

Synthesis, Characterization, and Reactivity of Coordinated Sulfenic Acids

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Received September 15, 1978

Several bis(ethylenediamine)cobalt(III) complexes containing chelated, S-bonded sulfenic acid ligands have been synthesized and characterized. $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2COO)]^+$ are prototypes of this class of complexes. The general preparative route to sulfenato complexes involves stoichiometric oxidation of the corresponding thiolato complex with a 2-equiv oxidant, e.g., H_2O_2 , in aqueous solution. Subsequent oxidation converts the sulfenato complex to the corresponding sulfinato complex. The ligand field strength and the electronegativity of the ligating sulfur atom increase monotonically along the thiolato-sulfenato-sulfinato series. The S-bonded sulfenato ligand exhibits a characteristic S-O stretch in the region $950-1000\text{ cm}^{-1}$ and a characteristic charge-transfer absorption at ca. 360 nm. Reversible protonation of the sulfenato ligand occurs in aqueous $HClO_4$ solutions; the protonation constant of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ at 25°C , $\mu = 4.0\text{ M}$, is $1.4 \pm 0.2\text{ M}^{-1}$. Sulfenato-cobalt(III) complexes slowly decompose in aqueous acidic media to yield a variety of products including cobalt(II). The single-crystal X-ray structure analysis of (2-sulfenatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) thiocyanate, refined to a conventional *R* factor of 0.030, is reported. The cobalt(III) center is approximately octahedrally coordinated (five N atoms and one S atom) while the sulfenato sulfur atom is three-coordinate (Co, C, and O). The Co-N bond trans to the sulfenato sulfur atom is significantly longer than the average of the cis Co-N bonds, $\Delta = 0.072(8)\text{ \AA}$. The rates of H_2O_2 oxidation of $[(en)_2CoS(O)CH_2CH_2NH_2]^{2+}$ in aqueous perchloric acid media are reported as a function of $[H_2O_2]$, $[H^+]$, and temperature. The mechanism of this reaction is discussed in terms of nucleophilic attack by the coordinated sulfur on the O-O bond of H_2O_2 , the coordinated sulfur atom having about the same nucleophilicity as the sulfur atom of SCN^- . The observed acid catalysis presumably reflects the greater reactivity of $H_3O_2^+$ as a nucleophilic substrate. This acid catalysis is significantly less effective in this system than in analogous H_2O_2 oxidations, implying that within the acid-catalyzed transition state there is an interaction between the proton and the sulfenato moiety which decreases the overall efficacy of this path.

Introduction

Free sulfenic acids are very unstable molecules,¹⁻⁴ few having ever been isolated.⁴⁻⁸ However, sulfenic acids are recognized to be important intermediates in many organic reactions such as hydrolysis of sulfonyl halides,^{1,9} decomposition of alkyl sulfoxides and thiosulfonates,^{2,8} autoxidation of thiols,¹⁰ etc. The instability of the sulfenic acid functionality is thought to be due to its high reactivity as either a nucleophile or electrophile.^{3,4,11,12} In a recent review⁴ Allison has compiled an impressive amount of indirect evidence making a strong case for the proposition that oxidation of certain protein thiol groups leads to sulfenic acids rather than the normally expected disulfides. This situation presumably obtains because within sterically confined protein environments both bimolecular formation of a disulfide and bimolecular decomposition of the sulfenic acid are energetically prohibitive. Therefore, the chemistry of sulfenic acids, which are inherently unstable as free small organic molecules, is important to the understanding of many organic reaction mechanisms as well as of the potential role of protein sulfenic acids in enzyme-catalyzed oxidations.

We,¹³ and others,¹⁴⁻¹⁶ have shown that controlled oxidation of thiols which are coordinated to cobalt(III) leads to coordinated, S-bonded sulfenic acids. Since the resultant sulfenato complexes are considerably more stable than the corresponding free sulfenic acid ligands, these complexes provide a means of investigating the chemistry of sulfenic acids. In this context we have undertaken a combined structural and mechanistic study of coordinated sulfenic acids. Our initial work, described in this paper, has focused on complexes such as $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2COO)]^+$ for three reasons. (1) The parent thiolato complexes $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ have been characterized by a variety of techniques, including single-crystal X-ray structural analysis.¹⁷ These complexes are designed for the explication of structural and mechanistic phenomena in that the first coordination spheres consist of a unique "soft" sulfur atom and five "hard" nitrogen or oxygen atoms. (2) Single-crystal X-ray structural analysis^{13,17} of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ shows that both thiolato sulfur and

sulfinato sulfur (formal oxidation states of -II and +II, respectively) induce significant structural trans effects (STE). It is therefore of interest to determine the extent of the STE exerted by sulfenato sulfur (formal oxidation state of 0) in $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. (3) These complexes do not contain a pendant carboxylate group, as in the cysteine derivative $[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]^{2+}$; such a pendant functionality can enter into complicated intraligand reactions¹⁸ and is likely to complicate the mechanistic interpretation of acid-dependent kinetic data.

In addition, because of the biochemical importance of H_2O_2 oxidations involving metal-sulfur enzymes,¹⁹ in this initial work we have chosen to probe the reactivity of coordinated sulfenic acids largely through an investigation of the kinetics and mechanism of the oxidation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ by hydrogen peroxide.

Experimental Section

Materials. All common laboratory chemicals were of reagent grade. Equivalent kinetic results were obtained using hydrogen peroxide solutions prepared from 30% H_2O_2 with and without added stabilizer. All kinetic experiments employed triply distilled water²⁰ and doubly vacuum-distilled perchloric acid (70-72%, G. F. Smith). Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate.²¹ Dowex 50W-X2 (200-400 mesh) cation-exchange resin was cleaned as previously described,²² Sephadex SP-C25 (sodium form) cation exchanger was prepared and stored as recommended by the manufacturer (Pharmacia). Perchlorate salts of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) and (2-sulfinatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) were available from previous studies.^{13,17,23,24} Perchlorate salts of (mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III) and (2-mercaptopropionato-*O,S*)bis(ethylenediamine)cobalt(III) were prepared by literature procedures.²⁵ The disulfides 2,2'-dithiodipropionic acid and 2,2'-dimethyl-2,2'-dithiodipropionic acid were prepared by H_2O_2 oxidation of the corresponding thiols; thiolactic acid was obtained from Aldrich, and thioisobutyric acid was kindly donated by H. J. Price of Eastman Kodak.

(2-Mercapto-2-methylpropionato-*O,S*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(SC(CH_3)_2COO)]ClO_4$. This complex is readily prepared by reduction of 2,2'-dimethyl-2,2'-dithiodipropionic acid with an ethylenediamine-cobalt(II) mixture according to the general procedure previously outlined.²³⁻²⁵ Reduction of this particular sterically hindered disulfide is slow, and the reaction mixture must

Table I. Visible-UV Spectrophotometric Parameters for Bis(ethylenediamine)cobalt(III) Complexes Containing Chelated Thiolato, Sulfenato, and Sulfinato Ligands^a

complex	λ_{\max} (ϵ)		
$[(en)_2Co]^{3+}$	465 (88)		
	Thiolato Complexes		
$[(en)_2Co(SCH_2CH_2NH_2)_2-N,S]^{2+}$	600 (44) sh	482 (142)	282 (13 800)
$[(en)_2Co(SCH_2CH(COOH)NH_2)_2-N,S]^{2+ c}$	600 (37) sh	483 (126)	283 (11 700)
$[(en)_2Co(SCH_2COO)-O,S]^+$		518 (152)	282 (11 700)
$[(en)_2Co(SCH(CH_3)COO)-O,S]^+$		515 (149)	280 (12 600)
$[(en)_2Co(SC(CH_3)_2COO)-O,S]^+$		514 (153)	282 (10 900)
	Sulfenato Complexes ^b		
$[(en)_2Co(S(O)CH_2CH_2NH_2)_2-N,S]^{2+}$	470 (500)	365 (6700)	284 (3700)
$[(en)_2Co(S(O)CH_2CH(COOH)NH_2)_2-N,S]^{2+ c}$	480 (600)	371 (5800)	287 (3750)
$[(en)_2Co(S(O)CH_2COO)-O,S]^+$	493 (350)	360 (6000)	285 (3100)
$[(en)_2Co(S(O)CH(CH_3)COO)-O,S]^+$	480 (390)	357 (6000)	287 (3500)
$[(en)_2Co(S(O)C(CH_3)_2COO)-O,S]^+$	486 (440)	364 (4500)	289 (4700)
	Sulfinato Complexes		
$[(en)_2Co(S(O)_2CH_2CH_2NH_2)_2-N,S]^{2+ d}$	432 (220)		288 (14 200)
$[(en)_2Co(S(O)_2CH_2CH(COOH)NH_2)_2-N,S]^{2+ c}$	430 (190)		287 (11 900)
$[(en)_2Co(S(O)_2CH_2COO)-O,S]^+$	448 (435)		294 (10 200)

