

for *trans*- and *cis*-Co(en)₂Cl₂⁺. Pecsok and Fletcher¹⁴ measured a value of $K = 6.9 \times 10^{-3} M$ for hydrolysis of Ti³⁺ in bromide media of 0.25–1.5 M. The closeness of this value to the K_h value measured here suggests that the acid-inverse term in rate laws 1–3 corresponds to the reaction of TiOH²⁺ with the Co(III) complexes and that the acid-independent term in rate laws 2 and 3 corresponds to reaction of Ti³⁺. TiOH²⁺ reacts 311 times faster than Ti³⁺ with *trans*-Co(en)₂Cl₂⁺ and 250 times faster with the *cis* isomer. TiOH²⁺ is relatively more effective with Co(NH₃)₅Cl²⁺, where the acid-independent path is not observed. One possible cause of this effect is that the higher charge of the latter oxidant favors the reductant of lower charge.

The relatively high rate of reaction of TiOH²⁺ may be understood in terms of the nature of the Ti(IV) product. Ti(IV) would be expected to have an acidity like that of V(IV) and to exist as TiO²⁺ and related polymeric species. A short Ti–O distance in such a species would provide a barrier to reaction which would be reduced for a deprotonated reductant like TiOH²⁺. The data presented here do not establish or disprove an inner-sphere mechanism for the reaction.

The rate of reaction of Ti(III) with Co(NH₃)₅Cl²⁺ reported here is several orders of magnitude less than that of Fraser et al.,¹⁵ who reported an acid dependence different from the one we observe. Their media contained ClO₄⁻ in high concentrations, and catalytic paths, perhaps involving radical intermediates, may have been important under the conditions they used.

Rosseinsky¹⁶ has rationalized the observation that reaction of Co^{III}L₄XY species with M²⁺ reductants showed decreased sensitivity to the nature of Y in the order (Fe²⁺ > Ru²⁺ > V²⁺) on the basis of the order of reducing power (Fe²⁺ < Ru²⁺ < V²⁺). Since electrode potential data indicate that TiOH²⁺

is intermediate in reducing power between Ru²⁺ and V²⁺, one would expect that the selectivity (with respect to variations in Y) of Ti(III) reductions should be more than that of V²⁺ reductions but less than that of Ru²⁺ reductions. The close similarity of redox rates between *cis*- and *trans*-dichloro Co(III) oxidants indicates an even lower selectivity than predicted on this basis. Among the many possible causes for such an effect (if it is real) is some Co^{III}–Ti^{III} overlap prior to the transition state.

Acknowledgment. This work was supported by the U.S. Air Force Office of Scientific Research under Grant AF 71-2003.

Registry No. Co(NH₃)₅Cl²⁺, 14970-14-0; *trans*-Co(en)₂Cl₂⁺, 14403-91-9; *cis*-Co(en)₂Cl₂⁺, 14875-15-1; Ti(III), 22541-75-9.

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Oxidation of Coordinated Cysteine. Formation of Sulfinato- and Sulfenatocobalt(III) Complexes

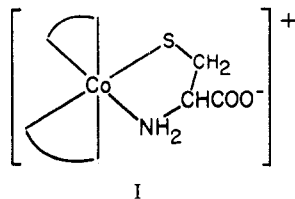
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Received December 17, 1974

AIC408345

Oxidation of (cysteinato)-*N,S*-bis(ethylenediamine)cobalt(III) perchlorate resulted in isolation of the corresponding sulfenato, [Co(en)₂[NH₂CH(COO)CH₂SO₂]]ClO₄, and sulfinato, [Co(en)₂[NH₂CH(COO)CH₂SO₂]]ClO₄, complexes. The products were characterized by elemental analysis and cation-exchange chromatography and by infrared, ¹H NMR, and uv-visible spectroscopy. The chemical and spectroscopic results are in accord with N and S bonding to cobalt in each complex. In the series thiolate, sulfenato, and sulfinato, an increase in the oxidation state of the coordinated sulfur ligand results in an increase in ligand field strength and an increase in deshielding of the methylene protons adjacent to sulfur.

Recently, Kothari and Busch¹ described a bis(ethylenediamine)cobalt(III) complex of cysteine for which it was shown that, of the three potential donor groups, it is the amine and thiolate functions that are coordinated. We have been in-



terested in the oxidation of thiolate sulfur to the sulfinate stage

in coordinated cysteine and it appeared that the above complex would be a useful choice for such a study. In particular, the nonlabile nature of a chelated cobalt(III) complex would maximize the chance that the sulfur function would remain coordinated during and after an oxidation reaction. The oxidation by hydrogen peroxide of a tris(cysteinato)cobaltate(III) complex, Co(CyS)₃³⁻,² to the corresponding cysteinesulfinato complex, Co(CySO₂)₃³⁻,² has been described, first by Schubert³ and more recently by Gillard and coworkers,⁴ and it seemed likely that I would undergo the same reaction.

A variety of sulfinato complexes have been prepared by oxidative addition, by SO₂ insertion into a metal-carbon bond, and by direct replacement of ligands by RSO₂⁻.^{5,6} Both

S-bonded and O-bonded isomers have been identified on the basis of infrared data. The S-bonded isomer is the more common and, to date, the only form observed in the case of Co(III).

