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Chemistry and Reactivity of S-Bonded Sulfenato–Cobalt(III) Complexes[1]

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The chemistry of cobalt(III) complexes containing S-bonded sulfenato ligands (Co–S(O)–R) is discussed in terms of the similar chemistries observed for noncoordinated sulfenate anions (R–S(O)$^-$) and noncoordinated sulfoxides (R–S(O)–R′). The energy of the charge-transfer band characteristic of the Co–S(O)–R linkage is shown to be markedly solvent dependent, ranging from 365 nm in water to 393 nm in acetonitrile. Indirect IR and visible–UV spectral evidence indicates that the prototype complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ coordinates to H^+ and BF_3 through the pendant oxygen atom but coordinates to palladium(II) through the sulfur atom to yield a 1/1 adduct in which the bridging sulfur atom is four-coordinate. Methylation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ by methyl iodide yields the N,O-chelated sulfoxide complex $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]^{3+}$, while methylation of $[(en)_2Co(S(O)CH_2COO)]^+$ results in formation of the thioether complex $[(en)_2Co(S(CH_3)CH_2COO)]^{2+}$; possible mechanisms for these reactions are presented. Reactions in which the sulfenato ligand undergoes 2-equiv reduction at sulfur, 2-equiv oxidation at sulfur, and transfer of oxidizing power from sulfur to an adjacent carbon atom are presented and discussed.

Introduction

Noncoordinated sulfenic acids, RSOH, are elusive species that are known to play crucial roles in the reactions of organosulfur compounds.[2] Although only a few have actually been isolated, sulfenic acids have been proposed, and identified, as transient intermediates in a wide variety of reactions[3] and have been shown to occur as metastable species in the protective folds of proteins.[4] They are thought to be involved in the antioxidant capacity of some sulfur compounds[5] and may function to regulate the catalytic activity of some enzymes.[4] In general, noncoordinated sulfenic acids are highly reactive species, being susceptible to both electrophilic and nucleophilic attack, which undergo a wide variety of synthetically useful reactions.[3]

When sulfenic acids are coordinated to cobalt(III) through sulfur, their reactivity is greatly reduced and the coordinated species are stable enough to be characterized by classical techniques. Several studies of S-bonded sulfenato–cobalt(III) complexes have been reported,[6] and two such species have been characterized by single-crystal X-ray structural analysis.[6a,d] Kinetic studies of the formation of coordinated sulfenates by the H_2O_2 oxidation of thiolato complexes, and of the subsequent oxidation of coordinated sulfenates to coordinated sulf*in*ates, have also been reported.[6a,b] Other efforts have been concerned with the stereochemistry of the S-bonded sulfenato–cobalt(III) moiety, separation of diastereomers proving that the coordinated sulfenato ligand possesses nonlabile chirality.[6d] In addition, it has been noted that the sulfenato ligand can undergo reversible protonation, and a pH-dependent decomposition has been described.[6a]

However, very little has been reported on the general reactivity of S-bonded sulfenato ligands. The chemical and physical properties of a sulfenato–cobalt(III) species (Co–S(O)–R) might be placed somewhere between those of a noncoordinated sulfenate anion (R–S(O)$^-$) and those of a noncoordinated sulfoxide (R–S(O)–R′) since, relative to R^+, a cobalt(III) center might be expected to induce similar, but smaller, effects on the S–O bond polarity and bond order. Thus the extensively investigated reactivities of both noncoordinated sulfenate anions and noncoordinated sulfoxides provide a framework within which we have investigated the reactivity of coordinated sulfenates and have attempted to better define the physical and chemical nature of this species.

Experimental Section

General Considerations. Although we have not experienced any explosions, all of the perchlorate salts described in this work are potentially explosive and should be carefully handled in only very small quantities. No attempt was made to resolve any of the optical isomers or diastereomers encountered in this work.

Materials. All common laboratory chemicals were of reagent grade. Doubly distilled perchloric acid (70–72%) was obtained from G. F. Smith Co. Dowex 50W-X2 (200–400 mesh) cation-exchange resin was cleaned as previously described.[7] Sephadex SP-C25 (Na^+ form) cation exchanger was treated with aqueous bromine as outlined previously[8] to eliminate a residual reducing capacity and then was stored as recommended by the manufacturer (Pharmacia). Methanol was purified by distillation and stored over 3-Å molecular sieves. $BF_3{\cdot}Et_2O$ (Eastman) was purified shortly before use by vacuum distillation.[9] Solutions of $[Pd(OH_2)_4](ClO_4)_2$ in 1.0 M $HClO_4$ were prepared from 99.99% palladium metal (Aldrich) by the method of Izatt and co-workers[10] and standardized spectrophotometrically (ϵ_{296} = 84.1 M^{-1} cm^{-1} in 5.8 M $HClO_4$).[10]

Perchlorate salts of (2-sulfenatoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$,[6a] (methyl 2-aminoethyl thioether-*N*,*S*)bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$,[11] (2-sulfinatoethylamine-*N*,*S*)-bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$,[12] and (2-sulfenatoacetato-*O*,*S*)bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(O)CH_2COO)]^+$,[6a] were prepared shortly before use by established procedures. Chloride and bromide salts of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ were prepared by successively sorbing a concentrated solution of the perchlorate salt (in 0.005 M $HClO_4$) onto a column of SP-C25 ion exchanger, washing the column with 0.01 M HX (X = Cl^-, Br^-), eluting the band with a 0.5 M solution of LiX in 0.01 M HX, reducing the volume of the eluent by rotoevaporation (temperature kept below 30 °C), and precipitating the halide salt by

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(1) Abstracted from: Lydon, J. D. Ph.D. Thesis, University of Cincinnati, 1982.

(2) (a) Davis, F. A.; Friedman, A. J.; Nadir, U. K. *J. Am. Chem. Soc.* **1978**, *100*, 2844. (b) Hogg, D. R. *Compr. Org. Chem.* **1979**, *4*, 261.

(3) (a) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65–76. (b) Jones, D. N.; Cottam, P. D.; Davies, J. *Tetrahedron Lett.* **1979**, 4977. (c) Chou, T. S.; Burgtorf, J. R.; Ellis, A. L.; Lammert, S. R.; Kukolja, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 1609. (d) Pal, B. C.; Vziel, M.; Doherty, D. G.; Cohn, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 3634–8.

(4) (a) Allison, W. S. *Acc. Chem. Res.* **1976**, *9*, 293–9. (b) Lin, W. S.; Armstrong, D. A.; Gaucher, G. M. *Can. J. Biochem.* **1975**, *53*, 298–306.

