1344 ms, 1314 m, 1230 s, 1191 vs, 1146 s, 1120 s, 1127 m, 1007 s, 981 s, 965 s, 931 vs, 870 s, 795 ms, 769 w, 699 vw, 672 w, 624 m cm^{-1}. ^{19}F NMR: ϕ 21.90 (NF_2, br), −101.6 (CF_2N, tr, $J = 2.07$ Hz), −112.7 (CF_2C, br). CI MS [*m/e* (species), intensity] 331 ($M^+ - F_5N$), 2.57; 319 ($M^+ - CF_5N$), 1.8; 293 ($M^+ - C_2F_5N_2$), 0.9; 281 ($M^+ - CF_7N$), 4.3; 269 ($M^+ - C_2F_7N$), 2.9; 231 ($M^+ - C_2F_9N$), 5.7; 219 ($C_5HF_6N_2O^+$), 7.9; 181 ($C_5HF_4N_2O^+$), 7.8; 169 ($C_4HF_4N_2O^+$), 16.3; 149 ($C_4F_3N_2O^+$), 4.2; 131 ($C_4HF_2N_2O^+$), 17.1; 119 ($C_3HF_2N_2O^+$), 23.6; 99 ($C_3FN_2O^+$), 6.4; 81 ($C_2F_3^+$, $C_3HN_2O^+$), 14.8; 69 (CF_3^+, $C_2HN_2O^+$), 100; 57 (CHN_2O^+), 66.1. Anal. Calcd for $C_8F_{12}N_6O_2$: C, 21.81; N, 19.09. Found: C, 21.32; N, 19.31.

Synthesis of 17 and 18. A large excess of phosgene was condensed on a solution of **9** (0.5 mmol) in diethyl ether at −196 °C. The temperature was raised slowly to and held at −20 °C for 30 min and then raised to 25 °C for 30 min with shaking. The solvent was removed under vacuum leaving **17** in approximately quantitative yield. Heating **17** at 120 °C for 4 h under vacuum gave nearly quantitative conversion to **18**.

Spectral data for **17**. IR (KBr disk): 3442 s, 3361 s, br, 3268 w, 3212 w, 1772 vs, 1675 vs, 1440 w, 1226 vs, 1134 vs, 970 s, 923 s, 870 w, 740 w, 700 vw, 625 vw cm^{-1}. NMR: ^{19}F, ϕ 19.00 (NF_2, br), −108.1 (CF_2); ^1H, δ 5.27 (NH_2). CI MS [*m/e* (species), intensity]: 226 ($M^+ + 3$), 2.6; 225 ($M^+ + 2$), 2.1; 224 ($M^+ + 1$), 7.5; 223 (M^+), 5.9; 204 ($M^+ - F$), 0.7; 185 ($M^+ - 2F$), 1.5; 173 ($M^+ - NF_2$, ^{37}Cl isotope), 12.4; 171 ($M^+ - NF_2$), 37.4; 160 ($M^+ - CClO$), 1.5; 102 ($NF_2CF_2^+$), 7.9; 92 ($C_2F_2NO^+$), 63.5; 91 ($C_2HF_2N_2^+$), 23.6; 83 ($NF_2CF_2^+$), 3.9; 78 ($C_2H_2F_2N^+$), 49.8; 65 ($C^{37}ClO^+$), 31.6; 63 ($C^{35}ClO^+$), 100; 42 ($CH_2N_2^+$), 47.5. Anal. Calcd for $C_3H_2ClF_4N_3O_2$: C, 16.14; H, 0.89; N, 18.83. Found: C, 15.53; H, 1.01; N, 19.27.

