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Synthesis of a Chiral O-Bound Sulfoxide from an S-Bound Sulfenate Ion

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Abstract: Methylation of the chelated sulfenate ion bis(ethane-1,2-diamine)(cysteamine sulfenate-*S*)cobalt(III) occurs at sulfur with complete retention of chirality at the S center. The crystal and molecular structures of one of the racemic diastereoisomeric products, $\Delta(R),\Lambda(S)$-bis(ethane-1,2-diamine)(cysteamine sulfoxide-*O*)cobalt(III) triiodide hydrate, have been determined by single-crystal X-ray diffraction techniques ($R = 0.040$, orthorhombic crystals, space group *Pbca* with $a = 23.755$ (2) Å, $b = 12.531$ (2) Å, $c = 13.453$ (1) Å). The structure consists of centrosymmetrically related enantiomers and iodide ions with one water molecule hydrogen bonded to an amino nitrogen of the cations. The sulfoxide moiety forms a six-membered ring with the oxygen bonded to cobalt. A rearrangement from S- to O-bonded sulfoxide following the alkylation is implied with a concomitant increase in ring size. The mechanism is discussed.

Thiolate ion coordinated to cobalt(III) retains some of the nucleophilic character of the sulfur center of the parent ion, RS^-.[2a-4] For example, $[(en)_2Co(S(CH_2)_2NH_2)]^{2+}$ readily undergoes the electrophilic addition of H_2O_2,[2b] Br^+, or Cl^{+3} in water to give the coordinated sulfenate $[(en)_2Co(SO(CH_2)_2NH_2)]^{2+}$ and ultimately the sulfinate $[(en)_2Co(SO_2(CH_2)_2NH_2)]^{2+}$ ion. Similarly it readily attacks alkyl halides to give thioethers of the type $[(en)_2Co(SR(CH_2)_2NH_2)]^{3+}$.[3,4] A feature of the chemistry is the control and stability imparted by the metal complex. For example, free sulfenate ions are notoriously unstable while their S-bonded metal complexes are apparently very stable.[2a] Futhermore, chiral cobalt(III) centers can direct the stereochemistry of the oxidation to give the chiral sulfur center which remains bonded to the metal ion.[2a,3] We were interested in utilizing these properties to prepare stereospecifically the first sulfur-bonded Co(III)–sulfoxide complex. In these attempts we found some unexpected and unusual reactions which are reported herein.

Experimental Section

Visible spectra were measured with a Cary 118C spectrophotometer. ^1H NMR spectra were recorded by using Varian T60 or JEOL Minimar 100-MHz spectrometers with an internal Me_4Si reference. Proton-decoupled ^{13}C NMR spectra were obtained with a Varian FX60 spectrometer using an internal deuterium lock. Positive chemical shifts are reported in ppm downfield from an internal dioxane reference. Solutions were evaporated under reduced pressure (~15 mmHg) by using a Büchi rotary evaporator so that the solution temperature did not exceed 25 °C.

The hydrogen peroxide oxidation of $[Co(en)_2(S(CH_2)_2NH_2)](ClO_4)_2$ gave major (80%) $\Delta(S),\Lambda(R)[Co(en)_2(SO(CH_2)_2NH_2)]NO_3ClO_4$ and minor (20%) $\Delta(R),\Lambda(S)[Co(en)_2(SO(CH_2)_2NH_2)](ClO_4)_2$ isomeric sulfenato products. The separation, purification, and characterization of these diastereoisomers will be given elsewhere.[5]

$\Delta(R),\Lambda(S)[Co(en)_2(SO(CH_3)(CH_2)_2NH_2)]^{3+}$ Salts. Methyl iodide (15 mL) was added to the orange-brown solution of $\Delta(S),\Lambda(R)[Co(en)_2(SO(CH_2)_2NH_2)]NO_3ClO_4$ (5.0 g) in Me_2SO (80 mL), and the mixture was allowed to stand overnight at ca. 20 °C. The orange-pink solution was diluted with water (400 mL), extracted with chloroform (3 × 30 mL) to remove I_2 and excess CH_3I, and then sorbed on a column of Dowex 50W-X2 (H^+ form, 200–400 mesh) cation-exchange resin. The column was washed (H_2O, 500 mL) and eluted (2 mol dm^{-3} NaCl) to remove unreacted sulfenato complex. Elution with 3 mol dm^{-3} HCl eluted the pink-red sulfoxide product. After removal of most of the HCl by evaporation, the addition of $HClO_4$ (70%) and cooling (5 °C, 12 h) produced pink *crystals* (4.1 g, 60%) of the triperchlorate hydrate salt. They were recrystallized twice from $H_2O/HClO_4$. Anal. Cacld for $C_7H_{27}Cl_3CoN_5O_{14}S$: C, 14.0; H, 4.5; N, 11.6; S, 5.3; Cl, 17.7. Found: C, 13.9; H, 4.3; N, 11.1; S, 5.4; Cl, 18.1. The chloride salt was obtained from the perchlorate by anion exchange (Dowex 1-X8, Cl^- form) and crystallization from $H_2O/HCl/MeOH/Me_2CO$. The triiodide salt was obtained by metathesis using NaI in water. ^1H NMR (D_2O) δ 2.77, s, SCH_3; ^{13}C NMR (D_2O) δ −21.28, −21.74, −21.88, −22.14 (4C, NCH_2 of en), −23.01 (1C, SCH_2), −31.98 (1C, NCH_2), −31.99 (1C, SCH_3); vis max ϵ_{513} 98.1 (H_2O). Anal. Calcd for $C_7H_{25}CoI_3N_5OS$: C, 12.6; H, 3.8; N, 10.5; S, 4.8; I, 57.1. Found: C, 12.8; H, 3.9; N, 10.5; S, 4.8; I, 56.1.