(5) Shelton, J. R. *Rubber Chem. Technol.* **1974**, *47*, 949–59.

(6) (a) Adzamli, I. K.; Libson, K.; Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303–11. (b) Herting, D. L.; Sloan, C. P.; Cabral, A. W.; Krueger, J. H. *Ibid.* **1978**, *17*, 1649–54. (c) Sloan, C. P.; Krueger, J. H. *Ibid.* **1975**, *14*, 1481–5. (d) Jackson, W. G.; Sargeson, A. M.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1976**, 934–5. (e) Schubert, M. P. *J. Am. Chem. Soc.* **1933**, *55*, 3336. (f) Dollimore, L. S.; Gillard, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, 933.

(7) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532.

(8) Lydon, J. D.; Elder, R. C.; Deutsch, E., manuscript in preparation.

(9) Zweifel, G.; Brown, H. C. *Org. React.* (*N.Y.*) **1963**, *13*, 28.

(10) Izatt, R. M.; Eatough, D.; Christensen, J. *J. Chem. Soc. A* **1967**, 1302.

(11) Elder, R. C.; Kennard, G. J.; Payne, M. D.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 1296–1303.

(12) Lange, B. A.; Libson, K.; Deutsch, E.; Elder, R. C. *Inorg. Chem.* **1976**, *15*, 2985–9.

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addition of excess ethanol and cooling to ca. −20 °C. The halide salts were dried in the dark in a vacuum desiccator over P_2O_5. The purity of the salts was established by visible–UV spectrophotometry and ion-exchange analysis.

Methyl 2-aminoethyl thioether, $H_3CSCH_2CH_2NH_2$, was prepared by methylation of 2-aminoethanethiol. In a typical preparation 31.0 g (0.267 mol) of $HSCH_2CH_2NH_2 \cdot HCl$ (Aldrich, ca. 98%) was dissolved in ca. 500 mL of methanol and the resulting solution was purged with a stream of nitrogen gas. Anaerobically and with stirring, 128.3 mL (0.535 mol) of a 25% solution of sodium methoxide in methanol was then added slowly (ca. 15 min), whereupon 38.7 g (0.267 mol) of methyl iodide in 75 mL of methanol was added dropwise. Precipitated sodium salts were removed by filtration, and then the solvent was removed by rotoevaporation to yield a light, straw colored oil. Subsequent vacuum distillation yielded a water-white oily liquid: picrate salt, mp 116–118 °C (lit.[13] mp 119 °C); ^1H NMR ($CDCl_3$) δ 1.98 (2 H, br s, exchangeable with D_2O, NH_2), 2.10 (3 H, s, CH_3), 2.72 (4 H, A_2B_2 m, CH_2CH_2).

Methyl 2-aminoethyl sulfoxide, $H_3CS(O)CH_2CH_2NH_2$, was prepared by H_2O_2 oxidation of the thioether. In a typical preparation ca. 1 g of $H_3CSCH_2CH_2NH_2$ was dissolved in 5 mL of H_2O, the solution was adjusted to pH ca. 5 with HCl, and 1.0 mol (30% solution) of H_2O_2/mol of thioether was added slowly (over ca. 15 min) with stirring. The mixture was allowed to stir for an additional 6 h and then rotoevaporated to yield an oil. This oil was dissolved in ca. 25 mL of methanol; the resulting solution was adjusted to pH ca. 9.5 with 25% sodium methoxide in methanol, filtered, and rotoevaporated to yield a water-white oily liquid, which was not purified further: IR (neat) ν_{NH_2} 1580–1670 br, $\nu_{S=O}$ 1015 s, br cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70 (3 H, s, CH_3), 3.03 (4 H, m, CH_2CH_2).

(Methyl 2-aminoethyl sulfoxide-*N*,*O*)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)](ClO_4)_3$, was prepared by (1) methylation of the S-bonded sulfenato complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ with CH_3I and (2) direct substitution of $CH_3S(O)CH_2CH_2NH_2$ on $[(en)_2Co(solvent)_2]^{3+}$. In a typical methylation reaction 20.0 g of $[(en)_2Co(S(O)CH_2CH_2NH_2)](ClO_4)_2$ was dissolved in 85 mL of *N*,*N*-dimethylformamide (DMF) and 100 g of methyl iodide was added. The mixture was stirred in the dark at ca. 25 °C for 3 days, and the product was then precipitated as an oil by addition of ca. 2 L of diethyl ether. The oil was dissolved in 100 mL of 0.01 M HCl, and the resulting solution was extracted with two 150-mL portions of chloroform. The aqueous solution was then loaded onto a column (3.5 cm i.d. × 50 cm) of Sephadex SP-C25 cation exchanger, and elution with 0.25 M LiCl yielded a small band of starting material and a major red band of formal charge ca. 3+. This latter band was displaced from the column with 0.5 M aqueous $Ba(ClO_4)_2$ (pH ca. 2), and cooling of this eluent to ca. −10 °C slowly yielded a fine red powder. Aqueous solutions of this solid exhibit the same visible–UV spectrum and ion-exchange behavior as does the original red eluent. The iodide salt $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]I_3$ was prepared from the perchlorate salt by metathesis with NaI in 0.01 M HCl. In a typical substitution reaction 1.0 g (2.86 mmol) of *trans*-$[(en)_2CoCl_2]ClO_4$ was dissolved in a minimum amount of sulfolane (purified by distillation and dried by passing through a column of 3-Å molecular sieves), and then 2.38 g (5.72 mmol) of dried $AgClO_4$ was added. The resulting mixture was stirred at 60 °C for 20 min, and the precipitated AgCl was removed by filtration. Then 1 mol of $CH_3S(O)CH_2CH_2NH_2$/mol of cobalt was added, and the mixture was heated at ca. 50 °C for 1.5 h. After cooling to ambient temperature, the product was separated by addition of excess diethyl ether and the resulting oil was taken up in 0.01 M HCl. Ion-exchange separation on Sephadex SP-C25 as above yielded a main band with the same physical characteristics as that obtained by the methylation route: Visible–UV λ_{max} (ϵ) 501 (87), 357 (110) nm, λ_{min} 416, 338 nm; IR (iodide salt) $\nu_{S=O}$ 980 cm^{-1}; ^1H NMR (D_2O, pD ca. 2, perchlorate salt) δ 2.95 ($\simeq$3 H, s, CH_3), 3.33 (4 H, m, SCH_2CH_2), 2.88 ($\simeq$6 H, br m, en–CH_2), 2.57 (2 H, en–CH_2). Anal. Calcd for $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)](ClO_4)_3 \cdot H_2O$: C, 13.96; H, 4.15; N, 11.62; S, 5.32; Co, 9.78; Cl, 17.65. Found: C, 14.15; H, 4.11; N, 11.46; S, 5.39; Co, 10.14; Cl, 17.70. Attempts to prepare this complex by substitution onto $[(en)_2CoCl_2]^+$ and $[(en)_2Co(OH_2)_2]^{3+}$ in water yielded only the N-coordinated sulfoxide complexes *cis*-$[(en)_2CoCl(NH_2CH_2CH_2S(O)CH_3)]^{2+}$ (Ia) and *cis*-$[(en)_2Co(OH_2)(NH_2CH_2CH_2S(O)CH_3)]^{3+}$ (Ib). Characterization of Ia: Co/S/Cl ratios = 1/1/1 by SEM X-ray fluorescence analysis of the bromide salt; visible–UV λ_{max} 525, 367 nm λ_{min} 420, 333 nm; IR (KBr, bromide salt) $\nu_{S=O}$ 1010 cm^{-1}; ^1H NMR (D_2O, pD ca. 2) δ 2.78 ($\simeq$3 H, s, CH_3), 3.23 ($\simeq$4 H, m, SCH_2CH_2), 2.88 ($\simeq$8 H, br m, en–CH_2); formal charge by ion-exchange characteristics ca. 2+. Characterization of Ib: visible–UV (pH 2) λ_{max} 485, 350 nm, λ_{min} 406, 320 nm, (pH 9) λ_{max} 494, 356 nm, λ_{min} 425, 320 nm; IR (KBr, chloride salt) $\nu_{S=O}$ 1005 cm^{-1}; ^1H NMR (D_2O, pD ca. 2) δ 2.80 ($\simeq$3 H, s, CH_3), 3.27 ($\simeq$4 H, br m, SCH_2CH_2), 2.90 ($\simeq$8 H, br m, en–CH_2); formal charge by ion-exchange characteristics ca. 3+. Treatment of the chloro complex Ia with $AgClO_4$ in water yields the aquo complex Ib, but similar treatment in sulfolane yields the N,O-chelated complex $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]^{3+}$. Attempts to prepare the N,O-chelated sulfoxide complex by oxidation of the N,S-chelated methyl thioether complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2]^{3+}$ were unsuccessful as the starting material proved to be highly resistant to attack by even strong oxidants such as H_2O_2 and molecular chlorine.