^a Wavelengths, λ , of maxima (max) and shoulders (sh) are in nm. Molar extinction coefficients, ϵ , given in parentheses, are in $M^{-1} cm^{-1}$. Spectra are recorded in dilute aqueous perchloric acid. ^b The sulfenato complexes are unstable in solution (vide infra) and therefore the reported extinction coefficients have relatively large uncertainties. Parameters reported in this work were obtained generating the sulfenato complex in situ. ^c Data from ref 14 and 15. ^d Data from ref 13.

be heated in order to obtain a reasonable yield. In a typical preparation 10 g of $Co(ClO_4)_2 \cdot 6H_2O$ was dissolved in 30 mL of H_2O and the solution deaerated; to this was added 3.6 mL of ethylenediamine and then 3.4 g of disulfide under anaerobic conditions. The reaction mixture was heated to ca. 90 °C for ca. 1 h while being brought to one-half volume under a stream of nitrogen gas. Refrigeration at 4 °C overnight yielded a brown precipitate which was collected and twice recrystallized from boiling water to yield 2.8 g of purple crystals. Anal. Calcd for $[(en)_2Co(SC(CH_3)_2COO)]ClO_4$: C, 23.17; H, 5.83; N, 13.51; S, 7.73; Cl, 8.55; Co, 14.21. Found: C, 23.14; H, 5.50; N, 13.55; S, 7.86; Cl, 8.63; Co, 14.20. Visible-UV spectrophotometric parameters are reported in Table I.

(2-Sulfenatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) Salts, $[(en)_2Co(S(O)CH_2CH_2NH_2)]X_2$, X = ClO_4 , NO_3 , and SCN . This complex is readily prepared by stoichiometric oxidation of the corresponding thiolato complex. In a typical preparation 20 g of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was dissolved in 275 mL of warm water and then 11 mL of 70% $HClO_4$ added. A stoichiometric amount (4.5 mL) of 30% H_2O_2 was added to this solution, leading to an immediate color change from brown to red-orange. Addition of 300 mL of saturated $NaClO_4$ solution and cooling to 4 °C led to crystallization of the desired product. This material was dissolved in a minimum amount of warm water, saturated $LiClO_4$ solution (in ethanol) was added until incipient precipitation, and then the solution was cooled to yield the recrystallized perchlorate salt (overall yield ca. 80%). The nitrate salt cannot be simply prepared from the perchlorate salt because of the peculiar insolubility of the mixed nitrate-perchlorate species $[(en)_2Co(S(O)CH_2CH_2NH_2)](NO_3)(ClO_4)$; the relative solubilities of the three salts perchlorate/nitrate/mixed are ca. 9/3/1 at room temperature. The nitrate salt can be prepared by H_2O_2 oxidation of $[(en)_2Co(SCH_2CH_2NH_2)](NO_3)_2$ as above, followed by subsequent recrystallization from $NaNO_3$ solutions. Either the nitrate or perchlorate salt can be converted to the thiocyanate salt by simple metathesis. Crystals of the thiocyanate salt suitable for X-ray analysis were grown by adding equal amounts (1.5 mL) of saturated, filtered solutions of $[(en)_2Co(S(O)CH_2CH_2NH_2)](NO_3)_2$ and $KSCN$ to one-third as much (1.0 mL) distilled water. Anal. Calcd for $[(en)_2Co(S(O)CH_2CH_2NH_2)](SCN)_2$: C, 24.80; H, 5.72; N, 25.31; S, 24.83; Co, 15.21. Found: C, 24.66; H, 5.90; N, 24.98; S, 24.65; Co, 15.09. Visible-UV and IR spectral parameters are reported in Tables I and II, respectively.

(2-Sulfenatoacetato-*O,S*)bis(ethylenediamine)cobalt(III), (2-Sulfenatopropionato-*O,S*)bis(ethylenediamine)cobalt(III), and (2-Sulfenato-2-methylpropionato-*O,S*)bis(ethylenediamine)cobalt(III) Complexes, $[(en)_2Co(S(O)C(CH_3)_n(H)_{2-n}COO)]^{+n}$ n = 0, 1, and 2. These complexes with O,S chelation are considerably less stable than the above 2-sulfenatoethylamine complex (an N,S chelate) and are not easily isolated as pure solids. However, they are readily generated

Table II. Infrared Sulfur-Oxygen Stretching Frequencies (cm^{-1}) for Sulfenato and Sulfinato Complexes^a

complex	$\nu(S=O)$	ref
Sulfenato Complexes		
$[(en)_2Co(S(O)CH_2CH_2NH_2)](SCN)_2$	986	b
$[(en)_2Co(S(O)CH_2CH_2NH_2)](NO_3)_2$	993	b
$[(en)_2Co(S(O)CH_2CH_2NH_2)](NO_3)(ClO_4)$	998	b
$[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]I_2$	953	c
$[(en)_2Co(S(O)CH_2COO)]Cl$	960	b
$IrCl_2(P(C_6H_5)_3)_2(CO)S(O)CH_3$	1013	d
Sulfinato Complexes		
$[(en)_2Co(S(O)_2CH_2CH_2NH_2)]I_2$	1220, ^f 1080 ^g	e
$[(en)_2Co(S(O)_2CH_2COO)]Cl$	1200, ^f 1055 ^g	b
$IrCl_2(P(CH_3)(C_6H_5)_2)_2(CO)S(O)_2CH_3$	1228, ^f 1076 ^g	d

^a Spectra obtained in Nujol mulls or KBr pellets. ^b This work. ^c Reference 14. ^d Reference 40. ^e Reference 13. ^f Asymmetric stretch. ^g Symmetric stretch.

in aqueous solution by stoichiometric H_2O_2 oxidation of the corresponding thiolato complex. The progress of the oxidation can easily be monitored in situ via the characteristic visible-UV or 1H NMR spectra of the sulfenato complexes (vide infra). A solid material containing largely $[(en)_2Co(S(O)CH_2COO)]ClO_4$ was prepared as follows. To a solution of 1 g of $[(en)_2Co(SCH_2COO)]ClO_4$ in ca. 200 mL of H_2O was slowly added slightly more than 1 mol equiv of H_2O_2 as a 0.25 M solution. The reaction was allowed to proceed for ca. 5 min at room temperature, and the solution was then loaded onto a Sephadex SP-C25 ion-exchange column. An orange band of formal charge 1+ was removed with 0.1 M $NaClO_4$; the eluant containing this band was evaporated under vacuum and cooled to yield dark orange crystals. Solid $[(en)_2Co(S(O)CH_2COO)]Cl$ may be prepared by the same general procedure, using 2-propanol to aid in precipitating the complex from the concentrated $NaCl$ eluant solution. This 2-sulfenatoacetato complex is further characterized by its oxidation to the yellow (2-sulfinatoacetato-*O,S*)bis(ethylenediamine)cobalt(III) complex with excess H_2O_2 .¹³ Anal. Calcd for $[(en)_2Co(S(O)_2CH_2COO)]Cl \cdot H_2O$: C, 20.33; H, 5.64; N, 15.80; S, 9.04; Cl, 10.00; Co, 16.62. Found: C, 19.95; H, 5.98; N, 16.14; S, 8.76; Cl, 10.04; Co, 16.65. Visible-UV, IR, and 1H NMR spectral parameters for these complexes are given in Tables I, II, and III, respectively.

Analyses. Elemental analyses of solid samples, and analyses of aqueous solutions for total sulfur content, were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Total cobalt analyses were performed by a modified Kitson procedure.^{26,27} Hydrogen peroxide stock solutions used for kinetic experiments were stored at 4 °C in the dark and standardized every 2 weeks by spectrophotometric

Table III. ^1H NMR Spectral Parameters for the Complexes $[(\text{en})_2\text{Co}(\text{S}(\text{O})_n\text{CH}_2\text{COO}-\text{O})_2\text{S}]^+$ Where $n = 0, 1,$ and 2^a

complex	protons	δ	character
thiolato	en-CH ₂	2.4–3.0	br mult ^b
	S-CH ₂	3.18	singlet ^c
sulfenato	en-CH ₂	2.7–3.5	br mult ^b
	S(O)-CH ₂	3.78	AB pattern ^c
sulfinato	en-CH ₂	2.4–3.4	br mult ^b
	S(O) ₂ -CH ₂	4.38	AB pattern ^c

^a Spectra determined in D₂O with DSS as internal standard. Values of δ are in ppm. Parameters for the NH₂ proton signals are not reported because of the very broad nature of these signals.

