Oxygen- and Sulfur-Bonded Thiosulfatopentaamminecobalt(III)

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The base hydrolysis of $[(NH_3)_5CoX]^{n+}$ *in 1.0 M* $Na_2S_2O_3$ *leads to both S- and O-bonded* $[(NH_3)_5Co(S_2O_3)]^+$. *The rate law for the subsequent reactions of the hitherto unknown O-isomer has been determined:* $-d[Co]/dt = k_s + k_{OH}[OH^-]$, *where* $k_s = (4.3 \pm 0.3) \times 10^{-4}\ s^{-1}$ *and* $k_{OH} = 0.185 \pm 0.006\ M^{-1}\ s^{-1}$, *25 °C,* $\mu = 3$ *M. Thus the O-isomer linkage isomerizes intramolecularly to the S-isomer by both the spontaneous (*k_s*) and base catalyzed paths (*k_{OH}*); competitive hydrolysis (43 ± 5%) is found for the* k_{OH} *route. The mechanisms are discussed in relation to other linkage isomerizations of this kind. The extent of total* $S_2O_3^{2-}$ *capture and the S-/O-bonded isomer ratios have been measured for the base hydrolysis reaction of* $[(NH_3)_5CoX]^{n+}$ *in 1 M* $S_2O_3^{2-}$ *using seven different leaving groups. For the 2+ cations, a constant % capture is observed, and a slightly higher % for the 3+ cations. In all cases a constant S-/O-isomer ratio is found (70 ± 3% S-, 30 ± 3% O-). This work complements a recent study where a fixed O-/N-ratio for* NO_2^- *capture was observed. The results support the case for a common but reactive five coordinate intermediate* $[(NH_3)_4(NH_2)Co]^{2+}$ *in the base hydrolysis reaction.*

Introduction

The base hydrolysis of $[(NH_3)_5CoX]^{n+}$ in the presence of excess Y^{m-} leads usually to some $[(NH_3)_5CoY]^{(n-m)+}$, along with $[(NH_3)_5CoOH]^{2+}$ [1, 2]. When ambidentate nucleophiles Y^{m-} such as SCN^- or NO_2^- are employed, both linkage isomers of $[(NH_3)_5CoY]^{(n-m)+}$ appear as immediate products [3, 4]. For both SCN^- and NO_2^-, the thermodynamically unstable isomers $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoONO]^{2+}$ are produced in excess over $[(NH_3)_5CoNCS]^{2+}$ and $[(NH_3)_5CoNO_2]^{2+}$ respectively. In the case of the thiocyanate complex, both acid [5] and base hydrolysis [3] of a suitable $[(NH_3)_5CoX]^{n+}$ complex in the presence of excess SCN^- affords a convenient synthesis of the sulfur bonded linkage isomer, previously unknown. The unstable oxygen bonded NO_2^- isomer may be prepared similarly [4], although an alternative and more convenient synthesis exists [6]. There was an interest in the thiosulfate ion $S_2O_3^{2-}$ as a competitor in the base hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$, and the expectation was that both sulfur and oxygen would be captured. This expectation has been realized. Despite reports to the contrary [7, 8], only the S-bonded $[(NH_3)_5CoSSO_3]^+$ ion appears to be known with certainty [9], and hence the observation of the O-isomer $[(NH_3)_5CoOS_2O_2]^+$ is of importance. Furthermore, since thiosulfate ion normally binds metal ions through the terminal sulfur atom, especially heavy metal ions such as Ag^+, the chemistry of an O-bonded metal complex isomer was of interest. Accordingly, evidence for the existence of $[(NH_3)_5CoOS_2O_2]^+$ is reported here, together with kinetic and thermodynamic data for the isomerization to the (known) S-bonded isomer in neutral and basic solution. The present work represents a further example of a spontaneous and base catalyzed linkage isomerization process, such as the S- to N-bonded isomerization of $[(NH_3)_5CoSCN]^{2+}$ [3] and O- to N-bonded isomerization of $[(NH_3)_5CoONO]^{2+}$ [6], affording further insight into the mechanism of these intramolecular processes [10].

Additional interest in the capture of both the S- and O-donor atoms of $S_2O_3^{2-}$ during the base hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$ in $OH^-/S_2O_3^{2-}$ media focuses on the leaving group (X) dependence [2] of the total percentage of $[(NH_3)_5Co(S_2O_3)]^+$ formed, and of the S-bonded/O-bonded isomer ratio. The problem was outlined in a preceding article for the NO_2^- system where both the O- and N-$[(NH_3)_5Co(NO_2)]^{2+}$ linkage isomers are formed in base hydrolysis [4]. The present work provides further evidence for the existence of a short-lived pentacoordinate intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ in the base hydrolysis reaction of $[(NH_3)_5CoX]^{n+}$.

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Experimental

Visible spectra were recorded on a Cary 210 instrument using matched 1 cm or 1 dm silica cells. ^1H NMR spectra were measured using a Varian T60 spectrometer at 35 °C, $Me_2SO\text{-}d_6$ as solvent and a tetramethylsilane reference. Ion-exchange chromatography was performed at ~22 °C using Dowex AG 50WX2 (Na^+ form; 200–400 mesh) resin. Some chromatography at ~2 °C was performed using jacketed columns cooled by circulating water from a Lauda thermostat bath. The use of the acid sensitive $S_2O_3^{2-}$ necessitated rigorous pre-washing of the normal H^+ form resin with Na_3PO_4 (0.5 *M*), Na_2HPO_4 (1 *M*), NaCl (1 *M*) and finally distilled water.

The complexes $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$, $[(NH_3)_5CoO_3SCH_3](ClO_4)_2$, $[(NH_3)_5CoONO_2](ClO_4)_2$, $[(NH_3)_5CoI](ClO_4)_2$, $[(NH_3)_5CoOC(NH_2)_2](S_2O_6)_{3/2}\cdot 1.5H_2O$, $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3\cdot H_2O$, and $[(NH_3)_5CoOP(OCH_3)_3](ClO_4)_3\cdot H_2O$ were from fresh batches used in concurrent work and fully characterized. This is described elsewhere [4].