$\Delta(S),\Lambda(R)[Co(en)_2(SO(CH_3)(CH_2)_2NH_2)]^{3+}$ Salts. A procedure similar to the above was followed with $\Delta(R),\Lambda(S)[Co(en)_2(SO(CH_2)_2NH_2)](ClO_4)_2$ (5.0 g) in place of $\Delta(S),\Lambda(R)[Co(en)_2(SO(CH_2)_2NH_2)]NO_3ClO_4$. The red complex was crystallized as the hydrated trichloride salt from $H_2O/MeOH/Me_2CO$ (2.90 g, 65%). Anal. Calcd for $C_7H_{28}Cl_3CoN_5O_{2.5}S$: C, 20.0; H, 6.7; N, 16.7; S, 7.6; Cl, 25.3. Found: C, 20.0; H, 6.1; N, 16.1; S, 7.8; Cl, 25.4. The perchlorate and iodide salts were obtained by metathesis in H_2O ($HClO_4$ or NaI). Anal. Calcd for $C_7H_{27}CoI_3N_5O_2S$: C, 12.3; H, 4.0; N, 10.2; S, 4.7; I, 55.6. Found: C, 12.5; H, 4.0; N, 10.3; S, 4.8; I, 55.7. ^1H NMR (D_2O) δ 2.80, s, SCH_3; ^{13}C NMR (D_2O) δ −21.28, −21.48, −21.81, −22.34 (4C, NCH_2 of en), −22.67 (1C, SCH_2), −30.98 (1C, NCH_2), −31.12 (1C, SCH_3); vis max ϵ_{499} 85.9 (H_2O).

Product Analyses. We were unable to separate mixtures of the sulfoxide isomers satisfactorily by ion-exchange chromatography. Therefore the products from the two methylation reactions above ($^1/_5$th scale) were sampled and examined by ^{13}C NMR and ^1H NMR spectroscopy (D_2O). A single O-bound sulfoxide diastereoisomer (>95%) was observed in each case.

Chlorine Oxidation. Solutions of the Cl^- salts of each of the O-sulfoxides in D_2O were saturated with Cl_2 (ca. 0.04 mol dm^{-3}) and sealed. No changes in the ^1H and ^{13}C NMR spectra were observed after 3 days at 20 °C.

X-ray Diffraction Study of $\Delta(R),\Lambda(S)$-Bis(ethane-1,2-diamine)(methylcysteamine sulfoxide-*O*)cobalt(III) Triiodide Hydrate. The crystals were grown from water as orange rectangular needles. The crystals appeared to have the same habitat, and all from a random selection were crystallographically identical. The crystal employed for data collection was of dimensions 0.32 × 0.19 × 0.04 mm mounted with a goniometer and [0, 1, 1] directions coincident. Approximate unit cell constants and group absences were determined from Weissenberg and precession photographs. The absences $h0l$, $l = 2n + 1$, $0kl$, $k = 2n + 1$, and $hk0$, $h = 2n + 1$, are consistent with the space group *pbca*(61).[6] Unit cell dimensions were adjusted by a least-squares treatment[7] of the setting

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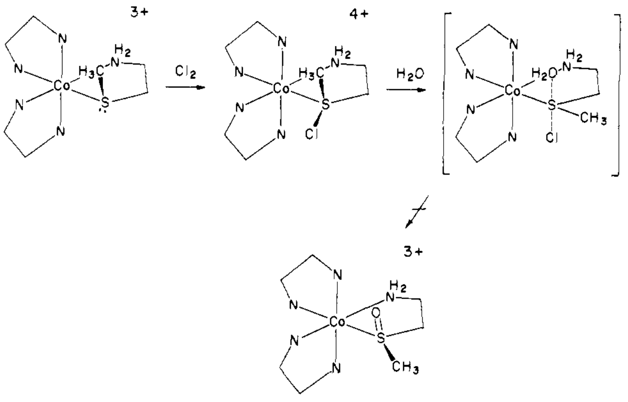
Scheme I



angles of 12 reflections centered automatically on a Hilger and Watts Y290 diffractometer, controlled by a PDP8/I computer. Crystal data (20 ± 1°): a = 23.755 (2), b = 12.531 (2), and c = 13.453 (1) Å: formula $C_7H_{27}CoI_3N_5O_2S$; M 685.0; cell volume 4004 Å^3; Z = 8; D_c = 2.27 g cm^{-3}; F(000) 2576; μ(Mo K_α) 56.7 cm^{-1}; λ(Mo K_α) 0.7107 Å.