Protonation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. Three methods were used to protonate the sulfenato complex and examine the resultant changes in the infrared spectrum. (1) DCl was added to a freshly prepared, concentrated solution of $[(en)_2Co(S(O)CH_2CH_2NH_2)]Cl_2$ in 0.05 M DCl to obtain samples in which $[D^+]$ was about 0.05, 1.0, 2.0, 3.0, 4.0, and 5.0 M. The IR spectrum of each solution was then obtained (1700–600 cm^{-1}) with use of Wilks AgCl mini-cells of path length 0.025 or 0.050 mm. A reference cell contained approximately the same concentration of DCl in D_2O. (2) Finely ground $[(en)_2Co(S(O)CH_2CH_2NH_2)]X_2$ ($X = ClO_4^-$, Br^-) was suspended on glass wool and treated in the dark with a stream of anhydrous HCl gas for ca. 10 m. The IR spectrum was then examined in KBr and in Nujol. (3) To a cooled, concentrated solution of $[(en)_2Co(S(O)CH_2CH_2NH_2)]Cl_2$ in water was added $HClO_4$ or HCl to give a final $[H^+]$ of about 6 M. Ethanol (for $HClO_4$) or 2-propanol (for HCl) was then added, and the mixture was cooled rapidly in a dry ice–2-propanol slush to yield a solid, which was collected by centrifugation and dried in vacuo over P_2O_5. The IR spectra of these solids were obtained in KBr or Nujol. For all three methods the protonation resulted in an elimination (or marked reduction in intensity) of the intense broad band at ca. 930 cm^{-1}, which is assigned to the S=O stretch of the coordinated sulfenato ligand, and the concomitant appearance of a much weaker broad band at ca. 800 cm^{-1}. The spectra in DCl–D_2O systematically exhibited these changes more dramatically as the $[D^+]$ was increased. Ion-exchange analysis and visible–UV spectrophotometry showed that the sulfenato complex did not undergo significant decomposition during the protonation studies.

Equilibration of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ with Palladium(II). The equilibria between palladium(II), as either $PdCl_4^{2-}$ or $[Pd(OH_2)_2]^{2+}$, and the sulfenato complex were examined spectrophotometrically by the method of continuous variations.[14] For the $PdCl_4^{2-}$ case, 5.03×10^{-4} M solutions (in 0.01 M HCl) of $[(en)_2Co(S(O)CH_2CH_2NH_2)](ClO_4)_2$ and K_2PdCl_4 were used to monitor the equilibrium at 475, 450, 425, and 400 nm; 8.05×10^5 M solutions were used to follow absorbance changes at 400, 350, 300, and 280 nm. At all wavelengths the Job plot showed an increase in absorbance upon complex formation and indicated the generation of a 1/1 equilibrium complex. An analysis of the data by the method of Likussar and Boltz yielded a conditional formation constant of 1.4 (1) $\times 10^4\ M^{-1}$.[14b] An increase in the chloride concentration to 0.05 M caused a substantial reduction in the observed absorbance changes. For the $[Pd(OH_2)_4]^{2+}$ case, increases in absorbance at 318, 287, and 260 nm, obtained with 1.10×10^{-2} M solutions (in 0.50 M $HClO_4$) also indicated a 1/1 complex formation. However, the resulting Job plots exhibited broader curvature than the plots describing the $PdCl_4^{2-}$ equilibrium, indicating a significantly smaller formation constant for the $Pd(OH_2)_4^{2+}$ case. The IR spectrum of a solid product isolated by mixing more concentrated solutions of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $PdCl_4^{2-}$ showed a loss of the $\nu_{S=O}$ band at 930 cm^{-1} and an increase in intensity in the 1040–1010-cm^{-1} region, which overlaps with a $\nu_{C\text{-}C}$ or $\nu_{C\text{-}N}$ band at ca. 1045 cm^{-1}.

