parameters[a] for $[(en)_2Co(S_2O_3)]^+ClO_4^-$

atom	*x*	*y*	*z*
Co	0.2899 (2)	0.2227 (2)	0.18072 (8)
S(1)	0.1964 (4)	0.0869 (4)	0.2879 (2)
S(2)	0.3113 (4)	0.2277 (5)	0.3574 (2)
O(1)	0.3759 (9)	0.3118 (8)	0.2817 (4)
O(2)	0.4213 (13)	0.1534 (14)	0.4104 (6)
O(3)	0.2236 (13)	0.3205 (13)	0.4076 (7)
N(1)	0.4573 (14)	0.0975 (8)	0.1717 (5)
N(2)	0.4038 (11)	0.3533 (11)	0.1024 (5)
N(3)	0.1864 (11)	0.1172 (9)	0.0861 (5)
N(4)	0.1265 (10)	0.3519 (9)	0.1828 (5)
C(1)	0.5477 (16)	0.1461 (14)	0.1005 (8)
C(2)	0.5507 (13)	0.3037 (15)	0.1030 (8)
C(3)	0.0323 (15)	0.1690 (15)	0.0887 (8)
C(4)	0.0253 (15)	0.3244 (14)	0.1063 (7)
Cl	0.7870 (4)	0.2374 (4)	0.3633 (2)
O(4)	0.6838 (10)	0.3316 (9)	0.3969 (6)
O(5)	0.9064 (12)	0.3261 (10)	0.3358 (7)
O(6)	0.8328 (12)	0.1343 (9)	0.4265 (6)
O(7)	0.7321 (14)	0.1619 (11)	0.2911 (7)

[a] The numbering for the cation is as shown in Figure 2.

Table VI. Selected Bond Lengths (Å) for $[(en)_2Co(S_2O_3)]^+ClO_4^-$

Co–N(1)	1.964 (10)	Co–N(4)	1.952 (10)
Co–N(2)	2.027 (9)	Co–S(1)	2.263 (3)
Co–N(3)	2.001 (9)	Co–O(1)	1.931 (7)
S(2)–S(1)	2.007 (5)	S(2)–O(2)	1.482 (12)
S(2)–O(1)	1.533 (8)	S(2)–O(3)	1.427 (12)
N(1)–C(1)	1.459 (16)	N(3)–C(3)	1.520 (17)
C(1)–C(2)	1.485 (19)	C(3)–C(4)	1.490 (19)
C(2)–N(2)	1.449 (16)	C(4)–N(4)	1.522 (15)
Cl–O(4)	1.410 (9)	Cl–O(6)	1.436 (9)
Cl–O(5)	1.458 (11)	Cl–O(7)	1.409 (11)

Å, *b* = 12.49 (1) Å, *c* = 17.28 (2) Å, and *β* = 89.74 (6)°, which are consistent with the monoclinic cell. With $Z = 4$, $d(\text{calcd}) = 1.83$ g/cm^3 and $d(\text{measd}) = 1.81$ g/cm^3. Further structural analysis was precluded by decomposition of the crystal in the X-ray beam.

Results and Discussion

Structural Results. The crystal structure of *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$ consists of discrete monomeric units within the unit cell. The geometry about the central cobalt is approximately octahedral with normal bite angles within the ethylenediamine chelates of ca. 85°, Table IV, and a Λδλ enantiomeric configuration of the ethylenediamine chelates, Figure 1. The S-coordination of the monodentate thiosulfato ligand is clearly established (Figure 1, Table III) with a Co–S(1) distance of 2.281 (3) Å, which is comparable to that of 2.287 (3) Å reported for the Co–S distance in $[(NH_3)_5CoS_2O_3]^+$.[21] The nitrito ligand is N-bonded to the cobalt with Co–N(5) = 1.91 (1) Å, which is comparable to those values, 1.89 (2) Å[22] and 1.929 (5) Å,[23] reported for the Co–NO_2 bond lengths in *cis*-$[(en)_2Co(NO_2)_2]^+$. The bonds between the cobalt and the amine nitrogens N(2) trans to the thiosulfato group and N(3) trans to the nitrito group, Co–N(2) = 2.000 (7) Å and Co–N(3) = 1.99 (1) Å, are longer than the mean distance, Co–N = 1.965 Å,[22] between the cobalt and the amine nitrogens, N(1) and N(4), that are trans to each other. The structural trans effects are consistent with those previously established for the thiosulfato ligand in Co(III) complexes[3] and for the nitrito-*N* ligand in *cis*-$[(en)_2Co(NO_2)_2]^+$[22,23] and are also consistent with the apparent trans-labilizing effect of the thiosulfato[3] and nitrito-*N*[13] ligands.