Details of Data Collection. The intensities were measured by using the θ and 2θ scan technique, with a scan step in θ of 0.01° and a counting time of 1 s. Each reflection was scanned through a range of 0.72° centered on the Mo K_α peak. The local background was measured for 18 s at each end of the scan range using the stationary-crystal, stationary-counter technique. For monitoring of the crystal and electronic stability, the intensities of three strong reflections well separated in reciprocal space were measured periodically throughout the experiment; only random fluctuations ($\leq\pm3\%$) in their mean values were observed.

All independent reflections in the sphere with $\theta \leq 23°$ were measured; the integrated intensities and their standard deviations were derived as described previously[8] with an "uncertainty" factor, p, of 0.05. The 1394 reflections having greater I than $3\sigma(I)$, used in the subsequent analysis, were corrected for absorption by the analytical method,[9] transmission coefficients on I ranging from 1.25 to 2.76.

Solution and Refinement of the Structure. The structure was solved[10] by conventional Patterson and difference Fourier calculations; the initial R, where R is $\sum||F_o| - |F_c||/\sum|F_o|$ and F_0, F_c are the observed and calculated structure factors, for the cobalt and iodine atoms was 0.20. All nonhydrogen atoms were located on the following difference Fourier map. Full matrix least-squares refinement was carried out minimizing the function $\sum w(|F_o| - |F_c|)^2$, where w was initially $1/r^2(F_o)$. The atomic scattering factors for Co, I, N, O, and C were taken from the usual tabulation[6] and those for H from Stewart et al.[11] The initial refinement without the water oxygen, in which all nonhydrogen atoms were refined with isotropic vibrational parameters, gave R = 0.115 and R' (weighted R factor) = 0.133 where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

The iodine and cobalt atoms were then refined with anisotropic thermal parameters leading to R 0.086, R' = 0.093. Analysis of the minimized function over ranges of $|F_o|$ and λ^{-1} sin j indicated the "diffractometer" weights were unsatisfactory. Absorption corrections were carried out and the weights recalculated as $w = 1/(170.0 + |F_o| + 5 \mid 10^{-6} |F_o|^3)$. Refinement with 18 atoms now converged in three cycles to R = 0.052, R' = 0.078.

The difference Fourier map showed three distinct peaks with relative integrated heights of 7:3:2 with the largest about 0.6 of the height of the last oxygen atom located. Several different refinement models were tried for these distinct atomic positions; all were consistent with the disorder of one oxygen atom into the three closely related sites. The water oxygens were included with population parameters fixed at 0.58, 0.25, and 0.17 (O(2), O(3), and O(4), respectively). Atoms S, O(1), C(1), and C(7) in the six-membered chelate also showed anisotropy in the map, and along with O(2) and O(3) were therefore refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined in their calculated positions (C–H 0.95 Å, N–H 0.87 Å, with B temperature factors of 4 Å^2); all corresponded to regions of positive density in the map. The refinement with 46 atoms and 379 variables converged in four cycles to a final R of 0.040 and R' of 0.044. The maximum shift/estimated standard deviation ratio was 0.4 (for atom O(4)) with the overall mean 0.03. Average values of the minimized function showed little dependence on $|F_o|$ and λ^{-1} sin θ. Examination of the final difference Fourier showed no significant features with all peaks within 1.3 Å of heavy atom positions.

The positional and vibrational parameters and their esd's obtained from the final cycle are listed in Table I.

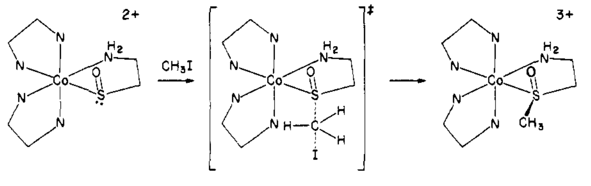
Table I. Atomic Positional Parameters for $\Delta(R),\Lambda(S)$Bis(ethane-1,2-diamine)(cysteamine sulfoxide-O)cobalt(III) Iodide Hydrate

anisotropic atoms			
atoms	10^4x	10^4y	10^4z
I(1)	2103.0 (5)	1796 (1)	1004.7 (8)
I(2)	3310.7 (5)	3735 (1)	3068.4 (9)
I(3)	5003.6 (5)	1791 (1)	4690.7 (9)
Co	3599.3 (8)	−108 (2)	3083 (2)
S	3526 (2)	130 (4)	720 (3)
O(1)	3432 (5)	−401 (9)	1725 (8)
C(1)	3792 (8)	1421 (14)	1034 (13)
C(7)	4156 (11)	−470 (18)	273 (17)
O(2)[a]	384 (9)	158 (22)	2540 (21)
O(3)[a]	223 (18)	−690 (41)	3260 (32)
O(4)[a]	700 (44)	260 (33)	1990 (81)