Analyses. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Total cobalt analyses were performed by using a modified Kitson procedure.[15] SEM X-ray

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(13) Müller, M.; Beck, W. *Justus Liebigs Ann. Chem.* **1912**, *386*, 337–41.

(14) (a) Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw-Hill: New York, 1961; Chapter 3. (b) Likussar, W.; Boltz, D. F. *Anal. Chem.* **1971**, *43*, 1265–72.

fluorescence measurements of atom ratios were kindly performed by Dr. C. J. Weschler of Bell Laboratories, Holmdel, NJ, using an AMR-100 instrument.

Equipment. Visible–UV spectra were recorded on a Cary 14 or a Cary 210 spectrophotometer. Infrared spectra were obtained on a Beckman IR-18A instrument, and ^{1}H NMR spectra were obtained on a Varian T-60.

Procedures. Formal charges on complexes were inferred from elution characteristics on Dowex 50W-X2 (H^+ or Na^+ forms) and Sephadex SP-C25 (Na^+ form) ion-exchange columns or determined by titrating the acid displaced from a H^+-form Dowex 50W-X2 column upon sorbing a known amount of complex. IR spectra were recorded in KBr pellets or Nujol mulls. ^{1}H NMR resonances were referenced to Me_4Si in $CDCl_3$ or to sodium 3-(trimethylsilyl)-1-propanesulfonate in D_2O.

Results and Discussion

Lewis Basicity. Both noncoordinated sulfenate anions ($R-S(O)^-$) and noncoordinated sulfoxides ($R-S(O)-R'$) are readily protonated. Sulfoxides can be titrated in acetic anhydride with perchloric acid,[16] and the pK_a values of the conjugate acids are slightly less than zero.[17] While the pK_a values of sulfenic acids have not been measured, aromatic sulfenic acids are known to be at least as acidic as phenol,[3a] and 1-methyluracil-4-sulfenic acid is deprotonated by weak bases in aqueous solution and can be regenerated from the silver(I) salt at pH 2.[3d] From these observations it is to be expected that S-bonded sulfenato ligands ($Co-S(O)-R$) can also be protonated to form the corresponding coordinated sulfenic acid, and indeed it has been shown that this protonation occurs more easily than does protonation of a coordinated thiolato ligand (Co–SR).[6a,18] This previous work also demonstrated that protonation of sulfenato and thiolato ligands affects the positions and intensities of the charge-transfer bands associated with these moieties; in particular, the transition at ca. 360 nm that is characteristic of the $Co-S(O)-R$ linkage is greatly diminished, or eliminated, upon protonation.[6a,18] However, the question as to whether sulfenato–cobalt(III) complexes are protonated on the coordinated sulfur atom or on the pendant oxygen atom was not addressed. There is a large body of literature concerned with whether free sulfoxides coordinate through sulfur or through oxygen[19–21,25] and how the mode of coordination is determined by the properties of the Lewis acid. Both noncoordinated sulfenate anions and noncoordinated sulfoxides are known to undergo protonation on oxygen,[3a,22] and on this basis alone protonation of sulfenato–cobalt(III) complexes is also expected to occur on oxygen.

Protonation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ causes the 930-cm^{-1} IR band assigned to $\nu_{S=O}$ to decrease in intensity at the expense of a new band appearing at 800 cm^{-1}. This observation is consistent with protonation at oxygen causing a decrease in S—O bond order. These IR spectral effects are analogous to those observed upon coordination of the oxygen atom of sulfoxides, e.g., in $(CH_3)_2S{=}O{-}BF_3$[19a] $(CH_3)_2S{=}O{-}CH_3^+$,[20b] and $(CH_3)_2S{=}O{-}M^{n+}$[20b,25] (where M represents a transition-metal center), which are again ascribed to a lowering of the S=O bond order upon oxygen coordination. However, the new band at 800 cm^{-1} in the IR spectrum of the protonated sulfenato complex cannot be unequivocally assigned to $\nu_{S=O}$ because of its relatively low intensity and the complexity of the spectrum in this region. An additional argument supporting protonation on oxygen is derived from the observation that both protons and BF_3 generate very similar changes in the visible–UV spectrum of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$; i.e., the 365-nm band that is characteristic of the S-bonded sulfenato ligand effectively disappears, and the sulfur-to-cobalt charge-transfer band at ca. 280 nm increases in intensity. Since BF_3 is known to be a "hard" Lewis acid that preferentially binds to oxygen over sulfur, and since BF_3 is known to form strong complexes with sulfoxides by bonding to oxygen,[19] it is presumed that BF_3 binds to the oxygen atom of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. Thus, the similar visible–UV spectrophotometric effects generated by H^+ and BF_3 imply that protonation also occurs on oxygen.

The marked affinity of BF_3 for "hard" bases is matched by the contrary affinity of palladium(II) and platinum(II) for "soft" bases. For example, a survey of transition-metal sulfoxide complexes shows that most contain O-bonded sulfoxides, but IR and structural studies conclusively demonstrate that palladium(II) and platinum(II) complexes often contain S-bonded sulfoxides.[23,25] Palladium(II) and $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ interact in dilute aqueous solution to form a 1/1 adduct, and while the visible–UV spectrum of the adduct cannot be completely interpreted, it is consistent with palladium coordination at sulfur; i.e., the intensity of the band in the 365-nm region increases, contrary to the decrease observed upon H^+ and BF_3 coordination. In addition, the IR spectrum of the adduct formed with $PdCl_4^{2-}$ shows a loss of the $\nu_{S=O}$ band at 930 cm^{-1} and an increased intensity in the 1010–1050-cm^{-1} region, which may result from a perturbed $\nu_{S=O}$ vibration of increased S—O bond order. The $\nu_{S=O}$ band of sulfoxides shifts in the same direction, by approximately the same amount, upon coordination through sulfur to palladium(II) or platinum(II) ($\nu_{S=O}((CH_3)_2S{=}O) = 1069$ cm^{-1}; $\nu_{S=O}$ (*trans*-$(PdCl_2[(CH_3)_2S{=}O]_2)$ = 1116 cm^{-1} [23]). An indirect argument supporting sulfur coordination in the sulfenato system arises from the observation that $PdCl_4^{2-}$ and the sulfinato complex $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ do not detectably interact in 0.01 M HCl. Since the sulfinato complex cannot coordinate through sulfur but could coordinate through oxygen, the lack of adduct formation implies that oxygen coordination to palladium(II) by either the sulf*i*nato or sulf*e*nato complexes is very unfavorable.