^b The en-CH₂ proton signals are partially split into two broad multiplets of approximate relative intensity 1:3. ^c These protons undergo deuterium exchange in basic D₂O media.

titration (350 nm) against 0.1000 M Ce(IV).

Equipment. Visible–UV and infrared spectra were recorded respectively on Cary 14 and Beckman IR-18A spectrophotometers at ambient temperature. Kinetic data were obtained on a Cary 118B spectrophotometer equipped with a thermostated sample compartment that maintained temperatures to ± 0.1 °C, the temperature being known with an accuracy of ± 0.2 °C. ^1H NMR spectra were obtained on a Varian T-60 instrument. X-ray data were collected with a Syntex PI diffractometer, equipped with a graphite monochromator and molybdenum target tube (Mo K α , λ 0.710 69 Å), at ambient temperature. Computer calculations were performed on an IBM 370/168 or AMDAHL 470/V6 located at the University of Cincinnati.

Kinetic Measurements and Calculations. All kinetic experiments were conducted in aqueous perchloric acid solutions maintained at constant ionic strength 1.00 ± 0.01 M with LiClO₄. Kinetics were monitored (a) at the characteristic 360-nm absorption band of the starting sulfenato complex (vide infra), (b) with initial concentrations of $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$ in the range $(1-2) \times 10^{-3}$ M, (c) with pseudo-first-order concentration excesses of H₂O₂ and H⁺ maintained over cobalt(III), and (d) for at least 4 half-lives. Two methods were used to calculate the pseudo-first-order rate constant, k_{obsd} , and its associated standard deviation, $\sigma_{k_{\text{obsd}}}$, for a given kinetic experiment. (1) For most experiments an infinite-time measurement, OD _{∞} , could be determined experimentally and plots of $\log(\text{OD}_t - \text{OD}_{\infty})$ vs. time gave straight lines for more than 95% reaction (linear least-squares analysis yielded values of k_{obsd} and $\sigma_{k_{\text{obsd}}}$). This observation establishes that the system follows first-order kinetics. (2) Some experiments proceeded too slowly to conveniently obtain an experimental OD _{∞} and in these cases the OD _{t} vs. t data were treated by the previously described²⁸ Kezdy time-lag method²⁹ (an exponential form of the Guggenheim treatment). Linear least-squares analysis yielded²⁸ values of k_{obsd} and $\sigma_{k_{\text{obsd}}}$; variation of the time interval chosen for the Kezdy analysis (from 1–3 half-lives) resulted in no significant variation in the calculated value of k_{obsd} . Data treated by the two methods always yielded values of k_{obsd} that agreed to within 2%, and, therefore, for internal consistency, all results reported in this work were obtained via the Kezdy procedure. Activation parameters were calculated within the Eyring formalism³⁰ using a previously described nonlinear least-squares procedure.³¹ In all calculations, individual values of k_{obsd} were weighted as $(1/\sigma_{k_{\text{obsd}}})^2$. Unless otherwise noted, all reported errors are standard deviations.

Procedures. Formal charges on complexes were inferred from the characteristics of their elution from Dowex 50W-X2 (200–400 mesh, H⁺ or Li⁺ form) ion-exchange columns which had been calibrated with ions of known formal charge.²⁰ The protonation constant $(1/K_a)$ of $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$ was determined spectrophotometrically at 365 nm by a standard procedure.²² The effective extinction coefficient, ϵ_{obsd} , of an $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{ClO}_4)_2$ solution was obtained as a function of $[\text{H}^+]$ at a constant ionic strength of 4.00 ± 0.04 M (LiClO₄); the resulting $\epsilon_{\text{obsd}}-[\text{H}^+]$ data were fit to expression 1, where ϵ_0 and ϵ_{H} represent respectively the extinction

$$\epsilon_{\text{obsd}} = (\epsilon_0 + \epsilon_{\text{H}}[\text{H}^+]/K_a)/(1 + [\text{H}^+]/K_a) \quad (1)$$

coefficients of the unprotonated and fully protonated species, by nonlinear least-squares techniques.³¹

X-ray Characterization of $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{SCN})_2$. Preliminary precession photographs exhibited systematic absences $h = \text{odd}$ for $h00$, $k = \text{odd}$ for $0k0$, and $l = \text{odd}$ for $00l$, indicating the space group³² $P2_12_12_1$, No. 19, acentric. An amber-colored crystal,

of approximate dimensions $0.22 \times 0.30 \times 0.30$ mm and general shape of a flattened octahedron, was mounted on the diffractometer and our usual procedures¹⁷ were followed to check the crystal quality (three axial-rotation photographs and mosaic-scan measurements), determine unit cell constants (15 reflections), and measure intensities. The crystal is of the orthorhombic class with $a = 9.353$ (4), $b = 11.668$ (3), and $c = 14.896$ (5) Å. With $Z = 4$, $d_{\text{calcd}} = 1.58$ g cm⁻³, and $d_{\text{measd}} = 1.59$ (2) g cm⁻³. The rate for the $\theta/2\theta$ scan varied between 1.0 and 8.0°/min depending on the intensity of the reflection being measured. The scan ranged from 0.7° in 2θ below the calculated K α_1 peak position to 0.8° above that calculated for K α_2 . Four standard reflections were monitored to check crystal stability and to account for long-term drift; the drift correction varied from 0.983 to 1.042 and indicated a gradual decay of ca. 2% in intensity over the time of data collection. Absorption corrections were not applied since $\mu = 14.78$ cm⁻¹ and the maximum relative error in the measured intensities was estimated to be less than 2.5%. Within the sphere $2\theta < 57^\circ$, 2598 reflections were measured; from these, 2280 unique reflections were obtained by averaging.³³ Of these, 2090 had $I > 2\sigma(I)$, where p , the ignorance factor used to calculate¹⁷ $\sigma(I)$, was set equal to 0.04.

Structure Solution and Refinement of $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{SCN})_2$. This structure was solved using normal Patterson techniques and refinement proceeded without difficulty. Hydrogen atoms were assigned isotropic temperature parameters³⁴ of $B = 4.0$ Å². Initial refinement using anisotropic thermal parameters for all nonhydrogen atoms and fixed hydrogen atom positions (N–H = 0.87 Å, C–H = 0.97 Å, tetrahedral geometry) converged with $R_1 = 0.031$ and $R_2 = 0.038$.³⁵ Equivalent refinement of the enantiomeric model (obtained by inversion of all coordinates through $1/2, 1/2, 1/2$) converged with $R_1 = 0.042$ and $R_2 = 0.055$.³⁵ Therefore, subsequent refinement was conducted using the original model. In the final cycles of least-squares refinement, 247 parameters were varied including the overall scale factor, positional parameters for all atoms, and anisotropic thermal parameters for all nonhydrogen atoms. Convergence was achieved with $R_1 = 0.030$ and $R_2 = 0.033$.³⁵ In the last cycle of refinement the maximum shift per error was 0.19 and the average shift per error was 0.02. A final difference map was essentially featureless, the largest peak being less than 0.47 e Å⁻³. Mean values of $w\Delta^2$ did not vary significantly with $(\sin \theta)/\lambda$ or $|F_o|$. Neutral atom scattering curves as given by Cromer³⁶ were used for Co, S, N, C, and O; those of Stewart³⁷ were used for H. Anomalous dispersion corrections³⁸ were made for Co and S. The values of $|F_o|$ and F_c are listed in Table A.³⁹

Results

Characterization. In addition to the X-ray structure analysis described below, the S-bonded sulfenatobis(ethylenediamine)cobalt(III) complexes prepared in this work are characterized by (1) their synthesis via stoichiometric H₂O₂ oxidation of S-bonded thiolato complexes, (2) their reaction with excess H₂O₂ to yield S-bonded sulfinato complexes,¹³ (3) elemental analysis of an isolated salt (see Experimental Section), (4) cation-exchange elution characteristics which are consistent with the assigned formal charges, and (5) the visible–UV, IR, and ^1H NMR spectral parameters given in Tables I, II, and III, respectively.