isotropic atoms			
atoms	10^3x	10^3y	10^3z
N(1)	400.1 (5)	122.7 (11)	280.0 (9)
N(2)	366.5 (6)	16.1 (11)	451.0 (10)
N(3)	288.0 (5)	63.8 (10)	319.8 (9)
N(4)	430.2 (5)	−92.9 (10)	302.3 (10)
N(5)	322.4 (5)	−149.6 (9)	331.9 (8)
C(2)	422.7 (7)	147.1 (12)	181.5 (12)
C(3)	326.5 (7)	100.4 (13)	479.9 (13)
C(4)	274.6 (7)	80.4 (14)	426.7 (13)
C(5)	414.4 (7)	−207.2 (13)	285.5 (12)
C(6)	366.3 (7)	−231.0 (13)	346.1 (12)
H(1)	428	127	324
H(2)	377	175	293
H(3)	442	216	184
H(4)	454	96	168
H(5)	348	184	126
H(6)	393	175	44
H(7)	401	36	467
H(8)	359	−42	485
H(9)	341	167	460
H(10)	321	101	548
H(11)	257	17	454
H(12)	249	138	436
H(13)	262	27	290
H(14)	290	126	290
H(15)	450	−87	359
H(16)	453	−70	255
H(17)	446	−255	303
H(18)	407	−220	216
H(19)	351	−300	328
H(20)	377	−234	414
H(21)	300	−166	281
H(22)	301	−146	385
H(23)	432	−10	−31
H(24)	446	−49	75
H(25)	404	−115	9

[a] Partial occupancy; see text.

Scheme II



Results and Discussion

We sought to construct the S-bound sulfoxide stereospecifically on the metal ion by using two different approaches, the oxidation

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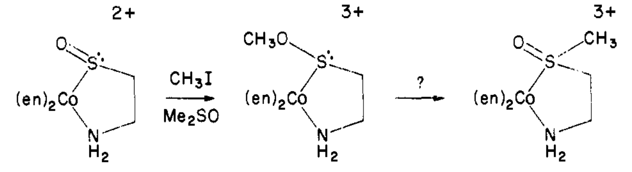
Scheme III



of the thioether (Scheme I) and the alkylation of the sulfenate ion (Scheme II). The chiral sulfur center in the thioether complex is not optically stable, but the methyl group is known to be stereospecifically oriented,[3] as shown in Scheme I. A similar orientation was observed in the S-methyl-(*R*)-cysteine analogue[12] (axially, between the en chelates). Therefore it was anticipated that oxidation at sulfur would lead to one epimer of the S-bonded sulfoxide product, the specificity arising from the presence of the chiral *cis*-Co(en)$_2$ moiety. These expectations were not realized. The thioether complex failed to oxidize with H_2O_2 and *N*-bromosuccinimide or even with chlorine (over 3 days). Uncoordinated thioethers RSR are oxidized very readily by these reagents to give first the sulfoxide RSOR and then the sulfone RSO_2R. While coordination must block the path to the sulfone, it is apparent that it also protects the thioether from oxidation, despite the availability of a lone pair on sulfur.

The second approach, addition of CH_3^+ to coordinated sulfenate ion, gave unexpected and interesting results. The chiral sulfur center of the starting material $[Co(en)_2(SO(CH_2)_2NH_2)]^{2+}$ is known to be stable to inversion,[2a,3] and the two S-bonded sulfenate diastereoisomers have been isolated.[3] The reaction of either sulfenate with MeI in Me$_2$SO produced a pink solution from which some unreacted orange-brown sulfenate (2+ ion, ~40%) and the pink-red product (3+ ion, ~60%) were separated easily by ionexchange chromatography. The products were crystallized readily as Cl$^-$, I$^-$, or ClO_4^- salts, and the elemental analyses and ^1H and ^{13}C NMR spectra were all consistent with the addition of one methyl group. A single but different product was obtained from each of the sulfenate diastereoisomers.

Two reaction pathways were envisaged: methylation at sulfur to give an S-bound sulfoxide (Scheme II) or methylation at oxygen to produce an O-bound sulfenate ester (Scheme III). In either case two diastereomeric products would be expected. The visible spectra of the two products were similar, and both the ^1H and ^{13}C NMR spectra indicated essentially identical chemical environments for the Me group in the two molecules, indicating that the products were diastereoisomers of essentially the same chemical species. Neither visible spectrum resembled that of the corresponding sulfenate complex,[2b,3] implying alkylation of the donor sulfur rather than at the more remote oxygen center. Sulfur-bonded cobalt(III) complexes typically show only one of the expected two ligand field bands;[2a-4] the second band is usually obscured by an intense charge transfer absorption in the near-UV which extends into the far-visible region. However the present complexes showed both ligand field bands and lacked the UV absorption characteristic of Co^{III}–$\ddot{S}$–charge transfer. The only reasonable structure consistent with these data is O-bonded sulfoxide or, much less likely,[13] O-bonded sulfenate ester. The visible spectra of the products closely resembled that of the *cis*-$[Co(en)_2(NH_3)(OSMe_2)]^{3+}$ ion,[14] while the chemical shifts for the methyl group in the ^1H NMR spectrum were also consistent with O-bonded sulfoxide. However, neither of the isomeric products reacted with aqueous chlorine (0.04 mol dm^{-3}, 3 days), and this remarkable insensitivity to oxidation is atypical of O-bonded sulfoxide.[16,17] For example, the complex $[Co(NH_3)_5OSMe_2]^{3+}$ reacts under the conditions above with $t_{1/2}$ ca. 2 s.[15] This conflicting chemical evidence led us to determine the molecular structure of one of the isomers by X-ray crystallography.