The dimensions of the thiosulfato ligand are comparable to those found in $[(NH_3)_5CoS_2O_3]^+$.[21] The bond distance S(1)–S(2) = 2.053 (3) Å is indistinguishable from that of 2.048 (2) Å reported for the corresponding bond in the pentaammine complex and is significantly longer than that of 2.013 (3) Å found in the free thiosulfate in $MgS_2O_3{\cdot}6H_2O$.[24] A marginally longer bond, 2.066 (6) Å, has been reported for the S–S bond in $[Pd(en)(S_2O_3)_2]^{2-}$.[25] The mean S–O distance, 1.453 (7) Å, agrees with the corresponding bond lengths in either the pentaammine complex, 1.463 (3) Å, or the free thiosulfate, 1.468 (4) Å. The Co–S(1)–S(2) angle, 109.8 (1)°, is approximately tetrahedral and is comparable to that of 110.20 (6)° found in the pentaammine complex. The deviations of the N(1)–Co–S(1) and N(4)–Co–S(1) angles from 90° allow the N(1) to bend away from the O(3) of the thiosulfato, to reduce steric crowding.

The crystal structure of $[(en)_2Co(S_2O_3)]^+ClO_4^-$ consists of discrete cationic and anionic units. The geometry about the central

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Table VII. Selected Bond Angles (deg) for $[(en)_2Co(S_2O_3)]^+ClO_4^-$

Metal Coordination Sphere			
N(1)-Co-N(2)	84.4 (4)	N(2)-Co-O(1)	89.7 (3)
N(1)-Co-N(3)	91.7 (4)	N(3)-Co-N(4)	87.0 (4)
N(1)-Co-S(1)	91.3 (3)	N(3)-Co-S(1)	93.4 (3)
N(1)-Co-O(1)	89.5 (4)	N(4)-Co-S(1)	92.0 (3)
N(2)-Co-N(3)	97.1 (4)	N(4)-Co-O(1)	92.1 (3)
N(2)-Co-N(4)	92.5 (4)	S(1)-Co-O(1)	79.8 (2)
Ligands			
Co-N(1)-C(1)	109.2 (7)	Co-N(3)-C(3)	105.9 (7)
N(1)-C(1)-C(2)	107.8 (1.0)	N(3)-C(3)-C(4)	111.3 (1.1)
C(1)-C(2)-N(2)	107.8 (1.0)	C(3)-C(4)-N(4)	106.2 (1.0)
C(2)-N(2)-Co	107.5 (7)	C(4)-N(4)-Co	111.2 (7)
O(1)-S(2)-S(1)	98.7 (3)	O(2)-S(2)-O(3)	113.1 (6)
O(1)-S(2)-O(2)	112.6 (6)	O(2)-S(2)-S(1)	110.2 (5)
O(1)-S(2)-O(3)	108.8 (6)	O(3)-S(2)-S(1)	112.6 (5)
Co-O(1)-S(2)	102.7 (4)	Co-S(1)-S(2)	78.8 (2)
Anion			
O(4)-Cl-O(5)	105.7 (6)	O(5)-Cl-O(6)	111.1 (6)
O(4)-Cl-O(6)	112.4 (6)	O(5)-Cl-O(7)	109.6 (7)
O(4)-Cl-O(7)	111.0 (7)	O(6)-Cl-O(7)	107.1 (6)