Spectral data for **18**. IR (KBr disk): 3500–2500 br, 1801 (ν_{CO}) br, s, 1673 ($\nu_{C=N}$) s, 1599 m, 1510 m, 1436 w, 1331 m, 1235 vs, 1200 w, 1175 vs, 1115 m, 976 m, 932 vs, 904 ms, 814 vw, 793 m, 747 m, 702 w, 675 w, 655 w, 615 w, 536 vw, 514 vw cm^{-1}. NMR: ^{19}F, ϕ 22.18 and 19.34 (NF_2, endo and exo), −104.0 and −107.8 (CF_2, endo and exo); ^1H, δ 5.46 (s, br). EI MS [*m/e* (species), intensity]: 161 ($M^+ - O$), 18.6; 149 ($M^+ - 2F$), 2.5; 123 ($C_2F_3N_3^+$), 2.3; 109 ($C_2F_3N_2^+$), 2.7; 91 ($C_2HF_2N_2^+$), 10.2; 90 ($C_2F_2N_2^+$), 5.9; 85 ($C_2HN_2O_2^+$), 60.4; 77 ($C_2HF_2N^+$), 7.6; 76 ($C_2F_2N^+$), 7.2; 52 (NF_2^+), 90.9; 44 (CO_2^+), 100. Anal. Calcd. for $C_3HF_4N_3O_2$: C, 19.25; H, 0.53; N, 22.45. Found: C, 19.08; H, 0.65; N, 22.52.

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Kinetics and Mechanism of the Oxidation of Coordinated Thiosulfate by Peroxymonosulfate

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Peroxymonosulfate, HSO_5^-, reacts cleanly with $[(NH_3)_5CoS_2O_3]^+$ to form $[(NH_3)_5CoS_2O_5]^+$. The reaction proceeds via two consecutive nucleophilic additions of the terminal peroxy oxygen to the coordinated thiosulfate. The kinetics of these reactions are reported along with an ^{18}O tracer study.

Introduction

The oxidation reactions of free thiosulfate have been examined by using a variety of oxidants.[1-3] Many important analytical procedures utilize these reactions.[4] The usual products are sulfate or tetrathionate, but in some cases, a mixture of these two products is obtained. A few studies involve the activation of thiosulfate by coordination to a metal ion.[5,6] For example, the oxidation of $S_2O_3^{2-}$ by molecular oxygen is known to be slow, but in the presence of a copper(II) ammine complex the reaction rates are dramatically increased. It was postulated that coordination of $S_2O_3^{2-}$ to the metal center catalyzed the redox reaction with O_2. However, in these systems, the metal ion is labile and no definitive structure–reactivity relationship can be elucidated. In order to further probe the effects of metal ions on thiosulfate oxidations, the reactions of a substitution-inert Co(III)–$S_2O_3^{2-}$ complex were investigated by using peroxymonosulfate, HSO_5^-, a versatile oxidizing agent.

Peroxymonosulfate is a strong oxidant and has been employed in a wide range of oxidation reactions.[7,8] Thus far, two major reaction pathways have been proposed. The most common involves a two-electron oxidation where transfer of the terminal peroxy oxygen occurs. For example, HSO_5^- reacts with $[(NH_3)_5CrN_3]^{2+}$ to form $[(NH_3)_5CrNO]^{2+}$ and N_2.[9] Recently, Thompson et al. have demonstrated the role of the sulfate radical ion, $SO_4^{\bullet-}$, in the reaction of HSO_5^- with VO^{2+}, a one-electron reductant.[10] Surprisingly, the kinetic results were relatively simple, which is in contrast with other radical-ion reactions.

In this paper, a study of the reaction of $[(NH_3)_5CoS_2O_3]^+$ with HSO_5^- is reported. Unlike the case of most other thiosulfate redox reactions, a simple kinetic pathway was observed and a new oxysulfur cobalt(III) complex produced.

Experimental Section

Peroxymonosulfate solutions were prepared from OXONE ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) purchased from Aldrich. Solutions were made as needed and standardized by using iodometric techniques.[10] No appreciable decomposition (<2%) of HSO_5^- was detectable after standing for a 24-h period.

$[Co(NH_3)_5S_2O_3](ClO_4)$ was prepared by the method of Ray[11] and was purified by using CM25 Sephadex cation-exchange resin.

The final yellow product from the reaction of the thiosulfate complex with HSO_5^- was isolated from the reaction mixture by adding solid $NaClO_4$. Recrystallization from water gave a pure compound. Elemental analysis was performed by Galbraith Laboratories.

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Table I. UV–Vis Data for Cobalt(III)–Sulfur Complexes

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	ref
$[Co(NH_3)_5SO_3]^+$	457, 278	148, 17 800	16
$[Co(NH_3)_5S_2O_5]^+$	464, 340	330, 15 400	this work
trans-$[Co(NH_3)_4(SO_3)_2]^-$	430, 327	490, 29 500	17
$[Co(NH_3)_5OSO_2]^+$ *a*	518, 330	88, 2100	16
$[Co(NH_3)_5S_2O_3]^+$	512, 289	64, 12 800	18

[a] Oxygen-bound-sulfite complex.