Table II. Bond Lengths

atoms	distance, Å	atoms	distance, Å
Co-O(1)	1.906 (11)	Co-N(1)	1.963 (13)
Co-N(2)	1.956 (14)	Co-N(3)	1.953 (14)
Co-N(4)	1.963 (13)	Co-N(5)	1.980 (12)
S-O(1)	1.524 (12)	S-C(1)	1.79 (2)
S-C(7)	1.78 (3)	N(1)-C(2)	1.46 (2)
N(2)-C(3)	1.47 (2)	N(3)-C(4)	1.49 (2)
N(4)-C(5)	1.50 (2)	N(5)-C(6)	1.47 (2)
C(1)-C(2)	1.48 (2)	C(3)-C(4)	1.45 (2)
C(5)-C(6)	1.44 (2)		

Table III. Bond Angles (Degrees)

atoms	angle	atoms	angle
O(1)-Co-N(1)	94.6 (5)	N(1)-Co-N(2)	90.3 (6)
O(1)-Co-N(2)	172.4 (6)	N(1)-Co-N(3)	91.9 (5)
O(1)-Co-N(3)	89.2 (5)	N(1)-Co-N(4)	91.4 (5)
O(1)-Co-N(4)	92.2 (6)	N(1)-Co-N(5)	176.8 (5)
O(1)-Co-N(5)	83.7 (5)	N(2)-Co-N(4)	93.6 (6)
N(3)-Co-N(4)	176.3 (6)	N(2)-Co-N(5)	91.7 (5)
N(3)-Co-N(5)	90.8 (5)	N(4)-Co-N(5)	85.9 (5)
O(1)-S-C(1)	103.7 (8)	Co-O(1)-S	137.4 (7)
O(1)-S-C(7)	103.8 (9)	Co-N(1)-C(2)	122 (1)
C(1)-S-C(7)	100 (1)	Co-N(2)-C(3)	109 (1)
Co-N(3)-C(4)	109 (1)	Co-N(4)-C(5)	107 (1)
Co-N(5)-C(6)	108 (1)	S-C(1)-C(2)	117 (1)
N(1)-C(2)-C(1)	112 (1)	N(2)-C(3)-C(4)	107 (1)
N(3)-C(4)-C(3)	109 (1)	N(4)-C(5)-C(6)	108 (1)
N(5)-C(6)-C(5)	110 (1)		

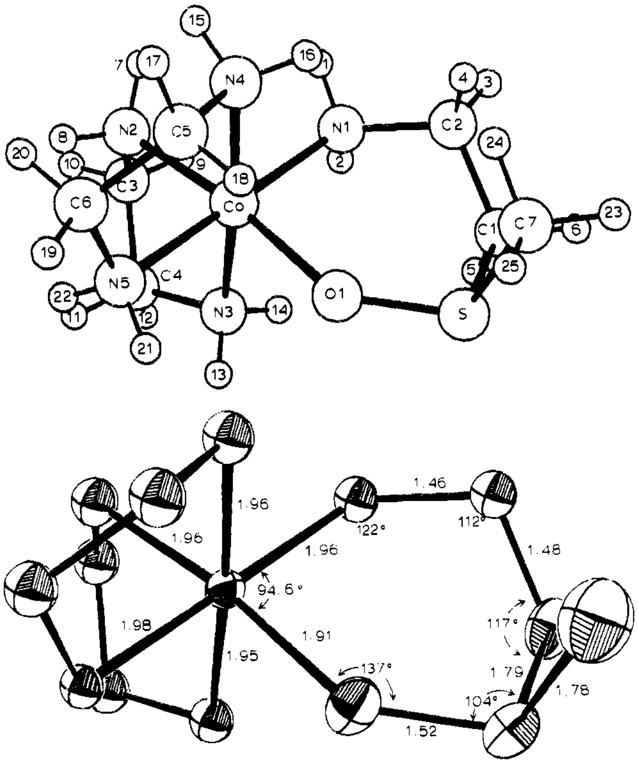


Figure 1. The molecular structure of the Δ(*R*)bis(ethane-1,2-diamine)(cysteamine sulfoxide-*O*)cobalt(III) cation.

Description of the Structure. Bond lengths and angles are given in Tables II and III, intermolecular contacts of significance in Table IV, and torsion angles and least-squares planes in Tables V and VI.