The S-bonded thiosulfato complex $[(NH_3)_5CoSSO_3]^+$ was prepared by several of the published methods [8, 9, 14], each involving aerial oxidation of a suitable Co(II) salt (Cl^- or NO_3^-) in the presence of the corresponding ammonium salt, sodium thiosulfate pentahydrate and excess aqueous ammonia. The only modification was the temperature employed for the oxidation, ~20 °C rather than ~0 °C. To check for the presence of any oxygen bonded $S_2O_3^{2-}$ isomer, a product sample (usually *all* from a small scale synthesis) from each preparative procedure was diluted with water, sorbed on and chromatographed from Dowex using neutral NaCl (0.5 *M*) eluent. In each case, a pink 1+ band was eluted free from excess Co(II), a higher charged brown dimeric peroxo complex and other material, including some brown-black insolubles. The visible and ultraviolet spectra (600–250 nm) of the 1+ bands were recorded. In other (larger scale) syntheses, the crystals of the Cl^- or NO_3^- salts which separated on cooling as described [14] were similarly chromatographed and their spectra recorded. Analytically pure material was obtained by recrystallizing the chloride salt several times from water using aqueous LiCl as precipitant, and cooling to ~5 °C. The perchlorate salt was obtained as deep burgundy plates by repetitive recrystallization of the NO_3^- salt from water at ~25 °C using $NaClO_4$. Both the chloride and perchlorate salts were obtained as monohydrates, although prolonged drying in vacuum resulted in efflorescence and noticeable collapse of the crystals to a purple-grey powder of the anhydrous perchlorate salt. This process was monitored by ^1H NMR and visible spectroscopy. A decrease in the signal at δ 3.38 ppm in the NMR spectrum was observed, attributable to a loss of two protons, while the increase in absorbance/gram indicated the expected decrease in formula weight corresponding to the loss of one H_2O molecule. Note that in the ^1H NMR spectrum, the lattice H_2O (2H) and trans-NH_3 (3H) signals are coincident, but may be separated by the addition of a little D^+. Restivo *et al.* [9] report $\epsilon_{512}^{\max}$ 64 and $\epsilon_{289}^{\max}$ 12800 for the perchlorate salt. A comparison with our values, $\epsilon_{512.5}$ 69.9 and $\epsilon_{289}^{\max}$ 14130, suggests that they probably isolated a hydrate also. *Anal.* Calcd for $[(NH_3)_5CoS_2O_3]ClO_4\cdot H_2O$: H, 4.59; N, 18.74; S, 17.16; Cl, 9.49. Found: H, 4.6; N, 19.0; S, 17.2; Cl, 9.4%.

The ^1H NMR spectrum of the anhydrous ClO_4^- salt in $Me_2SO\text{-}d_6$, δ 3.15 ppm (12H, *cis* NH_3) and δ 3.38 ppm (3H, *trans* NH_3), is similar to that found previously [9] for the S-bonded isomer. The corresponding chemical shifts for $[(NH_3)_5CoOSO_3]ClO_4\cdot H_2O$, which seems a reasonable model for the O-isomer, $[(NH_3)_5CoOS_2O_2]^+$, are δ 3.88 ppm and 2.58 ppm. No absorptions were observed in these regions.

The competition experiments were performed at 25 °C by directly dissolving solid complex (~200–800 mg) in 30–80 ml of 1.00 *M* $Na_2S_2O_3$ (AnalaR) which was 0.10 *M* in NaOH (Volucon). The complex dissolved and reacted rapidly on stirring. After 5.0 min, the reaction was quenched with NH_4Cl (1.0 g), diluted to 500 ml with water and sorbed on, washed (H_2O) and eluted from Dowex. The pink 1+ band $[(NH_3)_5CoSSO_3]^+$ was removed with 0.5 *M* NaCl (pH 3, HCl), and orange $[(NH_3)_5CoOH_2]^{3+}$ with 3.0 *M* HCl. The [Co] in the eluates was determined spectrophotometrically using $\epsilon_{490}^{\max}$ 47.7 for $[(NH_3)_5CoOH_2]^{3+}$ and $\epsilon_{512.5}^{\max}$ 69.9 for $[(NH_3)_5CoSSO_3]^+$ (10 cm cells). The thiosulfato complex ion was estimated more accurately using $\epsilon_{289}^{\max}$ 14130 (1 cm cell). Light was rigorously excluded in all experiments involving the S-bonded complex because of its appreciable photosensitivity*.

Some competition experiments were performed using the $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$ and $[(NH_3)_5CoO_3SCH_3](ClO_4)_2$ complexes reacted for shorter time periods: 1.0 min, and immediately following complete dissolution ($\lesssim$5 s). They were quenched with NH_4Cl and chromatographed at ~2 °C. The thiosulfato complex spectra were measured immediately and also after standing 24 hr at 25 °C in the dark.

For the O-urea and O-ureaMe$_2$ complexes, different eluents were required to separate some N-bonded urea complexes, $[Co(NH_3)_5NH\cdot CO\cdot NH_2]^{2+}$ (7%) and $[Co(NH_3)_5NH\cdot CO\cdot NMe_2]^{2+}$ (3%), respectively, which form in the base hydrolysis reaction together with $[(NH_3)_5Co(S_2O_3)]^+$ and $[(NH_3)_5Co-$

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*Solutions fade under both natural and normal laboratory lighting, and become turbid with the eventual deposition of insoluble brown material.

OH]$^{2+}$. Their separation and estimation are described elsewhere in connection with O- to N-bonded linkage isomerization reactions of urea complexes [11].

All experiments were performed at least in duplicate, and in all cases, the cobalt recovery from the ion-exchange columns exceeded 98.5%.