Table II. Stoichiometric Determinations

ratio added $[HSO_5]$:[Co(III)]	ratio $[HSO_5^-]$ consumed:[Co(III)][a]
10:1	1.95
50:1	2.01
100:1	2.11
	2.02 av

[a] Excess HSO_5^- determined iodometrically.

Table III. Kinetic Results for the HSO_5^-–$[(NH_3)_5CoS_2O_3]^+$ Reaction[a]

$10^3[HSO_5^-]$, M	$[H^+]$, M	k_{obsd}, s^{-1} [b]	k_{obsd}, s^{-1} [c]
0.10	0.10	0.46	0.10
0.50	0.10	0.72	0.12
1.0	0.10	1.1	0.14
2.0	0.10	2.0	0.18
5.0	0.10	3.6	0.30
0.10	0.50	0.43	0.11
2.0	0.50	1.8	0.19
5.0	0.50	3.9	0.28
2.0	0.75	2.0	0.18
5.0	0.75	4.4	0.31
0.50	1.0	0.79	0.12
2.0	1.0	1.9	0.20
5.0	1.0	4.1	0.30

[a] Ionic strength = 1.0 ($LiClO_4$), T = 25.0 °C, rates measured at λ = 320 nm, and $[[(NH_3)_5CoS_2O_3]^+] \sim 10^{-5}$ M. [b] k_{obsd} for the first step. [c] k_{obsd} for the second step.

The stoichiometry for the reaction of HSO_5^- with $[Co(NH_3)_5S_2O_3]^+$ was determined by addition of varying excess amounts of HSO_5^- to a known complex concentration. The amount of HSO_5^- remaining was determined iodometrically.

Oxygen-18 tracer studies were carried out with 2–8 times enriched ^{18}O water. The thiosulfate complex was dissolved in enriched water, HSO_5^- was added, and the final yellow product was isolated as the perchlorate salt. Pumping under a vacuum for 3 h and gentle heating with an air gun removed any water of hydration from the solid. The oxygens in the anhydrous solid were then converted into CO_2 by heating with dried $Hg(CN)_2/HgCl_2$ in a break-seal tube at 400 °C for 2 h. Isolation of the CO_2 was carried out by using gas chromatography. Isotopic analyses were performed on a Nucleide RMS-6 mass spectrometer.

The kinetic experiments utilized a Durrum Model D-110 stopped-flow spectrophotometer interfaced with a DASAR digital data collection module. The absorbance–time traces were biphasic, indicating the consecutive growth and decay of an intermediate. Rates were measured under pseudo-first-order conditions with respect to $[HSO_5^-]$ at 320 nm, the absorption maximum of the intermediate product. The two rates were well separated, and the observed rate constants were obtained directly from the trace by curve matching with a calibrated decay generator. The ambiguity associated with consecutive reactions[12] was resolved by computer simulation of the traces. An exact fit of the experimental data was given only for the case where the faster reaction is associated with the growth of the intermediate. This fit gave a constant value for the extinction coefficient of the intermediate of $(1.0 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}. Rate constants are the average of three to five runs and are precise to better than 10%.

Stock solutions of $LiClO_4$ and $HClO_4$ were prepared from anhydrous $LiClO_4$ and doubly distilled $HClO_4$, both purchased from the G. Frederick Smith Co. These solutions were standardized by using routine procedures described elsewhere.[13] All other chemicals were of reagent grade and were used as received. Water used in this study came from a Millipore ion-exchange system.

UV–vis spectra were obtained with a Beckmann Acta III spectrophotometer. The rapid-scan spectrophotometer was a Harrick rapid-scan monochromator interfaced with a Durrum stopped-flow spectrometer, as designed by Dr. R. DeSa (Olis Jefferson, GA).