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[13] O-bonded sulfenate ester is expected to hydrolyze very rapidly, by analogy with studies on free and O-coordinated $NH_2CH_2C(O)OR$.[15]

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Table IV. Close Intermolecular Contacts

I. Hydrogen Bonds

A–B–H···O	∠A–B···O, deg	∠B–H···O, deg	H···O, Å	B···O, Å	symmetry operation
Co–N(4)–H(16)···O(2)	120	136	2.30	3.00	$0.5 + x, y, 0.5 - z$
Co–N(4)–H(16)···O(3)	129	137	1.97	2.81	$0.5 + x, y, 0.5 - z$

II. Other Contacts (to 3.5 Å)

A···B	distance, Å	symmetry operation	A···B	distance, Å	symmetry operation
H(4)···O(2)	2.48	$0.5 + x, y, 0.5 - z$	H(5)···I(2)	3.42	x, y, z
H(24)···O(3)	2.25	$0.5 + x, y, 0.5 - z$	H(9)···I(2)	3.32	x, y, z
H(23)···O(3)	2.41	$0.5 - x, y, z - 0.5$	H(14)···I(2)	3.25	x, y, z
H(1)···I(3)	2.69	x, y, z	H(5)···I(1)	3.28	x, y, z
H(7)···I(3)	2.97	x, y, z	H(13)···I(1)	3.42	x, y, z
H(2)···I(2)	2.72	x, y, z	H(14)···I(1)	3.25	x, y, z

Table V. Torsion Angles (Degrees)

A-B-C-D	angle[a]
Co-O(1)-S-C(1)	−9.0
Co-O(1)-S-C(7)	94.7
O(1)-S-C(1)-C(2)	44.4
C(7)-S-C(1)-C(2)	−62.4
Co-N(1)-C(2)-C(1)	55.8
Co-N(2)-C(3)-C(4)	41.0
Co-N(3)-C(4)-C(3)	35.4
Co-N(4)-C(5)-C(6)	−41.2
Co-N(5)-C(6)-C(5)	−34.0
S-C(1)-C(2)-N(1)	−70.4
N(2)-C(3)-C(4)-N(3)	−49.5
N(4)-C(5)-C(6)-N(5)	50.0

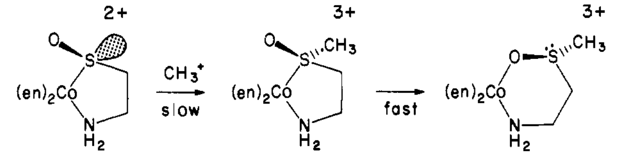
[a] The sign of the angle is positive if an anticlockwise rotation of the far bond C-D eclipses the near bond A-B.

Table VI. Least-Squares Planes

	planes					
	1	2	3	4	5	6
	equations $Px + Qy + Rz = S$ (LSQPL[10])					
P	21.96	21.16	18.54	11.32	20.79	3.36
Q	−4.64	−5.42	−7.83	10.63	−6.04	1.56
R	−1.22	−1.89	−0.11	−3.09	−0.50	13.21
S	7.56	7.17	6.55	2.94	7.37	5.26
	10^2x Deviations, Å[a]					
	Co 2	Co −8	N(1) −12	N(4) 1	N(2) −7	N(1) −3
	O(1) −4	S −9	C(2) 12	O(1) −1	N(1) 7	N(3) 3
	S 4	N(1) 10	S −12	N(2) −1	N(5) 8	N(4) 3
	C(1) −2	C(1) −11	O(1) 11	N(3) 1	O(1) −7	N(5) −3
	N(1) 32	*O*(1) −2	*Co* 18	*Co* 7	*Co* 3	*Co* 0
	C(2) 82	*C*(2) 64	*C*(1) −64	*N*(5) −190	*N*(4) 199	
	C(7) 176					

[a] Nondefining atoms in italics.

Scheme IV



The crystal structue consists of centrosymmetrically related enantiomers, one of which (Δ(*R*)) is illustrated in Figure 1, and iodide ions with one water molecule hydrogen bonded to an amino nitrogen of the cations (Table IV). The two significant features of the cation are the following: (1) O-bound sulfoxide is in a six-membered ring, and (2) for the Δ absolute configuration in the $Co(en)_2$ moiety, the chirality at sulfur is *R*,[18] with the ethylenediamine rings in the λδ[(lel)(ob)] conformation.

The six-membered chelate is best described as a distorted skew boat,[19] with an axial methyl group on the sulfur. The bond distances (Table II) are normal (e.g., Co–O(1) 1.906 (11) S–O(1) 1.524 (12),[20] S–C(1) 1.79 (2),[21] and S–C(7) 1.78 (3) Å) with some angular distortion at O(1) (Co–O(1)–S 137.4 (7)°)[20] and N(1)(Co–N(1)–C(2) 122 (1)°). Coordination around the sulfur is tetrahedral, and the atoms Co, O(1), S, and C(1) are all coplanar. All other distances and angles in the cation are normal.[1,4,22,23]

Reaction Mechanisms. The crystal analysis was made arbitrarily on the sulfoxide complex derived from the sulfenate isomer known[24-26] to be Δ(*S*)$[Co(en)_2(SO(CH_2)_2NH_2)]^{2+}$. A comparison of the present and previous crystal structures shows that CH_3^+ addition occurs with retention of the chirality at sulfur.[27] Note that the retention must be complete since each isomer gives a single isomeric sulfoxide product.