Isomerization and Hydrolysis Kinetics

Solutions (1.00 *M*) of AnalaR $Na_2S_2O_3 \cdot 5H_2O$ in 0.001, 0.005, 0.010, 0.020, 0.050, 0.075 and 0.1 *M* sodium hydroxide (Volucon) were prepared. Absorbance-time traces were recorded following dissolution of a small amount of solid complex in the $S_2O_3^{2-}/OH^-$ mixture in a thermostated (25.00 ± 0.05 °C) 1 cm silica cell housed in the Cary 210 instrument. Measurements at 290 nm (and in some runs, 300 nm) were commenced without delay, within ~20 s of dissolution. In all cases the absorbance increased with time (by ~15%), except for the reaction of $[(NH_3)_5CoI](ClO_4)_2$ where a very rapid and large absorbance decrease preceded the slower and subsequent rise. The complexes used as reactants are given in the Results and Discussion section. Most data were obtained for 0.1 *M* OH^-. The very labile [12, 13] $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$ complex was used exclusively for the variable $[OH^-]$ runs. Several runs were conducted at pH ~9 by quenching the reaction of the triflato complex with sufficient NH_4^+ (2.0 equiv) to neutralize the OH^- (pH ~ 9), and following the ensuing slow increase in absorbance (~20%) at 289 nm. The quenching was achieved by adding an equal volume of 0.02 *M* NH_4ClO_4/1.00 *M* $Na_2S_2O_3$ solution to the triflate complex immediately after its complete dissolution and reaction ($\lesssim$3 s) in 0.01 *M* NaOH/1.00 *M* $Na_2S_2O_3$ at 25.0 °C.

Results and Discussion

Since the primary aim of this work was to identify the previously unknown [9] oxygen-bonded thiosulfate complex $[(NH_3)_5CoOS_2O_2]^+$, and characterize it in terms of its solution properties, it is useful to first consider the evidence cited for the assignment of the known $S_2O_3^{2-}$ complex as the S-bonded isomer. Much of the history has been summarized by Restivo *et al.* [9]. The $S_2O_3^{2-}$ complex was first synthesized in 1930 and assigned as the O-bonded isomer [14]. Later, samples prepared by the original procedures were thought to be isomeric mixtures, 85% O- and 15% S- [8]. This followed from an analysis of the Cr(II) reduction data which indicated parallel reaction paths. Such analyses are fraught with ambiguities [15] and it does not surprise that these results have been refuted [9] by a later group who reexamined the Cr(II) reduction kinetics. More significant were the reports of the single crystal X-ray structure [9, 16], unambiguously establishing the S-bonded mode. Of course this does not testify to the homogeneity of the entire sample from which crystals were selected, and an active/inactive isomer mixture could still accommodate the revised Cr(II) reduction data. For the purposes of the present work it was important to establish the physical properties of at least one pure isomer. We prepared samples by several of the original procedures [14] and examined the *total* product by ion-exchange chromatography. Crude material was found to contain a range of impurities but exhaustively recrystallized samples, as various salts (Cl^-, NO_3^-, ClO_4^-) had constant properties (^1H NMR, visible and UV spectra) and chromatographed as a single 1+ band from both Sephadex and Dowex resins. For both crude and recrystallized material, a single 1+ band having $\epsilon_{290}/\epsilon_{512.5} = 202$ was always observed. It is concluded that either a single isomer is present, or a rapidly equilibrating mixture of isomers which elute together from the ion-exchange column. Ahead we note the rate of isomerization of the O-isomer obtained *in situ* via the base hydrolysis reaction and this is sufficiently slow ($t_{1/2}$ 27 min, 25 °C) to permit the separation of the O- and S-isomers by fractional crystallization procedures, at least in principle. We conclude that a single isomer is obtained *via* any of the original routes. The S-bonding for the solid state is established by the X-ray studies [9, 16]. In solution, the enormous adsorption at 289 nm (ϵ 14130) is characteristic of Co(III)-S bonding (*cf.* $(NH_3)_5CoSCN^{2+}$, ϵ_{288}^{max} 15600) [3], and the ^1H NMR spectrum in Me_2SO-d_6 is also consistent with the S-bonding mode (δ 3.38 ppm, *trans* NH_3; δ 3.15 ppm, *cis* NH_3). The *trans*-NH_3 chemical shift is especially sensitive to the donor atom X of $[(NH_3)_5CoX]^{n+}$ [17]; *e.g.*, the typical O-donor $[(NH_3)_5CoOSO_3]^+$ shows δ 2.58 ppm (*trans* NH_3), δ 3.88 ppm (*cis* NH_3). Thus the ^1H NMR spectrum also testifies to the isomeric purity of the thiosulfato complex since no additional absorptions in these regions were observed.

Identification of O-Bonded $S_2O_3^{2-}$ and its Linkage Isomerization to the S-Isomer

In preliminary competition experiments, $[(NH_3)_5CoO_3SCF_3]^{2+}$ and $[(NH_3)_5CoO_3SCH_3]^{2+}$ were base hydrolyzed in 1.00 *M* $Na_2S_2O_3$/0.1 *M* OH^- for periods of 5 s or 5 min. The reactions were quenched with excess NH_4^+ to reduce the pH (strong H^+ reacts with free $S_2O_3^{2-}$), and the $[(NH_3)_5Co(S_2O_3)]^+$ product was separated from $[(NH_3)_5CoOH]^{2+}$ by chromatography. The thiosulfate complex was estimated using ϵ_{289} 14130, the intense absorption maximum for the S-bonded isomer. The amount of observed competition seemed to depend upon reaction time, a variable 8.4 to 11.0% for the short reaction time and a constant 9.5% for the longer time examined (5.0 min). Since the pure S-isomer was found to be completely stable in 0.1 M OH^- under the conditions, and also since the base hydrolyses of the $CH_3SO_3^-$ and $CF_3SO_3^-$ complexes are complete ($>10\ t_{1/2}$) in $\leqslant 5$ s [12], it was clear that some process or processes subsequent to the initial hydrolysis reaction were occurring. Furthermore, while the complete vis-UV spectrum of $[(NH_3)_5Co(S_2O_3)]^+$ derived from the 5.0 min reaction matched that of the authentic S-isomer ($\epsilon_{289}/\epsilon_{512.5} = 202$), the spectra of the thiosulfato complex derived from the 5 s reaction showed a significantly lower $\epsilon_{289}/\epsilon_{512.5}$ ratio (~ 160) when freshly measured. Moreover, this ratio rose slowly to the value for the pure S-isomer on standing. This latter observation accommodates the variable % $S_2O_3^{2-}$ capture found for the short time reaction, since this result depends upon the temperature and the time for the chromatography and subsequent spectral measurements.