Results and Discussion

When aqueous solutions of HSO_5^- and $[(NH_3)_5CoS_2O_3]^+$ are mixed, a bright yellow solution is immediately formed that bleaches to a very pale yellow. The addition of solid sodium perchlorate results in the precipitation of a yellow solid. As may be seen in Table I, the absorption maxima of this complex corresponds closely with other oxysulfur complexes bound through a sulfur atom. The proton NMR spectrum gives the trans-NH_3 peak at 3.4 ppm and the cis-NH_3 at 2.6 ppm. This difference in chemical shift is consistent with a Co–S bond present in the complex.[14] The elemental analysis coupled with the UV–vis data support the formula $[Co(NH_3)_5S_2O_5]ClO_4{\cdot}H_2O$. Anal. Calcd: 4.20, H; 17.3 N; 15.8 S. Found: 4.20, H; 18.1, N; 15.8, S.

The stability of this complex is somewhat surprising considering the dissociation of free metabisulfite is almost complete at low $S_2O_5^{2-}$ concentrations:[15]

$$H_2O + S_2O_5^{2-} \rightleftarrows 2HSO_3^- \quad K \sim 15$$

Attempts to synthesize this complex starting with $[(NH_3)_5CoOH_2]^{3+}$ and $Na_2S_2O_5$ in aqueous media were unsuccessful and generally resulted in a sulfite salt of the beginning aquo complex. In nonaqueous media, however, the decomposition of $S_2O_5^{2-}$ to HSO_3^- is suppressed. When $(PNP)_2S_2O_5$ (PNP ≡ bis(triphenylphosphoranylidene)ammonium] and $[(NH_3)_5Co(trif)](trif)_2$ (trif ≡ $F_3CCO_2^-$) are mixed in dry sulfolane, a yellow solution is formed from which a solid can be isolated. The UV–vis characteristics of this solid in 0.1 M HCl are identical with those for the HSO_5^- reaction product described above. Since no other cobalt products were found by using ion-exchange chromatography, the metabisulfite complex appears to be formed exclusively.

When HSO_5^- was in excess, the reaction stoichiometry of HSO_5^- with $[(NH_3)_5CoS_2O_3]^+$ was shown to be 2:1 (Table II). No variation of this ratio was observed at different HSO_5^- concentrations (in excess) or with hydrogen ion concentrations between 0.1 and 1.0 M.

The net ionic equation for this reaction may be written as follows:

$$2HSO_5^- + [(NH_3)_5CoS_2O_3]^+ \rightarrow 2HSO_4^- + [(NH_3)_5CoS_2O_5]^+$$

The bright yellow intermediate formed upon mixing is too unstable to be isolated as a solid. However, it was characterized spectrophotometrically by using a rapid-scan spectrophotometer interfaced with a stopped-flow apparatus. The spectra are shown in Figure 1. Two peaks appear in 1 s after mixing with positions at 378 and 320 nm. After ~10 s, the peaks disappear and a single peak is observed at 340 nm. Rates of intermediate (int) formation and its slow subsequent decay measured at 378 and 320 nm were found to be the same, thereby indicating only one intermediate present during the oxidation reaction.

Kinetic data were obtained for both steps of this reaction:

$$HSO_5^- + [(NH_3)_5CoS_2O_3]^+ \rightarrow [int] \rightarrow [(NH_3)_5CoS_2O_5]^+$$

The first step follows the rate law

$$\frac{d[int]}{dt} = k_{obsd}[[(NH_3)_5CoS_2O_3]^+]$$

where $k_{obsd} = k_1[HSO_5^-] + k_{-1}$. The kinetic data are given in Table III. Plotting k_{obsd} vs $[HSO_5^-]$ gives a straight line with the slope and intercept equal to k_1 and k_{-1}, respectively. There