The data of Table I show that the visible–UV spectra of the sulfenato complexes exhibit d–d bands typical of cobalt(III) complexes, as well as intense ligand-to-metal charge-transfer (LTMCT) bands at ca. 280 nm which characteristically arise from coordination of sulfur to a potentially oxidizing center.²⁸ In addition, the visible–UV spectra of sulfenato complexes are characterized by an intense band at ca. 360 nm which is not present in the spectra of the corresponding thiolato and sulfinato complexes. Therefore, within the thiolato–sulfenato–sulfinato series, this 360-nm band is diagnostic for the S-bonded sulfenato moiety and the intensity of this band may be used as a gauge of the purity of the sulfenato complex. This gauge is conveniently expressed as $\epsilon_{360}/\epsilon_{280}$, with the actual wavelengths employed for a specific complex being those at which that complex exhibits maximum absorbance (see Table I); also, since the intensity of the 280-nm LTMCT band of the sulfenato complexes is less than half that of either the

Table IV. Fractional Atomic Positional Parameters for $[(en)_2Co(S(O)CH_2CH_2NH_2)](SCN)_2$, ^{a,b}

atom	x	y	z
Co	0.491 80 (4)	0.447 34 (3)	0.627 36 (2)
S	0.611 63 (9)	0.282 95 (6)	0.652 47 (5)
O(1)	0.530 81 (27)	0.216 12 (21)	0.726 92 (16)
N(1)	0.616 5 (4)	0.488 6 (3)	0.525 0 (2)
N(2)	0.395 3 (3)	0.601 2 (2)	0.601 0 (2)
N(3)	0.356 8 (3)	0.363 6 (2)	0.548 5 (2)
N(4)	0.352 9 (3)	0.413 6 (3)	0.721 9 (2)
N(5)	0.621 6 (3)	0.522 0 (2)	0.715 3 (2)
C(1)	0.611 3 (5)	0.614 5 (3)	0.511 1 (3)
C(2)	0.457 4 (4)	0.649 8 (3)	0.516 7 (3)
C(3)	0.244 5 (4)	0.306 4 (3)	0.602 2 (3)
C(4)	0.211 8 (4)	0.383 3 (3)	0.682 1 (3)
C(5)	0.697 2 (4)	0.439 0 (3)	0.774 0 (2)
C(6)	0.758 9 (4)	0.346 5 (3)	0.714 3 (2)
S(10)	0.379 0 (1)	0.447 0 (1)	0.944 0 (1)
S(11)	0.036 5 (1)	0.147 8 (1)	0.826 7 (1)
N(10)	0.588 5 (4)	0.603 3 (4)	1.000 6 (3)
N(11)	-0.019 3 (5)	0.096 2 (4)	0.647 4 (2)
C(10)	0.503 1 (4)	0.538 5 (3)	0.976 7 (2)
C(11)	0.005 7 (4)	0.118 1 (3)	0.720 5 (2)

^a The estimated errors in the last digit are given in parentheses. This form is used throughout. ^b The numbering scheme for the cation is shown in Figure 1.

thiolato or sulfinato complexes, this ratio is more sensitive to purity than the value of ϵ_{360} alone. For the (2-sulfenatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) complex, the LTMCT band occurs at 284 nm and the characteristic sulfenato band occurs at 365 nm; the highest $\epsilon_{365}/\epsilon_{284}$ ratio that we have observed for this complex is 1.86, most preparations having a ratio in the range 1.6–1.8. In strong perchloric acid solutions the intensity of the 360-nm band decreases with increased acid concentration. Over short time periods (several minutes at ambient temperature) this is a completely reversible phenomenon, and as described in the Experimental Section, the acid dependence of ϵ_{365} for $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is adequately expressed by the equation governing reversible protonation of a chromophore (eq 1). Nonlinear least-squares analysis of the $\epsilon_{365}-[H^+]$ data given in Table B³⁹ leads to values of the extinction coefficients of the protonated and unprotonated forms of 1600 ± 200 and $6600 \pm 100 M^{-1} cm^{-1}$, respectively, and a value of the protonation constant $1/K_a$ of $1.4 \pm 0.2 M^{-1}$ (25 °C, $\mu = 4.00 \pm 0.04 M$ (LiClO₄)). Over longer time periods (hours at ambient temperature) $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ undergoes irreversible decomposition reactions in strong perchloric acid solutions (vide infra).

The infrared spectra of S-bonded sulfinato complexes of the bis(ethylenediamine)cobalt(III) series exhibit an intense band which is not present in the spectra of the corresponding thiolato complexes. This band is therefore assigned as arising from the expected sulfur–oxygen stretch of the S-bonded sulfinato moiety. The frequencies observed for this band (in the region 950–1000 cm^{-1}) for the $(en)_2Co^{III}$ series are in agreement with the frequency reported (1013 cm^{-1}) for the only S-bonded sulfinato complex known to us which is not a member of this series, i.e., the oxidative addition adduct of methanesulfonyl chloride and an analogue of Vaska's iridium(I) complex (see Table II).⁴⁰ The symmetric and asymmetric sulfur–oxygen stretches of the corresponding S-bonded sulfinato complexes occur at higher frequencies (see Table II).^{13,41}

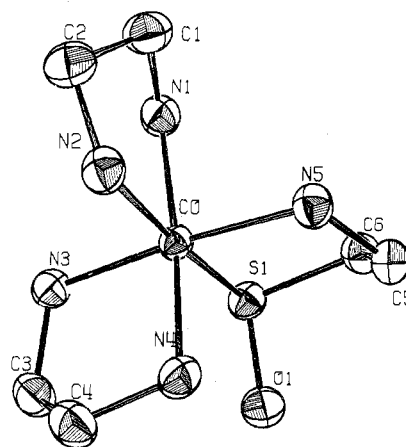
The data of Table III show that within the series of complexes $[(en)_2Co(S(O)_nCH_2COO)-O,S]^+$, where $n = 0, 1$, or 2, the chemical shift and the character of the ¹H NMR signal arising from the CH₂ moiety bonded to sulfur are dependent upon the oxidation state of the sulfur. Thus, the in situ successive oxidations of $[(en)_2Co(SCH_2COO)]^+$ to

Table V. Root-Mean-Square Displacements for $[(en)_2Co(S(O)CH_2CH_2NH_2)](SCN)_2$ (Å)

atom	min	med	max
Co	0.139	0.143	0.154
S	0.151	0.171	0.183
O(1)	0.170	0.200	0.220
N(1)	0.169	0.180	0.199
N(2)	0.162	0.175	0.197
N(3)	0.162	0.168	0.180
N(4)	0.157	0.183	0.195
N(5)	0.165	0.174	0.187
C(1)	0.173	0.211	0.219
C(2)	0.167	0.217	0.228
C(3)	0.166	0.190	0.217
C(4)	0.167	0.199	0.218
C(5)	0.163	0.189	0.197
C(6)	0.163	0.188	0.200
S(10)	0.186	0.210	0.245
S(11)	0.185	0.228	0.265
N(10)	0.199	0.236	0.263
N(11)	0.203	0.255	0.305
C(10)	0.178	0.182	0.217
C(11)	0.189	0.203	0.217

Table VI. Bond Lengths for $[(en)_2Co(S(O)CH_2CH_2NH_2)](SCN)_2$ (Å)

Co-S	2.253 (1)	Co-N(1)	1.980 (3)
Co-N(2)	2.048 (3)	Co-N(3)	1.982 (3)
Co-N(4)	1.956 (3)	Co-N(5)	1.987 (3)
S-O(1)	1.552 (3)	N(1)-C(1)	1.485 (5)
S-C(6)	1.815 (4)	N(2)-C(2)	1.495 (5)
C(1)-C(2)	1.499 (6)	N(3)-C(3)	1.480 (5)
C(3)-C(4)	1.521 (5)	N(4)-C(4)	1.490 (5)
C(5)-C(6)	1.513 (5)	N(5)-C(5)	1.484 (5)
S(10)-C(10)	1.650 (4)	C(10)-N(10)	1.156 (5)
S(11)-C(11)	1.645 (4)	C(11)-N(11)	1.143 (5)

**Figure 1.** Perspective view of $\Delta\lambda(S)\lambda\delta-[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. The ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity.

$[(en)_2Co(S(O)CH_2COO)]^+$ and then to $[(en)_2Co(S(O)_2CH_2COO)]^{2+}$ may be conveniently monitored by ¹H NMR spectroscopy.

Crystal Structure. Final fractional atomic positional parameters, and their estimated standard deviations, for non-hydrogen atoms are given in Table IV. The corresponding anisotropic thermal parameters may be found in Table C,³⁹ the root-mean-square displacements calculated therefrom are collected in Table V, and the associated ellipsoids for the complex cation are shown in Figure 1. Bond lengths and bond angles involving nonhydrogen atoms are found in Tables VI and VII, respectively. Table D³⁹ contains hydrogen atom positional parameters, while bond lengths and bond angles involving hydrogen atoms are given in Tables E³⁹ and F,³⁹ respectively.