cobalt is distorted from octahedral (Figure 2) with ethylenediamine bite angles of 84.4 (4) and 87.0 (4)° (Table VII). With a centrosymmetric space group, both Δ and Λ configurations occur; the configuration in Figure 2 is Δδδ. Chelation of the thiosulfato ligand is clearly shown (Table VI) with Co–S(1) = 2.263 (3) Å and Co–O(1) = 1.931 (7) Å and the restricted angles, O(1)–Co–S(1) = 79.8 (2)°, Co–S(1)–S(2) = 78.8 (2)°, and S(1)–S-(2)–O(1) = 98.7 (3)°. The dimensions of the chelated thiosulfato ligand differ from either the monodentate thiosulfato ligand or the free ligand. S(1)–S(2) = 2.007 (5) Å is the same as that value, 2.013 (3) Å, in the free ligand and is distinctly shorter than those values, 2.048–2.066 Å, given above for various monodentate thiosulfato structures. The endocyclic sulfur to oxygen distance, S(2)–O(1) = 1.533 (8) Å, in the chelate is greater than those distances, 1.48–1.50 Å, found in the less strained, 6-membered-ring structure of the sulfato-bridged cation, $[(en)_2Co(NH_2,SO_4)Co(en)_2]^+$.[26] The mean, exocyclic sulfur to oxygen bond length, $\overline{\text{S–O}}$ = 1.46 (3) Å, is comparable to the corresponding S–O bond lengths, 1.440–1.443 Å, found in the bridged-sulfato complex. The mean distance, $\overline{\text{Co–N}}$ = 1.96 (1), Å, between the cobalt and the two amine nitrogens trans to each other is the same as that distance, 1.96 (1) Å, found in *cis*-$[(en)_2Co(NO_2)(S_2O_3)]$, above. The cobalt–ammine bonds that are trans to the chelated sulfur, Co–N(2) = 2.027 (9) Å, and trans to the chelated oxygen, Co–N(3) = 2.001 (9) Å are both distinctly longer than the mean Co–N distance (above). This structural trans effect is consistent with the kinetic lability of this complex in aqueous solution.[5]

Preparation and Characterization

Cis Thiosulfato Complexes. Preparation of a nitrito-*N* complex by substitution of the chloro group in *trans*-$[(en)_2CoCl(NO_2)]NO_3$ with thiosulfate had been reported,[27] but the analytical data were manifestly in error and no confirmatory evidence was provided. The present method, anation of the cis aqua complex (eq 1), was

$$cis\text{-}[(en)_2Co(H_2O)(NO_2)]^{2+} + X^{2-} \rightarrow [(en)_2Co(NO_2)X] + H_2O$$

$$X = C_2O_4,\ S_2O_3 \qquad (1)$$

previously to prepare *cis*-$[(en)_2Co(NO_2)(C_2O_4)]$;[13] in the present case, this reaction is neither stereoretentive nor does it go to completion. In addition to the single-crystal X-ray structural determination and the elemental analysis, the complex is characterized by the following properties. The intense charge-transfer bands at 241 and 292 nm establish nitrito-*N*[13] and thiosulfato-*S*[28] coordination to Co(III). Weak doublets at 897, 876 cm^{-1} and at 792, 765 cm^{-1} are characteristic[29] of the *cis*-bis(ethylenediamine)cobalt(III) configuration. Elution from anion- or cation-exchange columns with H_2O confirms the charge neutrality of the complex, and the order of elution of a cis/trans isomeric mixture, trans before cis, further confirms the assigned configuration. Attempts to obtain a ^{13}C NMR spectrum of the complex were frustrated by its low solubility.

Reaction of *trans*-$[(en)_2Co(S_2O_3)_2]^-$ with Na_2SO_3 (pH ca. 10) yields some *trans*-$[(en)_2Co(SO_3)_2]^-$, as has been reported,[27] but the principal product is *cis*-$[(en)_2Co(SO_3)(S_2O_3)]^-$, which is separated from reactants and other (−1) complexes by elution with dilute (0.07 M) NaCl from an anion-exchange column. In addition to the elemental analysis, the complex is characterized by the intense charge-transfer bands at 272 and 289 nm, which are found in other well-characterized Co(III)–sulfito[6,29] and –thiosulfato[3,28] complexes. The cis configuration is supported both by the four resonances of roughly equal intensity in the ^{13}C NMR spectrum and by the asymmetric multiplet in the ^1H NMR spectrum.