The more interesting feature of the reaction is the rearrangement from a S- to an O-bonded complex with the concomitant increase in ring size from five to six membered. At no time did we observe S-bound sulfoxide or the sulfenate ester (Schemes I–III) even in partly reacted solutions (^1H and ^{13}C NMR spectra and chromatography). Free sulfoxides usually alkylate first at oxygen, with subsequent migration to sulfur. Likening the present S-bound sulfenate to a sulfoxide, it is clear at least that if *O*-precedes S-alkylation, then migration to sulfur is rapid and retentive and occurs without Co–S cleavage. Racemization would result if sulfur left the metal ion prior to complete development of the sulfoxide group. The inference is the methylation occurs at sulfur, with retention, and then the optically stable S-bound sulfoxide rapidly rearranges to the O-bound form (Scheme IV). Solvent (Me_2SO) participation is not implicated in this rearrangement since ring closure in *cis*-$[Co(en)_2(Me_2SO)(NH_2(CH_2)_2SOCH_3)]^{3+}$ is too slow ($t_{1/2} > 1$ h, 25 °C) on this time scale.[28] Therefore the five- to six-membered ring expansion

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(18) The product, although racemic, is a single diastereoisomer; it is the relative configurations about Co and S which are relevant here.

(19) See: Butler, K. R.; Snow, M. R. *J. Chem. Soc., Dalton Trans.* **1976**, 259. Kobayashi, A.; Marumo, F.; Saito, Y. *Acta Crystallogr. Sect. B*: **1973**, *B29*, 2443.

(20) See: Fergusson, J. E.; Page, C. T.; Robinson, Ward T. *Inorg. Chem.*, **1976**, *15*, 2270, and references therein.

(21) de Meister, P.; Hodgson, D. J. *J. Chem. Soc., Dalton Trans.* **1975**, 618.

(22) Gainsford, G. J.; Jackson, W. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 2388.

(23) Jackson, W. G.; Sargeson, A. M.; Tucker, P. A. *J. Chem. Soc., Chem. Commun.* **1977**, 199.

(24) Only one isomer (Δ(*S*)) has been reported.[25] We have prepared both and identified them by X-ray crystallography.[26]

(25) Adzamli, I. K.; Libson, K.; Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303.

(26) Elder, R. C., University of Cincinnati, personal communication.

(27) The opposite designations of the chirality at sulfur in reactant and product merely reflect changes in group priorities according to the usual rules for labeling chiral centers. They do not imply inversion at sulfur.

(28) Jackson, W. G.; Sargeson, A. M., to be published.

appears to be synchronous with this second step (Scheme IV).

Intramolecular linkage isomerizations are well documented, e.g., $[(NH_3)_5CoSCN]^{2+} \rightarrow [(NH_3)_5CoNCS]^{2+}$; $[(NH_3)_5CoONO]^{2+} \rightarrow [(NH_3)_5CoNO_2]^{2+}$.[29] None, however, have involved ambident functional groups incorporated into a chelate arm, and the present facile S- to O-sulfoxide rearrangement with synchronous ring expansion therefore assumes especial interest. It is also worthy of comment that while both O- and S-bound sulfoxide complexes are known, particularly for the noble metals, interconversion between these linkage isomers does not seem to have been observed. In this instance the cobalt(III) center is a rather hard acid and might be expected to prefer oxygen as the donor. Also the S-bound form is sterically crowded. Both would assist the rearrangement. Even so, it is a surprisingly rapid process.

A curious aspect of the chemistry is the resistance of the chelated sulfoxides toward chlorine oxidation. The crystallography establishes O-coordination for one of the two isomers in the solid state, and the lack of intense UV absorption typifying Co–S bonding indicates this linkage is retained in solution. It seems likely that chelation sterically inhibits sulfur from achieving the required trigonal-bipyramidal geometry which would result from addition of Cl^+ followed by the addition of H_2O to effect the oxidation to the sulfone. Oxidation of the monodentate sulfoxides, however, would not be inhibited in the same way, and it has been observed in at least two instances, i.e., $[(NH_3)_5CoO{=}S(Me)_2]^{2+}$ and $[(NH_3)_5CoO{=}\overline{S(CH_2)_3CH_2}]^{3+}$.[16]

A similar explanation may account for the difficulty in oxidizing the S-methylcysteamine chelate (Scheme I). An analogous trigonal bipyramid has to be achieved, and the chelate imparts a substantial restriction on the angles that can be adopted at the S atom during the process. The inverse process, however, is quite different. The oxidation of the bound mercaptide ion to the sulfenate ion and the subsequent use of the latter as a nucleophile for an alkyl halide require quite different and less demanding paths. The restrictions imposed by the chelate on the geometry about S do not impinge so effectively on this chemistry.