The above results are consistent with the initial formation of $[(NH_3)_5CoSSO_3]^+$ and an additional species, also a 1+ ion, in the base hydrolysis reaction of $[(NH_3)_5CoX]^{n+}$ in the presence of $S_2O_3^{2-}$. Moreover, the results indicate that this new 1+ ion leads to the formation of some more S-bonded isomer in 0.1 *M* OH^- solution, a reaction complete in 5 min and very largely incomplete in 5 s. For the NH_4^+ quenched reaction, this new ion again produces the S-bonded isomer but much more slowly at the lower pH. Also it appears that it produces more S-isomer at pH ~9 than in 0.1 *M* OH^-.

The results imply the initial formation of both S- and O-bonded $S_2O_3^{2-}$ in the base hydrolysis reaction. The O-isomer isomerizes spontaneously and completely to the S-isomer in aqueous solution, and the reaction is base catalyzed. Some hydrolysis accompanies the reaction in OH^-, or at least there is more competitive hydrolysis than in the spontaneous process. This interpretation of the data is consistent with detailed observations [10] on other linkage isomerization systems where both isomers are known (*e.g.* O- and N-bonded NO_2^- [6], S- and N-bonded SCN^-) [3].

As yet $[(NH_3)_5CoOS_2O_2]^+$ has not been isolated as a solid salt but the experiments described ahead leave little doubt as to its existence and properties. Furthermore, before a full range of $S_2O_3^{2-}$ competition experiments could be designed and fully interpreted, there was a need to know the rate of reaction of $[(NH_3)_5CoOS_2O_2]^+$ in neutral and basic solution. At the same time, to substantiate the claim to O-bonded $S_2O_3^{2-}$, this ion was generated using several different reactants, and properties independent of its source were sought.

The reaction of $[(NH_3)_5CoX]^{n+}$ in 1.00 *M* $Na_2S_2O_3$/0.1 *M* NaOH was expected to proceed by two consecutive reactions, the first with a rate constant dependent on X, and the second independent of X. Seven different substrates, for which the base hydrolysis rate constants cover six orders of magnitude, were studied. Only the second slower step was observed in each case except for $[(NH_3)_5CoI]^{2+}$ and, to a lesser extent, for $[(NH_3)_5CoONO_2]^{2+}$ and $[(NH_3)_5CoOS(CH_3)_2]^{3+}$, the more slowly reacting of the complexes. For the iodo complex the two step nature of the reaction was clearly evident as a very fast and large absorbance decrease at 289 nm, followed by a slower rise. In all cases the absorbance rise followed a single exponential function, and the first-order rate constants obtained by the usual least-squares analysis [18] are recorded in Table I. For some complexes ($X = I^-$, NO_3^- and $(CH_3)_2SO$) D,t data after 60 s had elapsed were used, while for the other complexes [2, 12], which are hydrolyzed essentially instantly in 0.1 *M* OH^-, all of the D,t data sets were used.

The absorbance (D_o) at the completion of the faster first step (base hydrolysis of $[(NH_3)_5CoX]^{n+}$) was obtained for each run by extrapolating the later time D,t data to zero time. The final absorbance (D_∞) was directly measured. For consecutive (pseudo) first-order reactions of this kind [15, 18] the zero time intercept D'_o is related to the true D_o by the relation,

$$D'_o - D_\infty = k_1(D_o - D_\infty)/(k_1 - k_2)$$

For the very labile complexes $k_1 \gg k_2$ and $D'_o = D_o$, but for $X = Me_2SO$, NO_3^- and I^- some small corrections were required to obtain the true D_o. The base hydrolysis rate constants $k_{OH} = 0.42$, 1.85 and 0.96 M^{-1} s^{-1} have been measured [19] for the Me_2SO, NO_3^- and I^- complexes in 1.00 *M* $Na_2S_2O_3$ at 25 °C, and were used in this analysis.

There are two important results to be gleaned from Table I. First, the measured rate constants are independent of X. It follows that the reaction rate corresponds to a species which does not contain X, namely the O-bonded $[(NH_3)_5CoOS_2O_2]^+$ complex [$k_{obs} = (1.7 \pm 0.2) \times 10^{-2}$ s^{-1}, $t_{1/2} \sim 39$ s at 0.091 *M* OH^-]. Second, the ratios of initial to final absorbances are constant, *i.e.*, independent of both X and [Co]. This important result establishes that the S-/O- isomer ratio produced by the base hydrolysis reaction is independent of the leaving group, a point taken up later (and see Appendix).

Using data obtained for the secondary reaction following the effectively instantaneous base hydrolysis of the extremely labile [12] $[(NH_3)_5CoO_3SCF_3]^{2+}$ ion in 1.00 *M* $Na_2S_2O_3$ at various $[OH^-]$ (pH ~ 9, and 0.001–0.1 *M* OH^-, Table II), values for k_s and k_{OH} were obtained by a standard least squares analysis as intercept and slope, respectively, of the linear plot of k_{obs} *vs.* $[OH^-]$. Thus the complete rate law for the reaction of $[(NH_3)_5CoOS_2O_2]^+$ in solution ($\mu = 3.1$ *M*, 25 °C) is

TABLE I. Kinetic Data for the Linkage Isomerization and Hydrolysis of $[(NH_3)_5CoOS_2O_2]^+$ following the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1.00 M $Na_2S_2O_3$/0.091 M NaOH at 25 °C.