A synthesis similar to our method has been used to form the bis(thiosulfato) complex,[6] and its isolation as a compound, nonstoichiometric salt, $Li(cis\text{-}[(en)_2Co(S_2O_3)_2])\cdot 6H_2O\cdot 1.6LiCl$, has been reported. In addition to the elemental analysis for the current preparation, the structure is indicated by the intense charge-transfer band at 289 nm, characteristic of Co(III)–sulfur coordination, and the weak doublets at 900, 880 cm^{-1} and at 765, 755 cm^{-1}, characteristic of the cis configuration. Attempts to obtain a ^{13}C NMR spectrum were frustrated by decomposition of the complex in the NMR tube. The cis assignment is additionally confirmed by the order of elution of the bis(thiosulfato) complexes, trans before cis, from an anion-exchange column, and by the relative intensities of the d–d transitions: ϵ_{545}(trans) = 85.5 (3), ϵ_{545}(cis) = 168.

The structural inferences drawn from the spectral characterization of the bidentate thiosulfato-*O*,S complex $[(en)_2Co(S_2O_3)]^+ClO_4^{-\,5}$ are amply confirmed by the single-crystal X-ray structural determination above.

Disulfanemonosulfonato Complexes. The complexes *cis*-$[(en)_2Co(NO_2)(S_3O_3)]$ and *trans*-$[(en)_2Co(H_2O)(S_3O_3)]^+$ are prepared by oxidation in subdued lighting of the corresponding *cis*-(thiosulfato)(nitrito-*N*) and bis(thiosulfato) complexes. The *cis*-(disulfanemonosulfonato)(nitrito-*N*) complex is relatively inert to substitution and is formed in the oxidation of the *cis*-(thiosulfato)(nitrito-*N*) complex with aqueous I_2 (eq 2). In contrast,

$$2cis\text{-}[(en)_2Co(NO_2)(S_2O_3)] + I_2 + 2H_2O \rightarrow cis\text{-}[(en)_2Co(NO_2)(S_3O_3)] + [(en)_2Co(H_2O)(NO_2)]^{2+} + 2H^+ + SO_4^{2-} + 2I^- \qquad (2)$$

the *trans*-(disulfanemonosulfonato)(aqua) cation, which is formed in the oxidation[7] of the bis(thiosulfato) anion by aqueous I_2 (eq 3), is kinetically labile and is isolated as the corresponding

$$cis\text{-}[(en)_2Co(S_2O_3)_2]^- + I_2 + 2H_2O \rightarrow trans\text{-}[(en)_2Co(H_2O)(S_3O_3)]^+ + 2H^+ + SO_4^{2-} + 2I^- \qquad (3)$$

trans-(disulfanemonosulfonato)(chloro) complex.

In addition to the elemental analyses and their preparative chemistry, the cis and trans disulfanemonosulfonato complexes are characterized by their intense, photosensitive, charge-transfer bands at 366 and 367 nm, respectively, corresponding to the Co(III)–$S_3O_3^{2-}$ linkage.[7] The 237-nm band in the cis complex confirms the nitrito-*N* coordination, and the charge on the aqueous complexes is confirmed by elution of the trans-(disulfanemonosulfonato)(aqua) cation from a cation column with 0.1 M $NaClO_4$ and by elution of the *cis*-(disulfanemonosulfonato)(nitrito-*N*) neutral complex from a cation column with H_2O. The geometric configuration of the complexes is established by the doublets at

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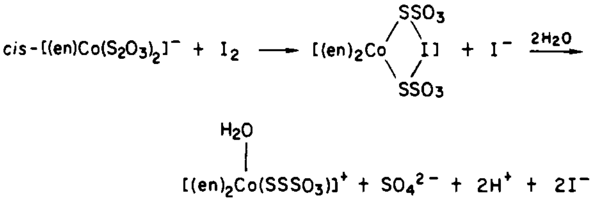
895, 875 cm^{-1} and at 775, 756 cm^{-1} for the cis nitrito-*N* complex and by the singlets at 860 and 800 cm^{-1} for the trans chloro complex. Additionally, we attribute the substitution lability of the *trans*-(disulfanemonosulfonato)(aqua) cation to a kinetic trans-labilizing effect of the disulfanemonosulfonate ligand.