Table VII. Bond Angles for $[(en)_2Co(S(O)CH_2CH_2NH_2)](SCN)_2$ (deg)

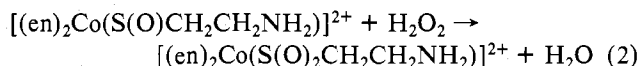
Metal Coordination Angles			
S-Co-N(1)	92.4 (1)	N(1)-Co-N(2)	84.2 (1)
S-Co-N(2)	176.1 (2)	N(1)-Co-N(3)	92.2 (1)
S-Co-N(3)	89.8 (1)	N(1)-Co-N(4)	174.3 (1)
S-Co-N(4)	92.3 (1)	N(1)-Co-N(5)	92.4 (1)
S-Co-N(5)	87.7 (1)	N(2)-Co-N(3)	92.2 (1)
N(3)-Co-N(4)	84.5 (1)	N(2)-Co-N(4)	91.3 (1)
N(3)-Co-N(5)	174.9 (1)	N(2)-Co-N(5)	90.7 (1)
N(4)-Co-N(5)	91.1 (1)		
Intrigand Angles			
Co-S-O(1)	107.7 (1)	N(1)-C(1)-C(2)	107.2 (3)
Co-S-C(6)	96.5 (1)	C(1)-C(2)-N(2)	108.4 (3)
O(1)-S-C(6)	102.3 (2)	C(2)-N(2)-Co	108.8 (2)
S-C(6)-C(5)	107.5 (2)	Co-N(3)-C(3)	110.7 (2)
C(6)-C(5)-N(5)	107.5 (3)	N(3)-C(3)-C(4)	107.5 (3)
C(5)-N(5)-Co	113.2 (2)	C(3)-C(4)-N(4)	105.8 (3)
Co-N(1)-C(1)	109.2 (2)	C(4)-N(4)-Co	110.5 (2)
Anion Angles			
S(10)-C(10)-N(10)	178.9 (6)	S(11)-C(11)-N(11)	178.1 (4)

This structure consists of discrete cationic complexes and thiocyanate anions with only very weak hydrogen bonds bridging the ions. The thiocyanate anions have reasonable bond lengths, thermal parameters, and bond angles, and these are entirely as expected from other structure determinations.^{17,42} The cobalt(III) center is six-coordinate (five nitrogen atoms and the sulfur atom of the sulfenato ligand) in an approximately octahedral configuration fully expected from the known structures of the analogous thiolato¹⁷ and sulfinato¹³ complexes. A ground-state structural trans effect is clearly apparent upon comparing the trans Co-N bond distance of 2.048 (3) Å (N(2) trans to S(1)) with the average cis Co-N bond distance of 1.976 (7) Å; the difference between cis and trans distances is 0.072 (8) Å. The sulfenato sulfur atom is three-coordinate (the cobalt atom, the carbon atom of the chelate ring, and the oxygen atom) in an approximately tetrahedral (counting the sulfur lone pair of electrons as occupying the fourth site) configuration. Since the three-coordinate sulfur atom is a chiral center, the stereochemical possibilities for the $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ cation are rather complex: the sulfur atom configuration may be either *R* or *S*; the wrapping of the chelate rings about the cobalt center may be either Δ or Λ ; the sulfenato chelate may adopt either a δ' or λ' conformation; the two ethylenediamine chelates may be $\lambda\lambda$, $\lambda\delta$, or $\delta\delta$. Combination of these component configuration possibilities leads to 24 overall possible configurations, i.e., 12 enantiomeric pairs of diastereoisomers. The particular crystal for which the structure was determined contains only the $\Delta\lambda'(S)\lambda\delta$ configuration (see Figure 1). In $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ ¹⁷ and $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$,¹³ wherein the sulfur atoms are not chiral, the cations both exhibit $\Delta\lambda\lambda\lambda$ configurations.

Decomposition. Coordinated sulfenic acids appear to be stable in the solid state; thus, within experimental error the same $\epsilon_{365}/\epsilon_{284}$ ratios are obtained for $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ salts when they are freshly prepared and after they have been stored for two years in the dark (room temperature, closed container, no desiccant). However, in HClO₄ solutions exposed to room light, coordinated sulfenic acids slowly undergo irreversible decomposition reactions that lead to a variety of products. (It has been reported¹⁵ that the decomposition of $[(en)_2Co(S(O)CH_2CH_2COOH)NH_2]^{2+}$ is light catalyzed.) In the range of acid concentrations 0.01–5.8 M, the rate of decomposition increases with increasing acid concentration; thus, in 1 h at 76 ± 1 °C $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ undergoes extensive decomposition in 5.8 M HClO₄ but suffers no detectable decomposition in 0.01 M HClO₄. Hexaaquocobalt(II) is a major decomposition product

of both $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2COO)]^+$. For $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ the major cobalt(III) decomposition product is a highly charged (3+ or 4+), red (λ_{max} 497 nm, ϵ_{max} 92 M⁻¹ cm⁻¹; λ_{sh} 350 nm, ϵ_{sh} 130 M⁻¹ cm⁻¹), metastable complex which appears to contain 2 sulfur atoms/cobalt atom. This red product is itself unstable at pH > 1 and under these conditions each mole of isolated red product quantitatively reconverts to 1 mol of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$.

Oxidation Kinetics. In the presence of excess hydrogen peroxide and acid, the decay of the 360-nm band of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ corresponds predominantly to the 2-equiv oxidation of the sulfenato ligand to a sulfinato¹³ ligand (eq 2). The observed specific rates for this process,



k_{obsd} , as a function of $[H_2O_2]$, $[H^+]$, and temperature are compiled in Table VIII. At any given $[H^+]$ and temperature, k_{obsd} is linearly dependent on $[H_2O_2]$ as in eq 3, where the

$$k_{obsd} = A + B[H_2O_2] \quad (3)$$

minor component represented by the intercept term presumably corresponds to the spontaneous decomposition of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ in acidic media (vide supra). Values of *A* and *B* are given in Table IX.

The slope term, *B*, represents the second-order rate constant governing the reaction of interest (eq 2). Values of *B* increase linearly with increasing $[H^+]$ at all temperatures investigated (eq 4). Table X gives the values of *a* and *b* resulting from

$$B = a + b[H^+] \quad (4)$$

linear least-squares analysis of the four sets of $B-[H^+]$ data of Table IX. Nonlinear least-squares analysis of all of the data of Table IX within eq 4 and the Eyring formalism leads to the following activation parameters: $\Delta H_a^* = 14.6 \pm 0.2$, $\Delta H_b^* = 14.4 \pm 0.7$ kcal/mol; $\Delta S_a^* = -26 \pm 2$, $\Delta S_b^* = -25 \pm 2$ eu.

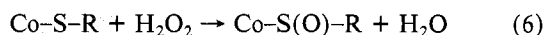
The intercept term, *A*, generally decreases with increasing $[H^+]$, except at 10 °C where there is no significant dependency on $[H^+]$. From a variety of functional forms chosen to fit the $A-[H^+]$ data, only the exponential form (5) does so adequately,

$$A = A_0 \exp(-\beta[H^+]) \quad (5)$$

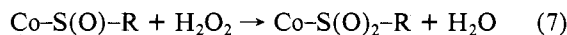
and this only when the 10 °C data is neglected. The temperature dependence of the $A-[H^+]$ data, expressed within eq 5, leads to the following derived parameters: $\Delta H_{A_0}^* = 23.6 \pm 0.2$ kcal/mol, $\Delta S_{A_0}^* = -0.6 \pm 0.7$ eu, $\beta = 0.35 \pm 0.2$ M⁻¹ with no temperature-dependent component.

Discussion

Synthesis and Characterization. The synthesis of a sulfenato complex from a thiolato complex involves 2-equiv oxidation of the coordinated sulfur. In a stoichiometric sense, this may be viewed as a formal oxygen atom transfer reaction, e.g. eq 6. Further reaction with excess oxidant converts the sulfenato



complex to the sulfinato complex, e.g., eq 7,¹³ and therefore



the preparative reactions are conducted under stoichiometric conditions. Oxidants other than hydrogen peroxide can be used; *N*-bromosuccinimide, chloramine-T, 2,2'-dithiodipyridine, Br₂, K₂S₂O₈, NaOCl, and KMnO₄ all generate sulfenato complexes in aqueous solution, although the yields and diversity of products vary markedly from one system to the next. Reactions 6 and 7 are analogous to the successive 2-equiv

Table VIII. Observed First-Order Rate Parameters for the H₂O₂ Oxidation of [(en)₂Co(S(O)CH₂CH₂NH₂)]²⁺ as a Function of Temperature, [H⁺], and [H₂O₂]^a