X	$10^2k_{obs}{}^a$, s^{-1}	D_o/D_∞ (obs)^{a,b}	D_o/D_∞ (Corr)^e
I^-	1.51 ± 0.26(3)	0.866 ± 0.022(3) (0.833 ± 0.021(3))^d	0.805
NO_3^-	2.16 ± 0.45(3)	0.848 ± 0.031(3) (0.831 ± 0.030(3))^d	0.789
$CH_3SO_3^-$	1.50 ± 0.05(2)	0.856 ± 0.005(2)	0.796
$CF_3SO_3^-$	1.68 ± 0.08(6)	0.868 ± 0.020(6) (0.856 ± 0.015(3))^c	0.807
$OSMe_2$	1.80 ± 0.05(2)	0.873 ± 0.012(2) (0.768 ± 0.010(2))^d	0.812
$OP(OMe)_3$	1.70 ± 0.05(2)	0.866 ± 0.004(2)	0.805
$OC(NH_2)_2$	1.80 ± 0.14(3)	0.847 ± 0.016(3)	0.788
Ave	1.74 ± 0.22	0.861 ± 0.010	0.800 ± 0.009

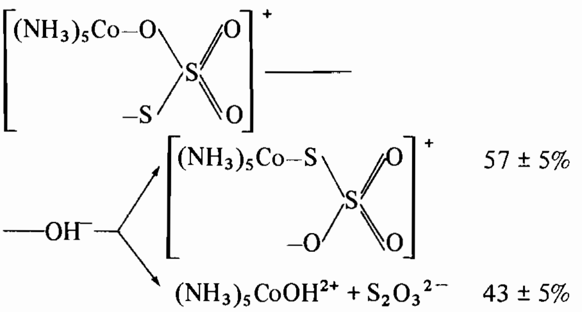
[a] Value in parenthesis is the number of determinations; standard errors are given [b] D_o/D_∞ is the ratio of the initial (immediately following the hydrolysis of $[(NH_3)_5CoX]^{n+}$) to final absorbance (289 nm) for any one run and is independent of the [Co] employed (5×10^{-4} to 2×10^{-3} M). It is also independent of the wavelength employed (289–300 nm). This ratio relates to the S- to O-bonded $[(NH_3)_5Co(S_2O_3)]^+$ ratio formed in the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ in $S_2O_3{}^{2-}$ media (see Appendix). [c] 299 nm. All other data, 289 nm. [d] Apparent D_o/D_∞. The unparenthesized values above are the actual D_o/D_∞; a small correction has been applied to allow for the (small) difference in rates between the hydrolysis of $[(NH_3)_5CoX]^{n+}$ and the subsequent reaction of $[(NH_3)_5CoOS_2O_2]^+$ which affect the determination of D_o (see text). [e] Corrected D_o/D_∞ values. Both D_o and D_∞ have been corrected for a small but significant contribution from $[(NH_3)_5CoOH]^{2+}$; D_o and D_∞ so corrected represent the absorbances due only to $[(NH_3)_5CoSSO_3]^+$ (see Appendix).

$$-d[Co]/dt = k_{obs}[Co] = k_s + k_{OH}[OH^-]$$

where $k_s = (4.3 \pm 0.3) \times 10^{-4}$ s^{-1} and $k_{OH} = 0.185 \pm 0.006$ M^{-1} s^{-1}. The results are means with standard deviations from the least squares analysis.

At 289 nm, the absorption maximum for the S-bonded $S_2O_3{}^{2-}$ complex, this ion is by far the most strongly absorbing (ϵ 14130) of the three light absorbing species present, S- and O-$[(NH_3)_5Co(S_2O_3)]^+$ and $[(NH_3)_5CoOH]^{2+}$. Indeed, the product distribution results for the reaction of $[(NH_3)_5CoOS_2O_2]^+$ in OH^-, can be quantified if it is assumed that the S-isomer, even at levels as low as 10% of the total [Co], is the *only* light absorbing species at 289 nm. As it happens, this is not quite true, since the relatively low absorption due to the major species present, $[(NH_3)_5CoOH]^{2+}$, is enhanced in the presence of $S_2O_3{}^{2-}$ (at the 1 M level). However, the results of the competition experiments together with the measured pure absorption spectra in 1 M $Na_2S_2O_3$ permitted the necessary small corrections (Appendix).

For the reaction of $[(NH_3)_5CoOS_2O_2]^+$ in OH^-, the total rise in absorbance at 289 nm systematically increased with decreasing $[OH^-]$, for any one run at a given [Co]. This fact, recorded as D_o/D_∞ (Table II), was used to deduce the course of reaction of the O-isomer in base:



Since the O-isomer was not isolated and this result could not be determined by direct measurement, in this analysis (Appendix) it had to be assumed that the O-isomer isomerized to the S-form by the spontaneous (k_s) pathway without competitive hydrolysis. This assumption is supported experimentally by the $S_2O_3{}^{2-}$ competition results, described ahead. It is at least certain that the O-isomer involves more competitive hydrolysis by the base catalyzed (k_{OH}) route.

The O-/S-isomer equilibrium must lie essentially fully to the side of the S-isomer for the following reasons. The (separated) product of the competition reaction showed $\epsilon_{289}/\epsilon_{512.5} = 202$, after the initial O-isomer component had been isomerized either by the spontaneous or base catalyzed route. This ratio is identical to that of the authentic S-isomer. Furthermore, if the equilibrium were detectably reversible, the pure S-isomer should isomerize to the equilibrium isomer distribution with the *same rate* as that measured for the O-isomer ($t_{1/2} = 37$ s in 0.1 M OH^-, $t_{1/2} \simeq 27$ min in neutral solution; 25 °C, $\mu = 3$ M). However no changes in the UV spectrum of $[(NH_3)_5CoSSO_3]^+$ were observed over at least 48 hr in neutral solution or 5 min in 0.1 M OH^-, although slow loss of $S_2O_3{}^{2-}$ and/or NH_3 does occur over longer periods in strong OH^-.

The O- to S-linkage isomerization reported here represents yet another reaction of the type which proceeds by both spontaneous and base catalyzed pathways [10]. Undoubtedly the catalysis arises by deprotonation of a coordinated amine to generate the reactive amido complex $[(NH_3)_4(NH_2)CoOS_2O_2]^+$,

TABLE II. Kinetic Data for the Isomerization and Hydrolysis of $[(NH_3)_5CoOSSO_2]^+$ in 1.00 *M* $Na_2S_2O_3$/NaOH ($\mu \simeq 3$ *M*) at 25 °C.