In the $PdCl_4^{2-}$ equilibrium with $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, increasing the chloride concentration from 0.01 to 0.05 M reduces the observed absorbance changes, implying that 10^{-2} M chloride and 10^{-4} M $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ effectively compete for coordination to palladium(II). Interestingly, $PdCl_4^{2-}$ (in 0.01 M HCl) does not detectably interact with the thioether complex $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$, and thus the affinities for palladium(II) qualitatively decrease in the order $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+} > Cl^- \gg [(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$. The sulfur atoms in both the sulf*e*nato and the thioether complexes are three-coordinate, and thus the reduced ligating ability of the thioether complex may be ascribed to either an electrostatic effect (3+ complex vs. a 2+ complex) or to an electronic effect resulting from the disparate nature of the groups bonded to sulfur (oxygen atom vs. CH_3^+). (Similarly the sulf*e*nate complexes can be oxidized to the sulf*i*nate analogues, but the thioether complex is highly resistant to oxidation to the coordinated sulfoxide.) That

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(15) (a) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664. (b) Hughes, R. G.; Endicott, J. F.; Hoffman, M. Z.; House, D. A. *J. Chem. Educ.* **1969**, *46*, 440.

(16) Wirner, D. C. *Anal. Chem.* **1958**, *30*, 2060–1.

(17) Laughlin, R. G. *J. Org. Chem.* **1960**, *25*, 864–5.

(18) Adzamli, I. E.; Nosco, D. L.; Deutsch, E. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1364–6.

(19) (a) Cotton, F. A.; Francis, R. *J. Am. Chem. Soc.* **1960**, *82*, 2986. (b) McGandy, L.; Eriks, K. *Diss. Abstr.* **1961**, *22*, 754.

(20) (a) Zimmerman, I. C.; Barlow, M.; McCullough, J. D. *Acta Crystallogr.* **1963**, *16*, 883. (b) Cotton, F. A.; Francis, R.; Horrocks, W. D.; Jr. *J. Phys. Chem.* **1960**, *64*, 1534–6.

(21) (a) Drago, R. S.; Meek, D. *J. Phys. Chem.* **1961**, *65*, 1446–7. (b) Kitching, W.; Moore, C. J.; Doddrell, D. *Aust. J. Chem.* **1969**, *22*, 1149.

(22) Modena, G. *Int. J. Sulfur Chem., Part C* **1972**, *7*, 95–102.

(23) (a) Cotton, F. A. *Acta. Crystallogr.* **1967**, *23*, 788. (b) Langs, D. A.; Hare, C. R.; Little, R. G. *J. Chem. Soc., Chem. Commun.* **1967**, 1080. (c) Kitching, W.; Moore, C. J.; Doddrell, D. *Inorg. Chem.* **1970**, *9*, 541–9.

Table I. Solvent Dependence of the Visible-UV Spectrum of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{+2}$ [a]

solvent	λ_{max} (ϵ)		
formamide	466 (640)	375 (6400)	290 (4100)
95% EtOH	470 (625)	375 (5800)	291 (3900)
MeOH	468 (675)	378 (5900)	294 (4100)
Me_2SO	478 (760)	385 (6390)	300 (4480)
DMF	474 (790)	387 (6350)	300 (4610)
acetone	480 (810)	393 (5650)	
acetonitrile	478 (835)	393 (5800)	304 (4900)
H_2O	470 (500)	365 (6700)	284 (3700)

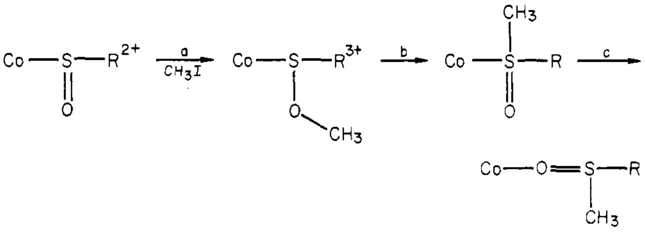
[a] Wavelengths, λ, are in nm. Molar extinction coefficients, ϵ, given in parentheses, are in M^{-1} cm^{-1}. Sulfenato complexes are unstable in solution,[6a] and therefore the reported extinction coefficients have relatively large uncertainties.

electrostatic effects are important in these equilibria is inferred from the Job plots governing the 1/1 adduct formation between $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and the cationic complex $[Pd(OH_2)_4]^{2+}$; the curvature of these plots indicates that this equilibrium is governed by a smaller formation constant than is the equilibrium with the anionic complex $PdCl_4^{2-}$.

Both silver(I) and mercury(II) have strong affinities for coordinated thiolates,[24] but neither bind detectably to the S-bonded sulf*e*nato ligands discussed here. This is consistent with the fact that Ag^+ and Hg^{2+} bind to the oxygen atom of free sulfoxides[25] and thus do not appear to have the great preference of palladium(II) and platinum(II) for sulfur coordination. The disparate affinities of silver(I) for the sulfur atoms of coordinated thiolates and coordinated sulf*e*nates provide the basis of an experimental technique to separate thiolato complexes from the sulf*e*nato and/or sulf*i*nato analogues that have similar ion-exchange elution characteristics. This separation is not utilized preparatively but rather is used to qualitatively identify thiolato complexes in the presence of sulf*e*nato/sulf*i*nato complexes, or vice versa. Elution of a mixture of complexes from a cation-exchange column with a solution of $NaClO_4$ and $AgClO_4$ causes the thiolato complex $[Co–SR]^{n+}$ to be retained as the stable, highly charged adduct $[Ag(CoSR)_2]^{(2n+1)+}$ while the uncomplexed, lower charged sulf*e*nato and/or sulf*i*nato complexes ($[Co–S(O)R]^{n+}$ and $[Co–S(O)_2R]^{n+}$) move with much higher R_f values.