<i>t</i> = 10 °C			<i>t</i> = 45.0 °C		
[H ⁺], M	[H ₂ O ₂], M	10 ⁴ <i>k</i> _{obsd} , s ⁻¹	[H ⁺], M	[H ₂ O ₂], M	10 ⁴ <i>k</i> _{obsd} , s ⁻¹
0.133	0.029	0.039 ± 0.001	0.133	0.029	3.53 ± 0.03
	0.067	0.080 ± 0.001		0.068	4.34 ± 0.02
	0.282	0.274 ± 0.001		0.290	8.13 ± 0.04
0.500	0.481	0.493 ± 0.003	0.500	0.492	12.0 ± 0.2
	0.029	0.053 ± 0.001		0.029	3.47 ± 0.02
	0.067	0.110 ± 0.001		0.068	4.70 ± 0.01
0.700	0.282	0.425 ± 0.001	0.700	0.290	11.18 ± 0.07
	0.481	0.755 ± 0.003		0.492	13.7 ± 0.2
	0.029	0.057 ± 0.001		0.029	3.39 ± 0.02
1.000	0.067	0.120 ± 0.001	1.000	0.068	4.79 ± 0.02
	0.282	0.475 ± 0.001		0.290	12.15 ± 0.08
	0.481	0.858 ± 0.004		0.492	17.7 ± 0.2
	0.029	0.068 ± 0.002		0.029	3.34 ± 0.02
	0.067	0.145 ± 0.001		0.068	4.82 ± 0.03
	0.282	0.571 ± 0.001		0.290	12.5 ± 0.2
	0.481	1.005 ± 0.007		0.492	20.0 ± 0.1

<i>t</i> = 25.0 °C			<i>t</i> = 36.8 °C		
[H ⁺], M	[H ₂ O ₂], M	10 ⁴ <i>k</i> _{obsd} , s ⁻¹	[H ⁺], M	[H ₂ O ₂], M	10 ⁴ <i>k</i> _{obsd} , s ⁻¹
0.050	0.047	0.411 ± 0.001	0.133	0.030	1.487 ± 0.007
	0.093	0.569 ± 0.002		0.070	1.902 ± 0.013
	0.279	1.221 ± 0.003		0.300	4.41 ± 0.02
0.100	0.465	1.913 ± 0.005	0.500	0.500	7.622 ± 0.035
	0.049	0.441 ± 0.003		0.000	1.096 ± 0.005
	0.098	0.639 ± 0.005		0.011	1.154 ± 0.006
0.200	0.298	1.382 ± 0.007	0.700	0.022	1.303 ± 0.005
	0.496	2.227 ± 0.010		0.030	1.497 ± 0.006
	0.047	0.444 ± 0.002		0.044	1.667 ± 0.006
0.300	0.093	0.649 ± 0.005	1.000	0.055	1.782 ± 0.008
	0.279	1.468 ± 0.002		0.066	1.895 ± 0.008
	0.465	2.222 ± 0.008		0.070	2.059 ± 0.011
0.700	0.049	0.489 ± 0.003	0.700	0.077	2.083 ± 0.009
	0.098	0.745 ± 0.005		0.088	2.160 ± 0.009
	0.298	1.716 ± 0.007		0.298	5.563 ± 0.003
1.000	0.496	2.986 ± 0.013	1.000	0.498	9.437 ± 0.039
	0.049	0.512 ± 0.003		0.030	1.410 ± 0.007
	0.097	0.836 ± 0.004		0.070	2.093 ± 0.012
	0.293	2.143 ± 0.006		0.298	6.19 ± 0.04
	0.488	3.707 ± 0.012		0.498	10.17 ± 0.07
	0.049	0.534 ± 0.002		0.030	1.450 ± 0.007
	0.097	0.920 ± 0.004		0.070	2.22 ± 0.02
	0.293	2.434 ± 0.005		0.252	5.04 ± 0.02
	0.488	4.529 ± 0.025		0.298	6.81 ± 0.05
				0.420	7.90 ± 0.04
				0.498	11.10 ± 0.05

^a Conditions: λ 360 nm; [Co(III)]₀ = (1.0–2.0) × 10⁻³ M; μ = 1.00 ± 0.01 M (LiClO₄).Table IX. Derived Rate Parameters Governing the [H₂O₂] Dependence for the H₂O₂ Oxidation of [(en)₂Co(S(O)CH₂CH₂NH₂)]²⁺ as a Function of Temperature and [H⁺]: *k*_{obsd} = *A* + *B*[H₂O₂]^a

<i>t</i> , °C	[H ⁺], M	10 ⁴ <i>A</i> , s ⁻¹	10 ⁴ <i>B</i> , M ⁻¹ s ⁻¹
10.0	0.133	0.015 ± 0.006	0.92 ± 0.03
	0.500	0.010 ± 0.006	1.49 ± 0.03
	0.700	0.008 ± 0.004	1.67 ± 0.03
	1.000	0.012 ± 0.002	1.99 ± 0.01
25.0	0.050	0.244 ± 0.007	3.54 ± 0.05
	0.100	0.247 ± 0.011	3.93 ± 0.06
	0.200	0.242 ± 0.009	4.36 ± 0.05
	0.300	0.22 ± 0.03	5.3 ± 0.2
36.8	0.700	0.17 ± 0.03	7.0 ± 0.2
	1.000	0.14 ± 0.04	8.0 ± 0.3
	0.133	1.1 ± 0.1	12.1 ± 0.8
	0.500	0.99 ± 0.02	15.3 ± 0.2
45.0	0.700	0.86 ± 0.03	18.2 ± 0.3
	1.000	0.84 ± 0.02	20.4 ± 0.3
	0.133	3.10 ± 0.06	17.6 ± 0.5
	0.500	2.8 ± 0.2	28 ± 2
	0.700	2.47 ± 0.09	33 ± 1
	1.000	2.31 ± 0.04	36.0 ± 0.6

^a *k*_{obsd}–[H₂O₂] data from Table VIII.Table X. Derived Rate Parameters Governing the [H⁺] Dependence of the Rate Law Term *B*[H₂O₂] for the H₂O₂ Oxidation of [(en)₂Co(S(O)CH₂CH₂NH₂)]²⁺ as a Function of Temperature: *B* = *a* + *b*[H⁺]^a

<i>t</i> , °C	10 ⁴ <i>a</i> , M ⁻¹ s ⁻¹	10 ⁴ <i>b</i> , M ⁻² s ⁻¹	av % diff ^b
10.0	0.82 ± 0.07	1.18 ± 0.08	3.4
25.0	3.35 ± 0.07	5.09 ± 0.34	3.1
36.8	10.4 ± 0.8	10.2 ± 1.2	2.2
45.0	15.0 ± 1.3	21.7 ± 2.0	5.0

^a *B*–[H⁺] data from Table IX. ^b Average % difference between observed values of *B* and values of *B* calculated from the optimized *a* and *b* parameters of this table.

oxidations of organic thioethers to sulfoxides and then sulfones, e.g., eq 8 and 9. Thus, while free sulfenic acids are notoriously

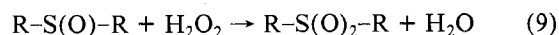
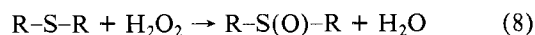
unstable,¹⁻⁴ a coordinated, S-bonded sulfenic acid enjoys stability similar to that of an organic sulfoxide. This constitutes a remarkable example of the stabilization of reactive organic ligands via coordination to a metal center.

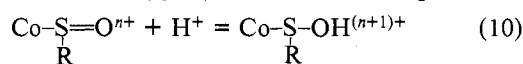
Table XI. Selected Bond Lengths (Å) for the Complexes $[(en)_2Co(S(O)_nCH_2CH_2NH_2)]^{2+}$ Where $n = 0, 1, \text{ and } 2$

bond	thiolato Co-S-R ^a	sulfenato Co-S(O)-R ^b	sulfinato Co-S(O) ₂ -R ^c
trans Co-N	2.001 (5)	2.048 (3)	2.027 (4)
av cis Co-N	1.960 (9)	1.976 (7)	1.978 (3)
STE	0.041 (10)	0.072 (8)	0.049 (5)
Co-S	2.226 (2)	2.253 (1)	2.191 (2)
S-C	1.818 (8)	1.815 (4)	1.803 (6)
S-O		1.552 (3)	1.456 (4)-1.476 (4)

^a Data from ref 17. ^b Data from Table VI. ^c Data from ref 13.

The properties of S-bonded sulfenato ligands (Co-S(O)-R) are expected to be intermediate between those of S-bonded thiolato (Co-SR) and S-bonded sulfinato ligands (Co-S(O)₂-R), and this is generally the case. As the formal oxidation state of the coordinated sulfur atom increases along the thiolato-sulfenato-sulfinato series (-II, 0, +II), the ligand field strength provided by the sulfur atom increases (Table I). Thus, in the cysteamine series, the thiolato, sulfenato and sulfinato complexes exhibit λ_{max} for the $^1A_{1g} \rightarrow ^1T_{1g}$ transition at 482, 470, and 432 nm, respectively; for the mercaptoacetato series of complexes, the corresponding transitions are at 518, 493, and 448 nm. Also, increasing the oxidation state of the coordinated sulfur increases the electronegativity of the RS(O)_n functionality. Thus the data of Table III show that the ¹H NMR signal for the protons attached to the carbon bonded to sulfur monotonically shifts to lower field (higher δ values) as the oxidation state of the sulfur increases; such shifts to lower field are well recognized^{43,44} to be due to increasing electronegativity of the group bonded to carbon.