The O-bonded sulfoxide diastereoisomers have been prepared independently from *cis*-$[Co(en)_2(Me_2SO)_2]^{3+}$ and (racemic) free ligand and also from *cis*-$[Co(en)_2X(NH_2(CH_2)_2SOCH_3)]^{n+}$ (X = Br^-, Cl^-, N_3^-, Me_2SO, OH_2) by ring closure with substitution of X. The products were separated by fractional crystallization and chromatography. The hope that five-membered ring formation (with S bonding) would be preferred to six-membered (with O bonding) was not realized, and this is consistent with the rearrangment observed in the oxidation. The starting material in all these cases was a ~50:50 mixture of epimers, and the product was a similar mixture of the chelated sulfoxides; i.e., ring closure occurs largely with retention of the configuration about cobalt.[28]

It appears that chiral chelate sulfoxides may be synthesized from resolved cobalt(III) mercaptide complexes, utilizing the methods for the stereospecific addition of oxygen and followed by the stereospecific addition of the alkyl group to the sulfenate as described here. However the generality of the method has yet to be explored and the specificity should be confined largely to the chelate systems.

Acknowledgment. We thank the Microanalytical Section of the John Curtin School of Medical Research, A.N.U., for the C, H, N, and S analyses.

Supplementary Material Available: Thermal parameters (Table VII), amplitudes of root mean square vibrations (Table VIII), and a listing of observed and calculated structure factors for the 1394 reflections used in the refinement (12 pages). Ordering information is given on any current masthead page.

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(29) Jackson, W. G.; Sargeson, A. M. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York 1980; Vol. 2, p 273.

Synthesis and Electrophile-Induced Disproportionation of the Neutral Formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO)

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Abstract: The crystalline, thermally stable neutral formyl (η-C_5H_5)Re(NO)(PPh_3)(CHO) (**3**) is synthesized by reaction of cation $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2a**) with either $Li(C_2H_5)_3BH$ in THF or $NaBH_4$ in THF/H_2O. Precursor **2a** is in turn prepared by the sequential treatment of $[(\eta\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (**1**) with $C_6H_5I^+O^-/CH_3CN$ (oxidative removal of CO) and PPh_3. At 50–105 °C in appropriate solvents, **3** decomposes (in variable yields) to rhenium hydrides. **3** is reduced by BH_3·THF to (η-C_5H_5)Re(NO)(PPh_3)(CH_3) (**4**). When **3** is reacted with CH_3SO_3F or CF_3CO_2H, facile formyl ligand disproportionation occurs: **4** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+$ salts form. Potential intermediates in these disproportionations are independently synthesized. Reaction of **4** with $Ph_3C^+X^-$ (X = PF_6, BF_4) at −78 °C affords the cationic methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+X^-$ (**5**), which can be isolated as a stable solid. **5** is further characterized by preparing $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{–}L^+)]$ adducts where L = pyridine (**6a**), 2,6-dimethylpyridine (**6b**), PPh_3 (**7a**), and P(n-C_4H_9)$_3$ (**7b**). Reaction of **5** or **6a** with excess CH_3O^- yields (η-C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3) (**8**). Addition of 0.5 equiv of CH_3SO_3F to **8** gives **4**, $(CH_3)_2O$, and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOCH_3)]^+SO_3F^-$ (**9a**) in a 1.0:1.0:1.1 ratio. On the basis of hydride transfer reactions observed between **3** and **5**, **3** and **9a**, and **8** and **5**, and low temperature ^1H NMR monitoring, the CH_3SO_3F-induced disproportionation of **3** is proposed to involve the sequence of intermediates **3** → **9a** → **8** → **5** → **4**. Reaction of **3** with CF_3CO_2H is suggested to occur similarly; initial formation of unstable hydroxymethylidene intermediate $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHOH)]^+X^-$ (X = CF_3CO_2, **10a**) can be observed by ^1H and ^{13}C NMR spectroscopy. When X = CF_3SO_3, this salt can be isolated. Attempts to prepare the proposed hydroxymethyl intermediate (η-C_5H_5)Re(NO)(PPh_3)(CH_2OH) (**11**) are detailed. Syntheses of (η-C_5H_5)Re(NO)(PPh_3)(COOH) (**2a** + NaOH) and (η-C_5H_5)Re(NO)(PPh_3)(H) (**2a** + $(CH_3)_3N^+O^-/LiAlH_4$) are also described, and the relevance of the above reactions to catalytic CO reduction is discussed.

Declining domestic crude oil reserves have prompted a renewed interest in the chemistry of CO/H_2 gas mixtures ("synthesis gas"), which are readily available from coal and can be transformed by metal catalysts into a variety of organic molecules (methane, methanol, higher alkanes and alcohols, glycols, and gasoline hydrocarbons) normally derived from petroleum.[2,3] In particular,

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