The potential Lewis basicity of both noncoordinated sulfenic acids and noncoordinated sulfoxides is manifested in many solvent-dependent properties; this solvent dependency is often presumed to result from hydrogen-bonding interactions between the solvent and the oxygen atom. Thus, the infrared spectrum of 2-methylpropanesulfenic acid shows substantial solvent effects,[26] while sulfoxides have been shown to have solvent-dependent infrared and ultraviolet spectra and to exhibit strong hydrogen-bonding tendencies.[27] Consistent with our expectation that sulfenato ligands should exhibit properties similar to those of noncoordinated sulfenates and noncoordinated sulfoxides, the visible–UV spectra of S-bonded sulfenato–cobalt(III) complexes are markedly solvent dependent (Table I). While the visible–UV spectra of other cobalt(III) complexes containing coordinated sulfur also show solvent-dependent effects, none of these effects is as large as those exhibited by the sulfenato complexes. Particularly dramatic is the wide range of energies observed for the charge-transfer transition characteristic of the Co–S(O)R linkage; this transition usually appears at ca. 365 nm in water but shifts to ca. 393 nm in acetonitrile (Table I). The marked dependence of the energy of this band on the nature of the solvent is consistent with assignment of this charge-transfer transition as originating from a molecular orbital that encompasses the oxygen atom of the sulfenato moiety.[8]

Scheme I



Methylation Reactions. Noncoordinated sulfenate anions and noncoordinated sulfenic acids are known to be highly reactive as both nucleophiles and electrophiles; the nucleophilicity of these species is manifested by reactions at both sulfur and oxygen.[3,26,28] Noncoordinated sulfoxides also function as ambidentate nucleophiles, the S-substituted product usually being thermodynamically favored and the O-substituted product often being kinetically favored.[29] It is thus likely that S-bonded sulfenato–cobalt(III) complexes can function as nucleophiles, and indeed it has been shown that H_2O_2 oxidizes the sulf*e*nato complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ to the sulf*i*nato complex $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$.[6a] This reaction could proceed by direct nucleophilic attack of the coordinated sulfur atom on the O–O bond of H_2O_2 or by initital nucleophilic attack of the pendant oxygen atom and subsequent rearrangement of the Co–S(O–O)–R intermediate to the Co–S(O)$_2$–R product. To further probe the nucelophilic reactivity of coordinated sulfenato ligands, we have investigated the reaction of CH_3I with $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2COO)]^{+}$.

(i) $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. The reaction of this sulfenato complex with a large excess of methyl iodide yields predominantly the complex containing N,O-chelated methyl 2-aminoethyl sulfoxide, i.e., $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]^{3+}$. No N,S-bonded products are detected. The N,O-chelated sulfoxide complex can also be independently prepared by direct substitution of $CH_3S(O)CH_2CH_2NH_2$ on the reactive center $[(en)_2Co(sulfolane)_2]^{3+}$. Substitution of $CH_3S(O)CH_2CH_2NH_2$ onto $[(en)_2CoCl_2]^+$ or $[(en)_2Co(OH_2)_2]^{3+}$ in water yields only monodentate N-bonded products, consistent with the generalization that O-bonded sulfoxides are weak ligands.[29] However, generation of $[(en)_2Co(sulfolane)(NH_2CH_2CH_2S(O)CH_3)]^{3+}$ leads directly to the N,O-chelated product, implying that O-bonded sulfoxide is at least competitive with sulfolane in terms of ligand strength.[29,39]

The product complex $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]^{3+}$ has an intense and broad band in the IR at 980 cm^{-1} that is characteristic of O-bonded sulfoxide ligands[20b,25,30] and is assigned to the S═O stretch. The visible–UV spectrum of this product shows only two characteristic d–d transitions, the lack of a charge-transfer band in the 280-nm region evidencing the absence of a Co–S bond.[31] The ^1H NMR spectrum exhibits a sharp singlet at δ 2.95 arising from the methyl group of the coordinated ligand. The cor-

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[24] (a) Heeg, M. J.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 2036–9. (b) Heeg, M. J.; Elder, R. C.; Deutsch, E. *Ibid.* **1980**, *19*, 554–6.

[25] Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 115–186.

[26] Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 207.

[27] (a) Szmant, H. H. "Sulfur in Organic and Inorganic Chemistry"; Senning, A., Ed.; Marcel Dekker: New York, 1971; p 122. (b) Passerini, R. C. "Organic Sulfur Compounds"; Kharasch, N., Ed.; Pergamon Press: New York, 1961; pp 67–8. (c) Koch, H. P. *J. Chem. Soc.* **1950**, 2892–4. (d) Gramstad, T. *Spectrochim. Acta* **1963**, *19*, 497.

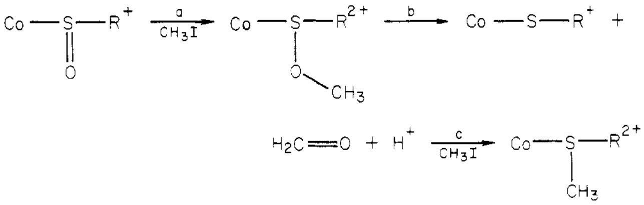
[28] (a) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; pp 26–31. (b) Chou, T. S. *Tetrahedron Lett.* **1974**, 725–8.

[29] Piriz Mac-Coll, C. R.; Beyer, L. *Inorg. Chem.* **1973**, *12*, 7–11.

[30] Smith, S. G.; Winstein, S. *Tetrahedron* **1958**, *3*, 317–21.

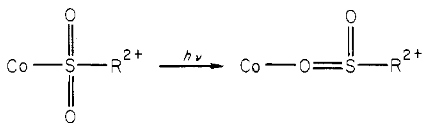
[31] Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.

Scheme II



responding resonance of the noncoordinated ligand occurs at δ 2.70 ($CDCl_3$), the coordination-induced deshielding effect being of the same magnitude observed in O-bonded dimethyl sulfoxide complexes of cobalt(III).[32] Similarly, the methylene protons that appear as a complex multiplet at δ 3.03 ($CDCl_3$) in the noncoordinated ligand are also deshielded in the sulfoxide complex, appearing as a similarly shaped multiplet centered at δ 3.33.[40]

A reasonable, albeit completely conjectural, mechanism for the conversion of the N,S-chelated sulfenato complex to the N,O-chelated sulfoxide complex involves (a) initial O-alkylation by CH_3I to give a metastable *O*-methyl ester, (b) internal CH_3^+ transfer to give the *S*-methyl sulfoxide, and finally (c) isomerization of the S-bonded sulfoxide to yield the O-bonded sulfoxide product (Scheme I). In Scheme I the initital step is proposed to be O-methylation, rather than direct S-methylation, in analogy to the reaction of dimethyl sulfoxide with methyl iodide, which proceeds by initial O-methylation and then subsequent conversion to the S-methylated product.[29] An equivalently reasonable scheme could be based about initital S-methylation and subsequent isomerization to the O-bonded sulfoxide. The proposed isomerization of the Co–S linkage to a Co–O linkage in the final step of Scheme I is reminiscent of the photoinduced isomerization of the sulf*i*nato complex $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$ reported by Adamson and co-workers:[33]



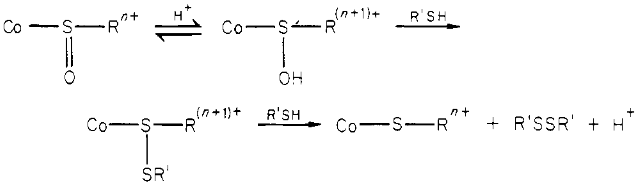
$$\mathrm{Co{-}\overset{O}{\underset{O}{S}}{-}R^{2+}} \xrightarrow{h\nu} \mathrm{Co{-}O{=}\overset{O}{S}{-}R^{2+}} \qquad (1)$$

However, in the sulf*i*nato system the five-membered, S-bonded ring is thermodynamically more stable whereas in the sulfoxide system the six-membered, O-bonded ring is more stable.