The R-S=O functionality is the essence of the sulfenato ligand. Table II shows that the characteristic infrared stretching frequency of this functionality (ca. 1000 cm⁻¹) is lower in energy than the frequencies resulting from the RSO₂ functionality of sulfinato ligands (ca. 1100 and 1200 cm⁻¹). This lower stretching frequency is consistent with the observed longer sulfur-oxygen bond length of the NH₂CH₂CH₂S=O⁻ ligand relative to the sulfur-oxygen bond lengths of the corresponding NH₂CH₂CH₂SO₂⁻ ligand (see Table XI). The R-S=O sulfenato functionality gives rise to a characteristic, intense band around 360 nm (Table I). While this is clearly a charge-transfer band, its origins are as yet unclear. Protonation of the R-S=O functionality of either $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ or $[(en)_2Co(S(O)CH_2COO)]^{2+}$ markedly decreases the intensity of this 360-nm band. If we assume that protonation occurs on oxygen rather than sulfur (eq 10), then

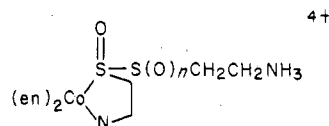


protonation decreases the double-bond character of the sulfur-oxygen bond and it would appear that the 360-nm band arises either from an intraligand charge-transfer characteristic of the R-S=O moiety or from a LTMCT originating from a molecular orbital primarily centered on the R-S=O functionality. The R-S=O group of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is a somewhat stronger Brønsted base than the acetato ligand of $[(H_2O)_5CrOOCCH_3]^{2+}$, the two complexes having protonation constants (25 °C) of 1.4 ± 0.2 and $0.20 \pm 0.02 M^{-1}$,²² respectively, in a medium of 4.0 M ionic strength. Following trends observed for the protonation of $[(H_2O)_5CrOOCCH_3]^{2+}$ as a function of ionic strength,²² we estimate that the protonation constant of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ at $\mu = 1.0 M$ is less than $0.1 M^{-1}$. The protonation constant of $[(en)_2Co(S(O)CH_2COO)]^{2+}$ is definitely larger than that of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, presumably due to the decreased formal positive charge on the complex, but the inherent instability of $[(en)_2Co(S(O)-$

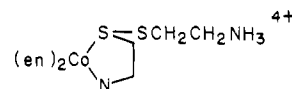
CH₂COO)]⁺ (vide supra) precludes the quantitative determination of this parameter.

Reactivity and Decomposition. Free sulfenic acids are very reactive as both nucleophiles and electrophiles.^{3,4,11,12} While coordination to cobalt(III) considerably masks this reactivity, coordinated sulfenic acids do react at reasonable rates with reagents that undergo characteristic reactions⁴ with free sulfenic acids, e.g., H₂O₂ (vide infra), CH₃I, ascorbic acid, and propionaldehyde. The hydrolysis of free sulfenate anions rapidly yields thiosulfinate esters^{1,4} (eq 11) whereas the $2RSO^- + 2H^+ \rightarrow 2[RSOH] \rightarrow R-S(=O)-S-R + H_2O$ (11)

aqueous decomposition of sulfenato ligands coordinated to cobalt(III) is considerably slower and much more complicated. The decompositions of both $[(en)_2Co(S(O)CH_2COO)]^{2+}$ and $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ in aqueous solution are promoted by high acid concentration but yield different products under different acidity conditions. Cobalt(II) is always a major product, suggesting that internal redox, i.e., cobalt(III) oxidation of the coordinated sulfenato ligand, is a primary decomposition route. The major cobalt(III) product resulting from the acid-promoted decomposition of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is itself metastable and has not been completely characterized; however, it has properties consistent with its tentative formulation as



where n can be 0, 1, or 2. The formulation with $n = 0$ is the analogue of the thiosulfinate ester resulting from hydrolysis of free sulfenic acids (eq 11). The three proposed product formulations contain a single oxygen atom bonded to the coordinated sulfur atom since each mole of the product decomposes to quantitatively regenerate 1 mol of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ (vide supra). This observation also establishes that the product is *not* the complex containing a coordinated disulfide



since this is a known species^{45,46} which does *not* decompose to $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$.

Structural Characterization. The salient structural characteristic of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is that the coordinated sulfur atom is bonded to one, and only one, oxygen atom (see Figure 1). This conclusively establishes that the isolated complex does indeed contain a coordinated sulfenic acid, and thus H₂O₂ oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ occurs without disruption of the primary coordination sphere of the cobalt center. Table XI contains selected structural data for the thiolato-sulfenato-sulfinato series of complexes $[(en)_2Co(S(O)_nCH_2CH_2NH_2)]^{2+}$ with $n = 0, 1, \text{ and } 2$. It is seen that the average cis Co-N bond distance of the sulfenato complex is entirely as expected for a bis(ethylenediamine)-cobalt(III) complex, while the trans Co-N bond distance is significantly longer than the average cis Co-N distance and marginally longer than the trans Co-N bond distances of the thiolato and sulfinato complexes. This leads to a structural trans effect (STE) for the sulfenato complex which is somewhat greater than the STE observed for the thiolato and sulfinato analogues. Although this difference in STE is small, it is clear that the STE is *not* correlated with (1) the oxidation state of the coordinated sulfur or (2) the ligand field strength of the sulfur ligand, since ligand field strength increases monotonically along the thiolato-sulfenato-sulfinato series

Table XII. Selected Bond Lengths (Å) for the Sulfenato Complexes $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]^{2+}$ ^a

bond	$[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$	$[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]^{2+}$	
		ion A	ion B
trans Co-N	2.048 (3)	2.036 (7)	2.048 (6)
av cis Co-N	1.976 (7)	1.968 (11)	1.970 (9)
STE	0.072 (8)	0.068 (13)	0.078 (11)
Co-S	2.253 (1)	2.225 (2)	2.237 (3)
S-C	1.815 (4)	1.796 (7)	1.824 (7)
S-O	1.552 (3)	1.523 (6)	1.499 (6)

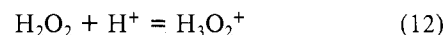
^a Data from Table VI and ref 16. The two ions of $[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]^{2+}$ are crystallographically independent and are joined by a H bond bridging the carboxylate groups; the net charge on the two cations is thus $3+$.¹⁶

(vide supra). The lack of correlation between trans effects and ligand field strength has been noted previously⁴⁷ in the pentaamminecobalt(III) series. Similarly, the fact that the Co-S bond length of the sulfenato complex is significantly greater than the Co-S bond lengths of the thiolato and sulfinato complexes demonstrates that Co-S bond length does not correlate with ligand field strength; a previous implication¹³ in favor of this correlation is now discounted. The data of Table XI also show that the S-C bond distances within the three structures are equivalent and that the S-O bond length of the sulfenato complex is significantly longer than the S-O bond lengths observed in the sulfinato complex (vide supra). In Table XII the selected structural data for $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ are compared with the equivalent data for $[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]^{2+}$ (two crystallographically independent ions joined by a H bond) recently reported¹⁶ by Jackson, Sargeson, and Whimp; the three structures are in good agreement.

Kinetics and Mechanism of H₂O₂ Oxidation. The mode of action of hydrogen peroxide as a 2-equiv oxidant has been extensively investigated and the relevant literature has been thoroughly reviewed, largely by Edwards and co-workers.⁴⁷⁻⁵⁰ It is generally accepted that H₂O₂ oxidation of nucleophilic substrates occurs via nucleophilic attack of the substrate on the O-O bond of H₂O₂.^{15,47-50} A wide variety of sulfur-containing substrates seem to react via this nucleophilic attack scheme, consistent with the well-established⁵¹ nucleophilic character of sulfur, and in fact a recent report⁵² presents evidence for the formation of a "R₂S=O-O" intermediate in the H₂O₂ oxidation of alkoxyulfuranes. Since a coordinated sulfur atom is known to have considerable nucleophilic character,^{42,53} in the following discussion we will assume that the H₂O₂ oxidation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ proceeds via this general nucleophilic attack scheme.