M			s^{-1}		
$[OH^-]_o$	$[Co]_o$	$[OH^-]$[a]	$10^4\ k_{obs}$[b,c]	10^4 k (calc)[c]	D_o/D_∞ (obs)[b,d]
9.10×10^{-2}	1.0×10^{-3}	9.01×10^{-2}	168 ± 8(6)	171	0.868 ± 0.020(6) (0.807)[e]
5.00×10^{-2}	1.1×10^{-3}	4.90×10^{-2}	95 ± 1.5(4)	95	0.857 ± 0.009(4)
1.00×10^{-2}	9.1×10^{-4}	9.1×10^{-3}	20.6 ± 0.4(2)	21.2	0.840 ± 0.015(2)
5.00×10^{-3}	1.1×10^{-3}	4.0×10^{-3}	12.0 ± 0.2(3)	11.7	0.838 ± 0.023(3)
1.00×10^{-3}	6.3×10^{-4}	4.4×10^{-4}	4.45 ± 0.21(2)	5.1	0.782 ± 0.003(2) (0.706)[f]
pH ≃ 9	$\sim 1.0 \times 10^{-3}$	~0	4.50 ± 0.15(4)	4.3	0.796 ± 0.003(3) (0.706)[f]

[a] $[OH^-] = [OH^-]_o - 0.89[Co]_o$; $[OH^-]_o$ = initial $[OH^-]$, $[OH^-]$ = the concentration *after* the hydrolysis of the generating $[(NH_3)_5CoO_3SCF_3]^{2+}$ complex which consumes 0.89 equivalents of OH^- in forming $[(NH_3)_5CoOH]^{2+}$ (89%) and $[(NH_3)_5Co(S_2O_3)]^+$ (11%). Further changes in $[OH^-]$ through partial (43%) hydrolysis of $[(NH_3)_5CoOS_2O_2]^+$ (30% of total $[(NH_3)_5Co(S_2O_3)]^+$) are negligible (at most, 43 × 0.11 × 0.3 = 1.4%$[Co]_o$).

[b] Mean and standard deviations; the number of determinations is given in parenthesis. For D_o/D_∞ the precision (reproducibility) was usually better than the accuracy, ±0.010.

[c] $k = k_s + k_{OH}[OH^-]$. Least squares analysis of the k_{obs}, $[OH^-]$ data gave $k_s = (4.32 \pm 0.31)\ 10^{-4}\ s^{-1}$, $k_{OH} = (0.185 \pm 0.006)\ M^{-1}\ s^{-1}$, and k_{calc} was obtained using the above equation and these mean values.

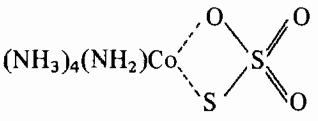
[d] The OH^- dependence of D_o/D_∞ (initial/final absorbance for any one run; independent of $[Co]_o$) defines the reaction course for $[(NH_3)_5CoOS_2O_2]^+$ (57% $CoSSO_2^+$, 43% $CoOH^{2+}$) (see Appendix).

[e] D_o/D_∞(corr): see Table I, footnote e.

[f] D_o/D'_∞(corr): see Table I, footnote e. The last two entries for D_o/D_∞ (0.782, 0.796) have been averaged and then corrected.

as appears to be the case for the base catalyzed linkage isomerizations of $[(NH_3)_5CoSCN]^{2+}$ [3] (to give $CoNCS^{2+}$) and $[(NH_3)_5CoONO]^{2+}$ (which yields $CoNO_2^{2+}$). All of these reactions are intramolecular processes. The isomerized product is thermodynamically unstable with respect to $[(NH_3)_5CoOH]^{2+}$ and the free anion, and hence freely dissociated ligand from $[(NH_3)_5Co(Y{-}Y')]^{n+}$ should lead to $[(NH_3)_5CoOH]^{2+}$ and Y–Y′ rather than $[(NH_3)_5Co(Y'{-}Y)]^{n+}$. Intimate or tight-ion-pair intermediates or transition states such as I have been proposed [10], as well as formally seven-coordinate species such as II:

$(NH_3)_4(NH_2)Co^{2+}{\cdot}S_2O_3^{2-}$ I



II

Although it is generally agreed that the pentaamminecobalt(III) linkage isomerization processes are essentially dissociative [10], there are some trends emerging which bear on the detailed mechanism. Discussion centres on the base catalyzed processes but similar considerations possibly apply to the spontaneous linkage isomerization reactions. First, there is a great deal of evidence to suggest that the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ proceeds *via* the reactive reduced coordination number amido intermediate $[(NH_3)_4(NH_2)Co]^{2+}$, which can capture nucleophiles present in solution such as $S_2O_3^{2-}$, SCN^- or NO_2^-, along with solvent water [2]. This intermediate cannot be of the same type as that involved in the linkage isomerization of $[(NH_3)_5CoSCN]^{2+}$, $[(NH_3)_4(NH_2)Co{\cdots}NCS]^+$, since the latter does not exchange NCS^- with $N^{14}CS^-$ present in the bulk solution [3]. This fact makes the process truly intramolecular, and the result is accommodated by some bond making by the incoming nucleophile in the activated state, presumably because of its close proximity to the metal ion in the ground state. Thus there is much less competitive hydrolysis in the linkage isomerization process than in the corresponding competition reaction and, quite likely, they are separate processes. Another interesting facet of these linkage isomerization reactions is the fact that there is more competitive hydrolysis by the base catalyzed path than by the spontaneous route. This is true of the SCN^- [3], $NH_2SO_3^-$ [20], NH_2CONR_2 [11] and FSO_3^- [21] systems as well as the present $S_2O_3^{2-}$ system. This is equivalent to noting that the acceleration afforded by OH^- is more significant for the hydrolysis reaction than for the linkage isomerization process. This trend is accommodated by recognizing the partly associative nature of the linkage isomerization reaction. For the spontaneous pathway, which lacks the dissociative labilization afforded by NH_2^- of the conjugate base route, nucleophilic assistance from the pendant S-atom of the ambidentate ligand should be more prominant.

Capture of $S_2O_3^{2-}$ in the Base Hydrolysis Reaction

The production and measurement of $[(NH_3)_5CoSSO_3]^+$ and $[(NH_3)_5CoOS_2O_2]^+$ for the reaction $[(NH_3)_5CoX]^{n+} + OH^- + S_2O_3^{2-}$ was generally carried out by allowing sufficient time in 0.1 *M* OH^-, (5.0 min 25 °C) for the O-isomer to decay completely to $[(NH_3)_5CoSSO_3]^+$ (57%) and $[(NH_3)_5CoOH]^{2+}$ (43%), and then simply measuring the total S-isomer produced. These results, coupled with the S-/O-isomer ratios deduced from the kinetics, enable a complete description in terms of the % S- and % O-isomer initially formed.