Reactivity

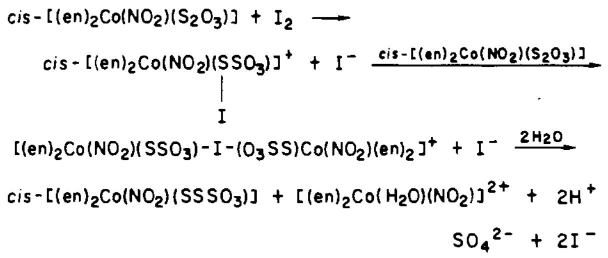
Cis Thiosulfato Complexes. Of the three cis thiosulfato complexes, the stability with respect to aquation, acid hydrolysis, or isomerization increases in the order bis(thiosulfato) < (thiosulfato)(nitrito-*N*) < (thiosulfato)(sulfito). The bis(thiosulfato) complex exhibits no detectible decomposition for up to 2 h at pH 5 or pH 1, but after 18 h in 0.1 M $HClO_4$, considerable decomposition is evident with production principally of $[(en)_2Co(H_2O)(SO_3)]^+$.[29] At either pH 5 or pH 1, in 12 h the nitrito-*N* and the sulfito complexes undergo <5% and undetectable decomposition, respectively. The stability of the latter contrasts notably with the lability of the *trans*-(thiosulfato)(sulfito) complex, which rapidly equilibrates with free thiosulfate and the *trans*-(sulfito)(aqua) cation in aqueous solutions.[30]

All three complexes are attacked by aqueous iodine and other oxidizing agents. The bis(thiosulfato) complex is rapidly oxidized in a 1:1 molar consumption ratio, yielding typically 75% *tran*-(disulfanemonosulfonato)(aqua) cation[7] (eq 3) and some Co^{2+}. Ceric ammonium nitrate solutions also oxidize the bis(thiosulfato) anion to produce the (disulfanemonosulfonato)(aqua) cation in up to 20% yield. Hydrogen peroxide reacts only slowly with the bis(thiosulfato) anion to give a distribution of products.

Aqueous iodine attacks the *cis*-(thiosulfato)(nitrito-*N*) complex somewhat less rapidly with a 1:2 consumption ratio (eq 2) to yield up to 0.35 *cis*-(disulfanemonosulfonato)(nitrito-*N*) complex per Co(III) and a mixture of *cis*- and *trans*-$[(en)_2Co(H_2O)(NO_2)]^{2+}$; some Co^{2+} and *trans*-(sulfito)(aqua) cation are also produced. In common with the bis(thiosulfato) anion, the (thiosulfato)(nitrito-*N*) complex is only slowly attacked by H_2O_2. Although we have no direct evidence for intermediate formation, we suggest a mechanism consistent with the formation of the $S_3O_3^{2-}$ moiety in these two oxidations by iodine. By analogy with the recently characterized I-bridged thiolato complex, $[(en)_2Co(cys)–I–(cys)Co(en)_2]^{5+}$,[31] we propose the formation of an iodinium intermediate, bridging intramolecularly (eq 4), or intermolecularly (eq 5).



$$cis\text{-}[(en)Co(S_2O_3)_2]^- + I_2 \longrightarrow [(en)_2Co(SSO_3)_2I] + I^- \xrightarrow{2H_2O} [(en)_2Co(H_2O)(SSSO_3)]^+ + SO_4^{2-} + 2H^+ + 2I^- \quad (4)$$



$$cis\text{-}[(en)_2Co(NO_2)(S_2O_3)] + I_2 \longrightarrow cis\text{-}[(en)_2Co(NO_2)(SSO_3I)]^+ + I^- \xrightarrow{cis\text{-}[(en)_2Co(NO_2)(S_2O_3)]} [(en)_2Co(NO_2)(SSO_3)\text{-}I\text{-}(O_3SS)Co(NO_2)(en)_2]^+ + I^- \xrightarrow{2H_2O} cis\text{-}[(en)_2Co(NO_2)(SSSO_3)] + [(en)_2Co(H_2O)(NO_2)]^{2+} + 2H^+ + SO_4^{2-} + 2I^- \quad (5)$$

Oxidation of the *cis*-(thiosulfato)(sulfito) anion is relatively slow, presumably because of the steric protection provided the sensitive cobalt-bonded sulfur by the surrounding $-SO_3$ groups. Over a period of hours, I_2, H_5IO_6 (pH 2), or H_2O_2 each oxidize the complex, generating principally *trans*-$[(en)_2Co(H_2O)(SO_3)]^+$. In the periodic acid oxidation, *cis*-$[(en)_2Co(SO_3)_2]^-$[6] is generated as a detectable intermediate that is subsequently oxidized. At pH 4, IO_4^- reacts with the complex more slowly and produces a distribution of products.