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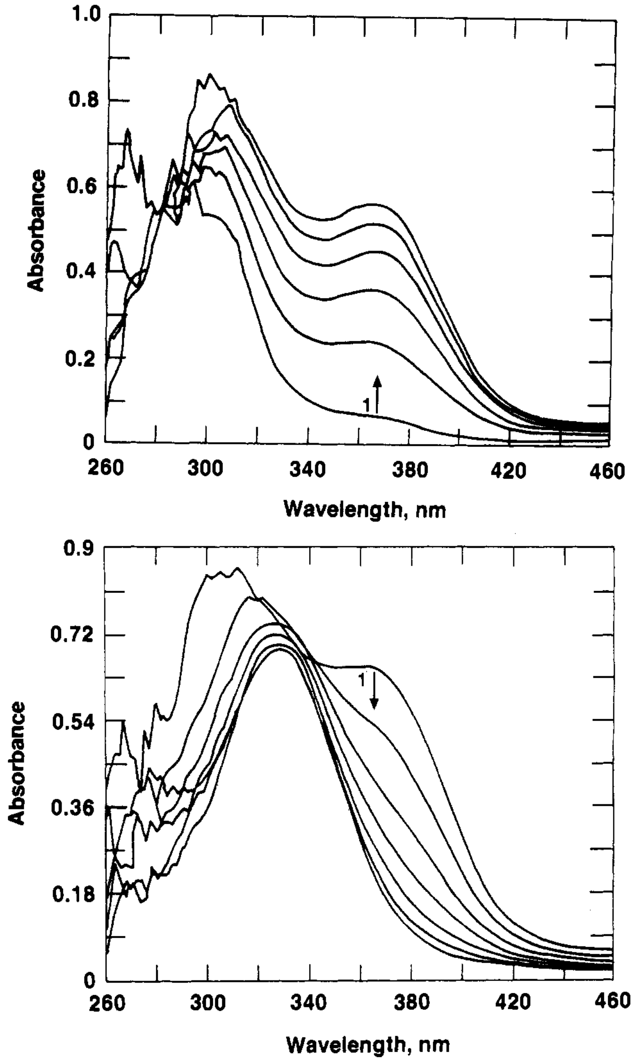


Figure 1. Top: Rapid-scan spectra for the formation of the intermediate complex (λ_{max} ~310–320 and 370 nm). The total scan time is 1 s (traces were taken every 0.16 s). Conditions: [Co] ~ 2×10^{-5} M, [HSO_5^-] ~ 5×10^{-3} M, [H^+] ~ 0.1 M ($HClO_4$), I = 1.0 M ($LiClO_4$), T = 25 °C. The noise in the 300-nm region is a result of instrumental limitations. Bottom: Rapid-scan spectra for the decay of the intermediate to the final product. The total scan time is 12 s (traces were taken every 1.7 s). Conditions: same as for the top spectra. The noise in the 300-nm region is a result of instrumental limitations.

is no hydrogen ion dependent term between 0.1 and 1.0 M acid. The values of these two rate constants are 700 ± 50 M^{-1} s^{-1} and 0.40 ± 0.05 s^{-1} [T = 25 °C, I = 1.0 ($LiClO_4$)], respectively. Since there is an increase in the absorbance change as the HSO_5^- concentration increases, the production of the intermediate must represent an equilibrium situation with K_1 = 1750 ± 250 M^{-1}. The possible effects of contaminants such as $S_2O_8^{2-}$, H_2O_2, and SO_4^{2-} were examined by adding small amounts of these reagents (~0.1 mM) to the reaction mixtures. These additions produced no change in the observed rate constants. However, at relatively high concentrations (~50 mM), SO_4^{2-} exerts a retarding effect on the rate. This further confirms the existence of an equilibrium.

Similarly, the second step obeys the rate law

$$\frac{-d[\text{int}]}{dt} = k_{obsd}[\text{int}]$$

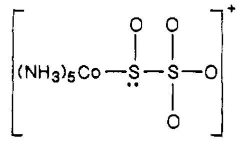
where $k_{obsd} = k_2[HSO_5^-] + k_{-2}$. Plotting k_{obsd} vs [HSO_5^-] allows determination of k_2 and k_{-2}. Again, no [H^+] dependence was observed between 0.1 and 1.0 M acid. The values of k_2, k_{-2}, and K_2 are 40 ± 3 M^{-1} s^{-1}, 0.10 ± 0.02 s^{-1}, and 400 ± 80 M^{-1}, respectively. The effect of $S_2O_8^{2-}$ was found to be negligible, but the inverse SO_4^{2-} dependence was much more pronounced than for the first reaction. At concentrations of ~10 mM SO_4^{2-} the second reaction is slowed by 50%.