The results for seven different leaving groups are compiled in Table III. There are two main features. First, the total % $S_2O_3^{2-}$ capture increases detectably with increasing formal charge on the complex, but is essentially constant within each set of 2+ and 3+ ions. The obvious and only exception is the unsubstituted O-urea complex; however this ion appears to react in the presence of 2– ions such as SO_4^{2-} and $S_2O_3^{2-}$ with significantly more C–O cleavage (~30%) than that observed [2] in the presence of 1– anions (2.5%). Anion competition cannot occur by this path, hence the apparent reduction (8.7%; *cf.* 10.6% for the other 3+ ions, Table III). This special problem is dealt with elsewhere [11, 19]. The explanation for the slight dependence of the % anion competition on the formal charge (but not the nature) of the leaving group has been given previously [2, 22]. It suffices to state here that the data are consistent with the production of the reactive intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ which samples an inherited environment richer in competing anion for the more highly charged substrates. The second and important feature of the results (Table III) is the constant S-/O-isomer ratio (70 ± 3% S-, 30 ± 3% O-). Its constancy, even under conditions where the total anion competition varies, strongly supports the case for the reactive $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate. Such an intermediate requires properties independent of the leaving group for the capture of the terminal S- or O- of $S_2O_3^{2-}$ from a constant ion-atmosphere, as found recently also for NO_2^- competition where both N- and O- compete [4].

The oxygen of $S_2O_3^{2-}$ is captured with close to the same efficiency as SO_4^{2-} (~5.0% [19]), when the results are statistically corrected (3:4). As found for SCN^-, the more poorly solvated terminal sulfur of $S_2O_3^{2-}$ is a significantly better competitor. This is consistent with the general picture for anion competition in the base hydrolysis reaction [2, 4].

It is timely to recapitulate on the competition results for the short and longer time reactions of $[(NH_3)_5CoO_3SR]^{2+}$ (R = CF_3, CH_3) in 1.0 *M* $Na_2S_2O_3$/0.1 *M* OH^- at 25 °C. The amount of $S_2O_3^{2-}$ capture found for the short term (5 s) reactions was 8.4 ± 0.4%, deduced from the freshly measured UV spectra (ϵ_{289}^{max} 14130) after chromatography at ~2 °C.

TABLE III. Product Distributions for the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1.00 *M* $Na_2S_2O_3$/0.10 *M* NaOH (μ = 3.1 *M*) at 25 °C.

X	$\%CoSSO_3^+$ (obs)[a]	$\%\Sigma(CoSSO_3^+ + CoOS_2O_2^+)$[b] %	D_o/D_∞(corr)[c]	$\%CoSSO_3^+$	$\%CoOS_2O_2^+$
Me_2SO	11.0, 11.0	12.6	0.812	72	28
$PO(OMe)_3$	10.7, 10.6	12.2	0.805	71	29
$OC(NH_2)(NMe_2)$	10.7, 11.1, 10.7, 10.0 (10.4, 10.8, 10.4, 9.7)[d]	12.2			
$OC(NH_2)_2$	7.7, 7.6, 8.4, 8.2, 7.9, 7.8, 7.8 (7.0, 6.9, 7.6, 7.4, 7.1, 7.0, 7.0)[e]	9.1	0.788	68	32
NO_3^-			0.789	68	32
I^-	9.7, 9.9	11.3	0.805	71	29
$CH_3SO_3^-$	9.6, 9.7	11.1	0.796	69	31
$CF_3SO_3^-$	9.3, 9.4	10.8	0.807	71	29
		Ave	0.800	70 ± 2	30 ± 2

[a] Observed % S isomer for a 5.0 min reaction time. This represents >10 $t_{1/2}$ for the reaction of the co-formed O-bonded isomer (30% of O- plus S-) which in 5 min produces more S- isomer (57% of O-) and $CoOH^{2+}$ (43% of O-). Data are ±0.4%. [b] Total $S_2O_3^{2-}$ capture; corrected for the loss of O- isomer through subsequent reaction (see Appendix). The other product is $CoOH^{2+}$. Data are ±0.4%. [c] Data from Table I; used to calculate the % S- and % O-isomer, recorded in the last two columns. [d] Observed values; numbers above are corrected for some C–O cleavage (2.5%, urea) and O- to N- urea linkage isomerization (7%, urea, 3% $ureaMe_2$) to give the competition for the Co–O bond cleavage pathway.

The spectra of the aged eluate solutions (pH ~ 5) yielded 11.0 (±0.4)%; the difference corresponds to 2.6% absolutely. It is important to note that the $\epsilon_{289}/\epsilon_{512.5}$ ratios (~200) for the spectra of the aged $[(NH_3)_5Co(S_2O_3)]^+$ solutions agree with that for the pure S-isomer, supporting the contention that the O-isomer isomerizes in neutral solution without the formation of significant amounts of $[(NH_3)_5CoOH_2]^{3+}$. Thus, if *all* the O-isomer (which is assumed to absorb negligibly at 289 nm) isomerizes to the S-form, the results correspond to an S-/O-isomer ratio of 8.4:2.6, *i.e.* 76% S, 24% O. This agrees well with the result deduced independently from the kinetic studies (70% S-, 30% O-). Furthermore, using the fact that ~57% of the O-isomer is converted to the S-isomer in strong OH^-, we calculate $8.4 + 0.57(2.6) = 9.9\%$ S-isomer for the long term (5 min) base hydrolysis reaction. Again, this agrees well with that directly observed (9.5 (±0.4)%, Table III). In early experiments, the % $S_2O_3^{2-}$ capture found for 5 s and 5.0 min reactions were, fortuitously, very similar. The chromatography (at ~20 °C) took ~1 hr, sufficient time for $\gtrsim$ half of the O-isomer to isomerize to the S-form.