(ii) $[(en)_2Co(S(O)CH_2COO)]^+$. The reaction of this sulfenato complex with excess methyl iodide yields a mixture of products, the methyl thioether complex $[(en)_2Co(S(CH_3)CH_2COO)]^{2+}$ being one of the major components. This product is readily identified by comparison to an authentic sample.[11] Ion-exchange analysis using a $NaClO_4$–$AgClO_4$ eluent (vide supra) shows that the initital sulfenato complex is not contaminated with the thiolato complex $[(en)_2Co(SCH_2COO)]^+$, and thus the thioether product does not arise from methylation of a thiolato impurity. None of the observed reaction products could be assigned as O-bonded or S-bonded sulfoxide complexes.

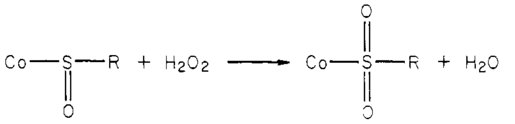
A possible mechanism for the conversion of the sulfenato complex to the thioether complex could plausibly involve (a) initial O-alkylation by CH_3I to give a metastable *O*-methyl ester, (b) disproportionation of this intermediate to yield formaldehyde and the thiolato complex, similar to the Kornblum reaction of sulfoxides,[34] and finally (c) alkylation of the thiolato complex by CH_3I to yield the thioether complex (Scheme II). The disproportionation reaction in the second step of Scheme II presumably involves the acidic hydrogen atoms on the activated α-carbon atom of the mercaptoacetato chelate ring since the methylation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, which does not contain an activated α-carbon atom, does not give rise to a thioether product (vide supra). Other examples have been noted wherein the chemistries exhibited by $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ and their derivatives are markedly different.[8,35] The last step of the Scheme II is totally consistent with the chemisty of thiolato–cobalt(III) complexes, which are known to undergo rapid methylation in the presence of excess methyl iodide.[11]

Scheme III

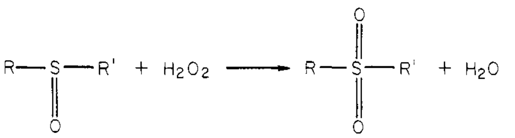


Reduction Reactions. Both noncoordinated sulfenic acids and noncoordinated sulfoxides are susceptible to nucleophilic attack, and concomitant reduction, by thiols.[3,36] Analogously, the sulfenato complexes $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2COO)]^+$ are reduced to the respective thiolato complexes by excess thiol in *N,N*-dimethylformamide. However, this reduction proceeds at a reasonable rate only in the presence of acid (ca. 2 M methanesulfonic acid). This acid dependence is consistent with protonation of the oxygen atom of the sulfenato moiety, causing it to be a better leaving group, and with the fact that the reduction of noncoordinated sulfoxides by thiols is also acid catalyzed.[37] A reasonable mechanism for thiol reduction of sulfenato ligands is shown in Scheme III. The intermediate disulfide complex proposed in this scheme is not observed during the reaction since coordinated disulfides are readily cleaved by excess thiol to yield the corresponding thiolato complex and a noncoordinated disulfide.[8] The reduction of sulfenato complexes by thiols proceeds more rapidly with mercaptoethanol than with 2-methylpropanethiol, consistent with nucelophilic attack by the thiol (as either in the second or third step of Scheme III) being a rate-determining step.

Oxidation Reactions. The H_2O_2 oxidation of S-bonded sulf*e*nato ligands to S-bonded sulf*i*nato ligands has already been mentioned;[6a] this reaction is similar to the H_2O_2 oxidation of noncoordinated sulfoxides to sulfones (eq 2, 3). Noncoordinated sulfoxides are also known to undergo reactions that result ultimately in transfer of oxidation from the sulfur atom to an adjacent carbon atom. The familiar Pummerer rearrangements are examples of this type of reaction[36] (eq 4a, b).



$$\mathrm{Co{-}\underset{O}{S}{-}R} + H_2O_2 \longrightarrow \mathrm{Co{-}\overset{O}{\underset{O}{S}}{-}R} + H_2O \qquad (2)$$



$$\mathrm{R{-}\underset{O}{S}{-}R'} + H_2O_2 \longrightarrow \mathrm{R{-}\overset{O}{\underset{O}{S}}{-}R'} + H_2O \qquad (3)$$

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[32] Lantzke, I. R.; Watts, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 816.

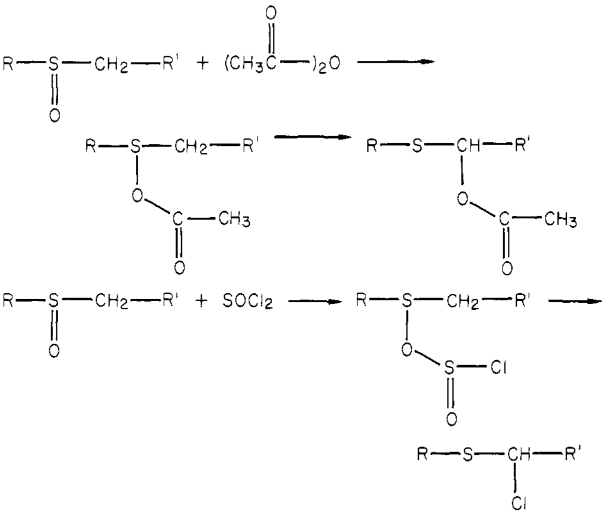
[33] Adamson, A. W.; Houlding, V. *J. Am. Chem. Soc.* **1980**, *102*, 6889–91.

[34] Oae, S. "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; pp 419–24.