A reasonable mechanism may be written for the HSO_5^-–[$(NH_3)_5CoS_2O_3$]$^+$ reaction involving two consecutive equilibria:

$$HSO_5^- + [(NH_3)_5Co\text{-}S_2O_3]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{int} + HSO_4^-$$

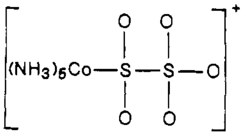
$$\text{int} + HSO_5^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(NH_3)_5CoS_2O_5]^+ + HSO_4^-$$

Since the final product is formed from the addition of two oxygens to the coordinated thiosulfate, the intermediate is most likely the first oxygen adduct. A possible structure involving a coordinated "isodithionite" is given as follows:



$$\left[(NH_3)_5Co\text{—}\overset{O}{\underset{\cdot\cdot}{S}}\text{—}\overset{O}{\underset{O}{S}}\text{—}O\right]^+$$

It might be anticipated that [$(NH_3)_5CoSOSO_3$]$^+$ would survive as a reaction intermediate since the symmetrical dithionite itself is a sluggish reducing agent toward Co(III) complexes and predominantly reacts via the dissociated SO_2^- radicals.[19] The proposed intermediate can then accept an additional oxygen to form the final product:



$$\left[(NH_3)_5Co\text{—}\overset{O}{\underset{O}{S}}\text{—}\overset{O}{\underset{O}{S}}\text{—}O\right]^+$$

The two oxygens added to the thiosulfate ligand will arise from either the solvent water or the terminal peroxy group from two HSO_5^- species. In order to determine from which source they originate, a series of ^{18}O tracer studies were carried out.

Initially, the reactant and product complexes were examined for their ability to exchange oxygens with the solvent water. Dissolution of these complexes in enriched water and reprecipitation as a perchlorate salt showed that no exchange occurred after 1 h of exposure time. Furthermore, it has been previously demonstrated that HSO_5^- does not exchange its oxygens in this time frame.[9]

The tracer experiment was performed by adding an aliquot of HSO_5^- to [$(NH_3)_5CoS_2O_3$]$^+$ dissolved in enriched water. The mixture was allowed to stand until the reaction was complete, and solid $NaClO_4$ was added until precipitation occurred. In every sample analyzed, no enrichment of the ^{18}O content was found. Enrichment would be observed only if solvent water was incorporated during the oxidation reaction. This could occur by oxygen exchange of the intermediate or by outer-sphere oxidation by HSO_5^-. Since no enrichment occurred, both of these reaction pathways may be eliminated.

Thus, we conclude that the oxygens added to the coordinated thiosulfate must come from the HSO_5^- ion in an inner-sphere oxidation. Behavior of this nature has been postulated to occur with HSO_5^- by others.[9] In a particularly definitive experiment by Thompson and Appleman, the terminal oxygen of the peroxy group was shown to be transferred during the oxidation of azidopentaamminechromium(III) using specifically labeled HSO_5^-.[9]

$$O_3S\text{-}O\text{-}{}^*OH^- + [(NH_3)_5CrN_3]^{2+} \rightarrow [(NH_3)_5CrNO^*]^{2+} + HSO_4^- + N_2$$

It seems reasonable to assume a similar process for the thiosulfate reaction.

Examination of other oxidants, such as $Fe(CN)_6^{3-}$ and Ce^{4+}, did not show analogous redox reactions toward [$(NH_3)_5CoS_2O_3$$^+$]. However, when 4-nitroperoxybenzoic acid was combined with the thiosulfate complex, formation of a yellow complex occurred. The UV–vis spectrum was identical with that obtained by using HSO_5^-; therefore, the peroxy acid may be reacting in a manner similar

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Inorg. Chem. **1988,** *27,* 3107-3112

to that of the peroxymonosulfate ion. The reactions of other peroxy species with $[(NH_3)_5CoS_2O_3]^+$ may also produce the $S_2O_5^{2-}$ species, and their investigation is anticipated.

In summary, HSO_5^- reacts with S-bonded thiosulfate to produce S-coordinated $SOSO_3^{2-}$. This reacts with a further HSO_5^- ion to produce the coordinated metabisulfite complex. In each case, the oxygen addition occurs via a nucleophilic attack of HSO_5^- and transfer of the terminal peroxy oxygen.

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Registry No. HSO_5^-, 12188-01-1; $[(NH_3)_5CoS_2O_3]^+$, 44982-28-7.