Finally, it is noted that this report represents the first strong evidence for monodentate oxygen-bonded thiosulfate, although in passing $S_2O_3^{2-}$ functioning as an O,S-chelate in $[Co(en)_2(S_2O_3)]^+$ [23] warrants mention.

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Appendix

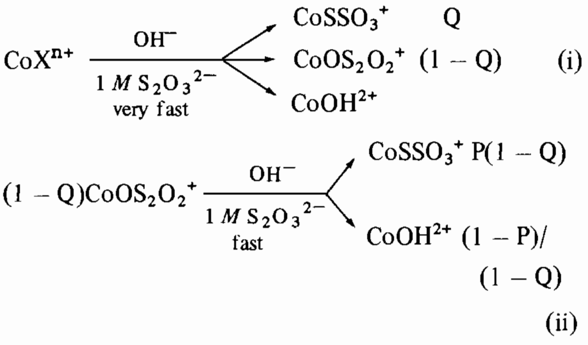
In the following it is assumed that $[(NH_3)_5CoSSO_3]^+$ dominates the light absorption at 289 nm for mixtures with $[(NH_3)_5CoOH]^{2+}$ and $[(NH_3)_5CoOS_2O_2]^+$. This is not strictly true, but becomes so when the absorbances have been corrected for a contribution (23–31%) from $[(NH_3)_5CoOH]^{2+}$ and an almost negligible (<1.5%) contribution from $[(NH_3)_5CoOS_2O_2]^+$. This was possible using the results from competition experiments (which directly provided the relative amounts of the two major light absorbing species), and the measured molar extinction coefficients for the three cations in 1.00 *M* $Na_2S_2O_3$. The complex $[(NH_3)_5CoOSO_3]^+$ was used as a model for the O-bonded $S_2O_3^{2-}$ complex $[(NH_3)_5CoOS_2O_2]^+$ but since at $\lesssim$3% of total [Co] it contributes negligibly to the absorbance, inaccuracy here is immaterial.

$$[(NH_3)_5CoSSO_3]^+ \quad \epsilon_{289}\ 14130\, M^{-1}\, cm^{-1}$$

$$[(NH_3)_5CoOSO_3]^+ \quad \epsilon_{289}\ 747\, M^{-1}\, cm^{-1}$$

$$[(NH_3)_5CoOH]^{2+} \quad \epsilon_{289}\ 535\, M^{-1}\, cm^{-1}$$

Consider the reaction sequences (P, Q are mole fractions):



$$\mathrm{CoX}^{n+} \xrightarrow[\substack{1\,M\,\mathrm{S_2O_3}^{2-}\\ \text{very fast}}]{\mathrm{OH}^-} \begin{array}{ll} \mathrm{CoSSO_3}^+ & Q \\ \mathrm{CoOS_2O_2}^+ & (1-Q) \\ \mathrm{CoOH}^{2+} & \end{array} \qquad \text{(i)}$$

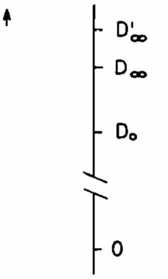
$$(1-Q)\mathrm{CoOS_2O_2}^+ \xrightarrow[\substack{1\,M\,\mathrm{S_2O_3}^{2-}\\ \text{fast}}]{\mathrm{OH}^-} \begin{array}{ll} \mathrm{CoSSO_3}^+ & P(1-Q) \\ \mathrm{CoOH}^{2+} & (1-P)/(1-Q) \end{array} \qquad \text{(ii)}$$

$$(1-Q)\mathrm{CoOS_2O_2}^+ \xrightarrow[\text{slow}]{\mathrm{H_2O}} \mathrm{CoSSO_3}^+ \quad (1-Q) \qquad \text{(iii)}$$

The problem was to determine P, and values of Q for each leaving group X.

Reaction (ii) occurs subsequently to and much more slowly than (i), in the same medium. Reaction (iii) proceeds when (i) is quenched with excess $\mathrm{NH_4}^+$ immediately following its completion. It involves no competitive aquation.

D_o, D_∞ and D'_∞ are the absorbances (289 nm) at the completion of reactions (i), (ii) and (iii), respectively. D_∞ and D'_∞ were directly measured experimentally; D_o was obtained by extrapolating the absorbance-time data for reaction (ii) to t = 0 (see Experimental).



It is intuitively obvious and can be proved readily that the rise in absorbance from D_∞ to D'_∞ due to reaction (iii) is directly proportional to the amount of O-isomer formed in (i), while D_o is proportional to the amount of S-isomer formed in (i). Thus, the S-/O-isomer ratio for reaction (i) is

$$D_o/(D'_\infty - D_\infty) \text{ i.e., } Q = D_o/D'_\infty \qquad \text{(iv)}$$

It is also clear that D_∞ is lower than D'_∞ by an amount proportional to the amount of CoOH^{2+} produced in reaction (ii); and it is easily shown that

$$P = (D_\infty - D_o)/(D'_\infty - D_o) = \frac{1 - 1/(D_o/D_\infty)}{1 - 1/(D_o/D'_\infty)} \qquad \text{(v)}$$

The quantities D_o and D_∞ were determined in a single experiment (*i.e.*, [Co] = constant) and the result recorded as D_o/D_∞ since this is independent of [Co]. This ratio was measured for at least three runs at different [Co] and the results averaged. Similarly, D_o and D'_∞ were measured in single experiments, the results were recorded as D_o/D'_∞ and values averaged over several runs.

In the $\mathrm{S_2O_3}^{2-}$ competition experiments, the actual Σ(%S- + %O-) is related to the observed %S-isomer (5.0 min reaction) as follows:

$$\begin{aligned} \Sigma(\%\text{S-} + \%\text{O-}) &= [\%\text{S-(obs)}]\,[1/(Q + P(1-Q))] \\ &= [\%\text{S-(obs)}]\,[1/(Q + 0.57(1-Q))] \\ &= [\%\text{S-(obs)}]\,[1/(0.57 + 0.43Q)] \end{aligned}$$

and since Q = %S-/(%S- + %O-) = 0.70 in all cases,

$$\Sigma(\%\text{S-} + \%\text{O-}) = [\%\text{S-(obs)}] \times 1.15$$