[35] (a) Weschler, C. J.; Sullivan, J. C.; Deutsch, E. *Inorg. Chem.* **1974**, *13*, 2630–6. (b) Lydon, J. D.; Mulligan, K. J.; Elder, R. C.; Deutsch, E. *Ibid.* **1980**, *19*, 2083–7. (c) Gainsford, G. J.; Jackson, W. G.; Sargeson, A. M. *Aust. J. Chem.* **1980**, *33*, 707–15.

[36] Oae, S. "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; pp 406–13.

[37] Oae, S. "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; p 404.



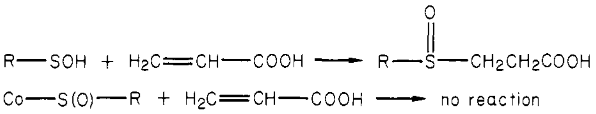
(4a)

(4b)

This chemistry is mimicked in the reaction of $[(en)_2Co(S(O)CH_2COO)]^+$ (in DMF) with electrophiles such as *N*-chlorosuccinimide, *N*-bromosuccinimide, and acetic anhydride to give small yields (3–5%) of the monothiooxalato complex $[(en)_2Co(SC(O)COO)]^+$. This product is readily identified by comparison to an authentic sample.[35b,c] The major products of the reaction are yet uncharacterized but predominantly consist of complexes that do not contain a Co–S bond. While the low yield of this reaction makes generalizations difficult, the production of $[(en)_2Co(SC(O)COO)]^+$ is reproducible and can be shown *not* to be the result of oxidation of a possible $[(en)_2Co(SCH_2COO)]^+$ impurity in the $[(en)_2Co(S(O)CH_2COO)]^+$ starting material.

The oxidation of $[(en)_2Co(S(O)CH_2COO)]^+$ to $[(en)_2Co(SC(O)COO)]^+$ involves formally a 4-equiv oxidation of carbon and a 2-equiv reduction of sulfur, and thus during the reaction 2 equiv of oxidation are transferred from sulfur to carbon. This demonstration of the transfer of oxidizing power from sulfur to the adjacent carbon atom supports the previously proposed mechanism for the oxidation of the thiolato complex $[(en)_2Co(SCH_2COO)]^+$ to $[(en)_2Co(SC(O)COO)]^+$.[35b,38] The oxidation of $[(en)_2Co(SCH_2COO)]^+$ by a variety of 1- and 2-equiv agents has been presumed to proceed by initial oxidation of the coordinated thiolato sulfur atom to a thiyl or sulfenyl intermediate, followed by transfer of the oxidizing power from sulfur to carbon.[35b,38]

Addition Reactions. Noncoordinated sulfenic acids are known to undergo facile addition to activated olefins and acetylenes to generate sulfoxides, and in fact this reaction is commonly used to trap reactive sulfenic acid intermediates.[3,26] However, sulfenato–cobalt(III) complexes do not appear to undergo similar addition reactions, even in the presence of acid; thus, no reaction is observed with $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and either acrylic acid or propynol in DMF solvent, with and without added methanesulfonic acid (eq 5a, b). Thus, with regard to addition reactions sulfenato–cobalt(III) complexes are more similar to noncoordinated sulfoxides, which do not readily add to activated olefins.



$$R{-}SOH + H_2C{=}CH{-}COOH \longrightarrow R{-}\overset{O}{\overset{\|}{S}}{-}CH_2CH_2COOH \quad (5a)$$

$$Co{-}S(O){-}R + H_2C{=}CH{-}COOH \longrightarrow \text{no reaction} \quad (5b)$$

Summary

Many of the physical properties of S-bonded sulfenato ligands such as the S—O bond length, the $\nu_{S=O}$ infrared stretching frequency, and the solvent dependence of visible–UV spectrophotometric parameters are similar to those of noncoordinated sulfenate anions and sulfoxides. It is therefore not surprising that the chemical reactivity of sulfenato–cobalt(III) complexes mimic the reactivity of these noncoordinated species. This is illustrated by (1) oxygen coordination to "hard" Lewis acids such as BF_3 and H^+, (2) sulfur coordination to "soft" Lewis acids such as palladium(II), (3) nucleophilic reactivity by probably both sulfur and oxygen, (4) 2-equiv reduction at sulfur to yield the corresponding thiol, (5) 2-equiv oxidation at sulfur, and (6) transfer of oxidizing power from sulfur to an adjacent carbon atom. Coordination to cobalt(III) introduces several complicating features to the chemistry of the sulfenato moiety such as potential isomerization of the Co–S linkage to a Co–O linkage and possible internal oxidation of the ligand by cobalt(III) and also reduces the nucelophilic reactivity of the coordinated sulfur atom. Despite these metal ion effects, it appears to be generally true that sulfenato–cobalt(III) complexes display reactivity intermediate between that of noncoordinated sulfenate anions and that of noncoordinated sulfoxides.

Acknowledgment. Financial support by the National Science Foundation, Grant No. CHE79-26497, is gratefully acknowledged. We thank Dr. Charles Weschler of Bell Laboratories for performing the X-ray fluorescence measurements.

Registry No. Ia, bromide salt, 81688-32-6; Ib, chloride salt, 81688-33-7; $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)](ClO_4)_3$, 80136-79-4; $[(en)_2Co(S(O)CH_2CH_2NH_2)](ClO_4)_2$, 68645-83-0; $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]I_3$, 80136-81-8; $[(en)_2Co(S(O)CH_2CH_2NH_2)]Cl_2$, 81688-92-8; $[(en)_2Co(S(O)CH_2CH_2NH_2)]Br_2$, 81688-91-7; *trans*-$[(en)_2CoCl_2]ClO_4$, 14407-65-9; $PdCl_4^{2-}$, 14349-67-8; $[Pd(OH_2)_4]^{2+}$, 22573-07-5; $H_3CS(O)CH_2CH_2NH_2$, 49773-19-5; $H_3CSCH_2CH_2NH_2$, 18542-42-2; CH_3I, 74-88-4.

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(38) Sullivan, J. C.; Deutsch, E.; Adams, G. E.; Gordon, S.; Mulac, W. A.; Schmidt, K. H. *Inorg. Chem.* **1976**, *15*, 2864–8.

(39) Hurst, J. K.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1174.

(40) After submission of this paper, Sargeson and co-workers reported[41] the single-crystal X-ray structural characterization of $[(en)_2Co(O{=}S(CH_3)CH_2CH_2NH_2)]^{3+}$ prepared by methylation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$.

(41) Gainsford, G. J.; Jackson, W. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1982**, *104*, 137–141.