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$[Co(NH_3)_6][LAS]_3$ (LAS = Lasalocid A). A Second-Sphere Complex Involving a Natural Carboxylic Ionophore

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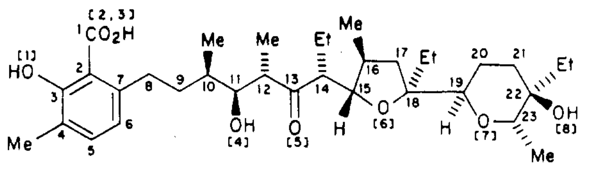
$[Co(NH_3)_6]$[lasalocid A]$_3$ crystallizes in the monoclinic space group $P2_1$ with a = 12.772 (3) Å, b = 29.811 (7) Å, c = 16.602 (3) Å, β = 109.79 (3)°, and Z = 2. Least-squares refinement of the 7115 independent, observed [$I_o \geq 3\sigma(I_o)$] reflections was carried out to R = 0.0808 and R_w = 0.1064. Hydrogen atoms, in their idealized positions, were included during refinement. The second-sphere complex consists of a $Co(NH_3)_6^{3+}$ ion surrounded by three lasalocid A anions, each of which is in a cyclic conformation maintained by intraligand hydrogen bonds. The backbone conformation of one of the lasalocid A anions is unusual and has been found in only one previous structure. The complex has approximate 3-fold symmetry. Two water molecules reside within the complex. A network of hydrogen bonds between the $Co(NH_3)_6^{3+}$ ion, the water molecules, and the lasalocid A oxygens maintains the second-sphere coordination. The complex may be regarded as a sphere with hydrophobic groups on the exterior, thus accounting for its solubility in solvents of low polarity.

Lasalocid A (formerly X-537A) (I)[1] is a bacterially produced, carboxylic ionophore capable of serving as a transmembrane mobile carrier for a variety of metal and amine cations.[2-5] The antibiotic activity of lasalocid A is attributed to its ability to perturb transmembrane ion gradients, thereby interfering with natural transport systems for ions such as H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}. Lasalocid A has proven useful as a laboratory tool for transport studies involving both natural and artificial membranes, and it has been exploited commercially as a feed additive in the poultry industry because of its anticoccidial activity.[5] Furthermore, it has been shown that lasalocid A has pronounced cardiovascular effects.[5]



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The current mechanistic view of lasalocid-mediated cation transport involves formation within the membrane of a hydrophobic lasalocid–cation complex in which the lasalocid A anion (hereafter abbreviated LAS) surrounds the cation with its polar groups, leaving a hydrophobic exterior.[4,5] This model is supported by a number of X-ray crystallographic studies of LAS complexes of mono- and divalent metal cations.[6] Because of the relatively small size of lasalocid A, dimeric (2:2 cation:anion) structures are usually found for complexes of the monovalent cations Na^+ and Ag^+ in order to provide a sufficiently large hydrophobic "shell" about the cation. A 1:2 complex is formed with Ba^{2+}, and the Cs^+ complex is polymeric.[6] In all these structures the LAS ligand adopts a cyclic conformation maintained by intramolecular hydrogen bonding. The five oxygens, O_4, O_5, O_6, O_7, and O_8, are involved in cation binding in nearly all these structures, but the carboxylate group is not always directly bound to the cation, and binding by the phenolic oxygen is rare. A crystallographic study of the 1:1 complex of LAS with the cation of the amine (R)-(+)-1-amino-1-(4-bromophenyl)ethane revealed hydrogen bonds from the $-NH_3^+$ group to O_2, O_6, and O_8 of LAS, which was found in the usual cyclic conformation.[7]

Structures of LAS complexes in the solution phase are not as well established, but there is considerable evidence that these differ from the solid-state structures.[8] NMR studies in this laboratory have shown that the LAS oxygens used for binding to divalent and trivalent cations depend upon both the charge of the cation and the polarity of the solvent, and in some cases fluxional behavior is observed.[8,9] Also, the Na^+ complex, which is dimeric in the solid state and in solutions of nonpolar solvents, becomes monomeric in polar solvents.[10]

Colquhoun and co-workers have shown that crown ether ionophores such as 18-crown-6 and its analogues form M–N–H···O hydrogen-bonded adducts with transition-metal–amine complexes.[11] These observations, combined with the fact that LAS forms adducts with a variety of organic amine cations,[2-5,7,12,13]

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