Disulfanemonosulfonato Complexes. Both *trans*-$[(en)_2CoCl(S_3O_3)]$ and *cis*-$[(en)_2Co(NO_2)(S_3O_3)]$ are more stable in the solid form than in solution; the trans chloro complex exhibits no decomposition after 3 weeks in the dark, and the cis nitrito–*N* complex is unchanged after 2 weeks under laboratory illumination. The photoacoustic spectrum of the solid trans chloro complex has maxima at 600 and 350 nm and a minimum at 500 nm, which account for its green color. In H_2O the solid slowly dissolves, liberating one Cl^-/Co(III) and generating the yellow-brown cation *trans*-$[(en)Co(H_2O)(S_3O_3)]^+$. In solution both the trans aqua and the cis nitrito-*N* complexes are notably photosensitive (see below); in the dark, solutions of either at pH 5 or at pH 1 are stable to aquation of the $S_3O_3^{2-}$ group for 1 h or more, but each becomes turbid on standing overnight and gives a positive test (acetone–SCN^-) for Co^{2+}.

The trans aqua cation displays evidence for the lability in aqueous solutions of the site trans to the $S_3O_3^{2-}$ ligand. When mixed with azide, thiocyanate, nitrite, or thiosulfate, a solution of the trans aqua cation undergoes distinctive, reversible color changes and the original cation can be recovered by sorption of the mixture on a cation-exchange column and elution of the anions with H_2O. These results are consistent with dynamic equilibrium (eq 6). In contrast the cis nitrito-*N* complex exhibits no evidence

$$trans\text{-}[(en)_2Co(H_2O)(S_3O_3)]^+ + X^{-/2-} \Leftrightarrow trans\text{-}[(en)_2CoX(S_3O_3)]^{0/-}$$
$$X = NO_2,\ SCN,\ N_3,\ S_2O_3 \quad (6)$$

of dissociation, and the complex is recovered intact following elution from a cation column with water.

Aqueous solutions of either the trans aqua or the cis nitrito-*N* complex are rapidly photolyzed at pH 5 or at pH 1 by 350-nm radiation. For the trans aqua complex at pH 5 in aerated solutions, the principal cobalt-containing product is $[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$.[32] In 0.1 M HCl, the quantum yield is 0.44 ± 0.04, with production of Co^{2+} and $S_6O_6^{2-}$ (eq 7).[10] In 0.1 M HCl the

$$trans\text{-}[(en)_2Co(H_2O)(S_3O_3)]^+ + 2H^+ \xrightarrow{h\nu} Co^{2+} + 2enH^+ + H_2O + {}^1/_2S_6O_6^{2-} \quad (7)$$

quantum yield for photolysis of the *cis*-(disulfanemonosulfonato)(nitrito-*N*) complex at 350 nm is 0.26 ± 0.03.

In the absence of a definitive single-crystal X-ray structural determination, the mode of the $S_3O_3^{2-}$ ligand coordination to cobalt, $CoSSSO_3$ or $CoS(S)SO_3$, can only be inferred. The well-known catalysis[33] by pendant sulfur atoms of the oxidation of azide by aqueous iodine (eq 8) provides a means of distinguishing between these bonding modes. In the presence of either the trans aqua or the cis nitrito-*N* complex, the oxidation of azide by aqueous I_2 proceeds rapidly with the evolution of a colorless gas. In contrast, the *cis*-(nitrito-*N*)(thiosulfato) complex, which has no pendant sulfur atom, does not catalyze this oxidation. We conclude that the bonding mode of the disulfanemonosulfonato ligand in these complexes is most likely $CoS(S)SO_3$.

$$I_2 + 2N_3^- \xrightarrow{R\text{-}S} 2I^- + 3N_2 \quad (8)$$

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Supplementary Material Available: Tables A–H, listing all observed and calculated structure factors, anisotropic thermal parameters, root-mean-square displacements, and hydrogen atom fractional positional parameters (31 pages). Ordering information is given on any current masthead page.

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