Spontaneous decomposition of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ (vide supra) competes with H₂O₂ oxidation, leading to the two-term rate law $k_{obsd} = A + B[H_2O_2]$ (eq 3) for the disappearance of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$. The

A term results from several complicated decomposition reactions (and possibly medium effects) and is not amenable to kinetic analysis. The available $A-[H^+]-T$ data have been fit to an arbitrary functional form merely for convenience—the resulting parameters have no chemical or mechanistic significance. The *B* term, on the other hand, arises from the reaction of interest, reflecting the composition of the activated complex for nucleophilic attack of the coordinated sulfur atom on the O-O bond of H₂O₂. As is typical for reductions of H₂O₂ by a variety of nucleophilic substrates,^{47,50} the *B* term is linearly dependent on acid concentration: $B = a + b[H^+]$, eq 4. The value of the acid-independent parameter, *a*, is $(3.35 \pm 0.07) \times 10^{-4} M^{-1} s^{-1}$ (Table X, 25 °C, $\mu = 1.00 M$), in good agreement with the specific rate reported¹⁵ by Krueger et al. for the H₂O₂ oxidation of $[(en)_2Co(S(O)CH_2CH(COOH)NH_2)]^{2+}$ ($k = (2.0 \pm 0.3) \times 10^{-4} M^{-1} s^{-1}$ at 25 °C, $\mu = 0.1$ and 0.28 M, and pH 5-7; at this pH the $b[H^+]$ term will be negligible with respect to the *a* term). Selected rate parameters and activation parameters for the acid-dependent H₂O₂ oxidation of a variety of sulfur-containing substrates are given in Table XIII and compared to the analogous data for the H₂O₂- $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ reaction. There are three points to be made from this comparison: (1) A coordinated sulfenato sulfur atom maintains considerable nucleophilicity toward H₂O₂, the acid-independent rate parameter, *a*, being just about equal to that of SCN⁻. (2) The activation parameters for the H₂O₂- $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ reaction are very similar to those observed for the other systems, implying that this reaction proceeds by the same general mechanism operating in the other systems. (3) The ratio of *b/a* is significantly smaller than observed for any of the other sulfur systems and indeed for any of the other nucleophilic systems tabulated by Hoffman and Edwards.⁴⁷ It is generally accepted that the acid dependence of H₂O₂ oxidations of nucleophilic substrates arises from protonation of H₂O₂⁴⁷⁻⁵⁰ (eq 12). H₂O functions as a better leaving group



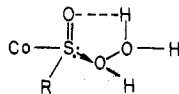
from H₃O₂⁺ than OH⁻ does from H₂O₂ and therefore protonation facilitates nucleophilic attack. However, in the H₂O₂- $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ reaction, an ambiguity in mechanistic interpretation arises because both H₂O₂ and $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ are weak bases; there is no a priori way of determining (1) if the proton is brought into the activated complex by H₃O₂⁺ or by $[(en)_2Co(S(OH)CH_2CH_2NH_2)]^{3+}$ or (2) on which site the proton is actually located within the activated complex no matter how the proton was brought into the activated complex. It is, however, very unlikely that protonation occurs solely on the sulfenato ligand since it is unreasonable for a protonated ligand to be more nucleophilic than an unprotonated ligand. The unusually small observed *b/a* ratio for the H₂O₂- $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ reaction (Table XIII) implies that the proton has a role in this reaction which disfavors reaction through the protonated path (relative to normal nucleophilic

Table XIII. Selected Kinetic Data for the Acid-Catalyzed H₂O₂ Oxidation of Sulfur-Containing Nucleophiles: Rate = $(a + b[H^+]) [H_2O_2] [Nuc]$ ^{a-c}

Nuc	<i>a</i>	ΔH_a^*	ΔS_a^*	<i>b</i>	ΔH_b^*	ΔS_b^*	<i>b/a</i>
S ₂ O ₃ ²⁻	0.025			1.7			68
SCN ⁻	5.2×10^{-4}	15	-25	0.025	11	-32	48
(HOCH ₂ CH ₂) ₂ S	2.2×10^{-3}			0.023			10
O(CH ₂ CH ₂) ₂ S	2.6×10^{-3}	13	-27	0.035	11	-29	14
(NH ₂) ₂ C=S	0.07	15	-14	1.42	10	-26	20
$[(en)_2Co(NO_2)(NCS)]^+$	4.6×10^{-5}			1.3×10^{-3}			28
$[(NH_2)_5CoNCS]^{2+}$	5.3×10^{-5}	17	-17	9.8×10^{-4}			19
$[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ ^d	3.4×10^{-4}	15	-26	5.1×10^{-4}	14	-26	1.6

^a Data taken from compilation of ref 47. ^b Conditions: 25 °C, H₂O solvent, variable ionic strength. ^c *a* is in M⁻¹ s⁻¹, *b* is in M⁻² s⁻¹, ΔH^* is in kcal/mol, and ΔS^* is in eu. ^d This work.

substitution on H_3O_2^+). This could occur through an activated complex configuration such as



wherein internal hydrogen bonding to the sulfenato oxygen atom would make OH_2 a poorer leaving group and lower the overall efficacy of H_3O_2^+ as a substrate for nucleophilic attack. This hypothesis of a special role for the proton in the $\text{H}_2\text{O}_2\text{-}[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$ reaction is supported by an additional piece of negative evidence. For a wide variety of nucleophilic substrates that obey the general rate law $B = a + b[\text{H}^+]$ (eq 4), Hoffmann and Edwards⁴⁷ have shown that a plot of $\log b$ vs. $\log a$ is linear with a slope of 0.95. This implies a similar transition state (i.e., nucleophilic attack on the O—O bond) for both the a and b paths. However, the a and b terms for the $\text{H}_2\text{O}_2\text{-}[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)]^{2+}$ reaction do not fit on this linear free-energy plot, supporting the view that within the protonated transition state the proton has some definite interaction with the sulfenato moiety.

Acknowledgment. Financial support by the National Science Foundation, Grant No. CHE 76-19681, is gratefully acknowledged.

Registry No. $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{ClO}_4)_2$, 68645-83-0; $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{NO}_3)_2$, 68645-82-9; $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{SCN})_2$, 68645-81-8; $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{COO})]\text{ClO}_4$, 68645-80-7; $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}(\text{CH}_3)\text{COO})]^+$, 68645-78-3; $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{C}(\text{CH}_3)_2\text{COO})]^+$, 68645-77-2; $[(\text{en})_2\text{Co}(\text{S}(\text{O})_2\text{CH}_2\text{COO})]\text{Cl}$, 68698-56-6; $[(\text{en})_2\text{Co}(\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2)](\text{NO}_3)(\text{ClO}_4)$, 68645-76-1; $[(\text{en})_2\text{Co}(\text{S}(\text{CO})\text{CH}_2\text{COO})]\text{Cl}$, 68698-55-5; $[(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)](\text{ClO}_4)_2$, 40330-50-5; $[(\text{en})_2\text{Co}(\text{SCH}_2\text{COO})]\text{ClO}_4$, 26743-67-9; $[(\text{en})_2\text{Co}(\text{SCH}(\text{CH}_3)\text{COO})]^+$, 60828-74-2; $[(\text{en})_2\text{Co}(\text{SC}(\text{CH}_3)_2\text{COO})]\text{ClO}_4$, 68645-87-4; $[\text{Co}(\text{en})_3]^{2+}$, 23523-25-3.

Supplementary Material Available: Tables A–F giving $[F_{00}]$ and F_{00} , anisotropic thermal parameters, positional parameters, bond lengths and bond angles involving hydrogen atoms, and $\epsilon_{365}^{\text{obsd}} - [\text{H}^+]$ data (14 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Dimethyltellurium Tetraiodide, $(\text{CH}_3)_2\text{TeI}_4$

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Received September 22, 1978

$(\text{CH}_3)_2\text{TeI}_4$ crystallizes in the space group $\text{P}\bar{1}$ with $a = 7.460(3) \text{ \AA}$, $b = 12.600(5) \text{ \AA}$, $c = 6.592(3) \text{ \AA}$, $\alpha = 82.83(3)^\circ$, $\beta = 103.54(3)^\circ$, $\gamma = 106.45(3)^\circ$, $V = 576.6 \text{ \AA}^3$, and $Z = 2$. The crystal structure was determined with diffractometer data and refined to $R_1 = 0.061$ using anisotropic thermal parameters for all atoms. The compound is an adduct of $(\text{CH}_3)_2\text{TeI}_2$ with I_2 linked by intermolecular I—I bonds and weak Te—I bonds and does not contain Te(VI).

Introduction

Dialkyltellurium tetraiodides are prepared by the reaction of the corresponding dialkyltellurium diiodides with molecular iodine.¹⁻³ The chemical behavior and the spectra give no evidence for an oxidation state of +6 for tellurium but are in agreement with a weakly bound adduct of R_2TeI_2 with I_2 .^{4,5}

Smith and Thayer suggested an interaction between the central tellurium and the molecular iodine, as the Te—I stretching bands in the IR spectrum do not change going from R_2TeI_2 to R_2TeI_4 .⁴ But in $\alpha\text{-}(\text{CH}_3)_2\text{TeI}_2$ the tellurium already forms intermolecular Te—I bonds.⁶ Additional bonding of the tellurium is not possible without breaking these intermolecular