In the peroxide oxidation of a coordinated thiolate a sulfenato complex $M(\text{OSCH}_2\text{R})$ is a potential intermediate, although free alkyl sulfenates are notoriously elusive species. In this paper we describe the preparation and characterization of both the cysteinesulfinato complex and the novel cysteinesulfenato complex derived from oxidation of $(\text{en})_2\text{Co}(\text{CyS})^+$. To our knowledge, the only previous report of a sulfenato complex is that due to George and Watkins⁷ in which $\text{IrCl}_2(\text{CH}_3\text{SO})(\text{CO})(\text{PR}_3)_2$ was prepared by reaction of $\text{CH}_3\text{S}(\text{O})\text{Cl}$ with $\text{IrCl}(\text{CO})(\text{PR}_3)_2$, $\text{PR}_3 = \text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$.

Experimental Section

L(-)-Cystine was obtained from Matheson Coleman and Bell. H_2O_2 (30%) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were Mallinckrodt reagent grade. Cysteinesulfenic acid monohydrate was Calbiochem A grade. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of (Cysteinato)-N,S-bis(ethylenediamine)cobalt(III) Perchlorate (I). This compound, first reported as the iodide,¹ was synthesized using an approach described for related complexes.⁸ Cystine (3.6 g, 15 mmol) was added with stirring to 40 ml of 10% aqueous ethylenediamine (60 mmol) which had been purged for 30 min with nitrogen. To this mixture a total of 7.2 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (30 mmol) was added in small portions over 1 hr. The reaction mixture was continuously purged with N_2 and the pH maintained at ~ 9 by addition of concentrated NaOH as required. After an additional 3 hr, the product was precipitated as the perchlorate by addition of 4.2 g $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (30 mmol). The resulting brown solid was recrystallized using a minimum of boiling water and then washed with methanol and dried over P_2O_5 . Anal. Calcd for $[\text{Co}(\text{en})_2\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{S}\}]\text{ClO}_4$: C, 21.14; H, 5.32. Found: C, 21.15; H, 5.47. Although we experienced no difficulty, the perchlorate complexes described herein should be handled with caution.

Preparation of (Cysteinesulfenato)-N,S-bis(ethylenediamine)cobalt(III) Perchlorate (II). Cysteinatobis(ethylenediamine)cobalt(III) perchlorate (1.00 g, 2.5 mmol) was stirred for ~ 10 min in 15 ml of water and then a solution consisting of 0.28 ml of 30% H_2O_2 (2.8 mmol) diluted to 10 ml was added dropwise over a 50-min period. The starting material went into solution as it reacted with the peroxide. The mixture was allowed to react for 1 additional hr, with stirring, during which time only a small amount of oxygen evolution was noted. The approximately 10% stoichiometric excess of H_2O_2 employed was designed to compensate for decomposition of the peroxide but to be sufficiently small to minimize subsequent oxidation to the sulfinato complex (vide infra). The product mixture was filtered to remove any unreacted solid and diluted with 200 ml of 2-propanol. After 3 hr, the orange solid was filtered and washed with ether. The crude product (~ 0.2 g) was recrystallized by dissolving it in 4 ml of water, followed by addition of 8 ml of 2-propanol. After 5 hr the solid was filtered, washed several times with ether, and dried over P_2O_5 . The recrystallization from 2:1 2-propanol-water resulted in a 2-propanol-free product, as shown by proton NMR analysis; higher 2-propanol:water ratios, while improving the yield, lead to a 2-propanol-containing product. Samples prepared as above typically lost 0.2–0.4 equiv of water on heating to 110° . Further heating in vacuo at 75° for 4–5 hr caused no detectable weight loss, which was taken to indicate that the product is not a hydrate. Anal. Calcd for $[\text{Co}(\text{en})_2\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{SO}\}]\text{ClO}_4$: C, 20.32; H, 5.12; N, 16.93; S, 7.75. Found: C, 19.98; H, 5.30; N, 16.72; S, 7.40.

Preparation of (Cysteinesulfinato)-N,S-bis(ethylenediamine)cobalt(III) Perchlorate (III). Cysteinatobis(ethylenediamine)cobalt(III) perchlorate (1.00 g, 2.5 mmol) was stirred for ~ 10 min in 15 ml of water and then a solution consisting of 0.83 ml of 30% H_2O_2 (8.3 mmol) diluted to 10 ml was added dropwise over a 40-min period. If significant decomposition of peroxide was noted or if a sample uv-visible scan failed to reveal the 430-nm peak arising from the product, another 3 mmol of H_2O_2 was added. The mixture was allowed to react overnight, after which 200 ml of acetone was added. The yellow product separated slowly and, after 24 hr, was collected and washed with ether. In the several preparative runs a tendency

for formation of variable quantities of a gummy, brown solid was noted. This dark solid, which was removed from the desired yellow product, was not characterized, although dilute solutions of it and the yellow solid possess identical uv-visible spectra. The yellow product (~ 0.3 g) was recrystallized by dissolving it in 5 ml of water and slowly adding 8 ml of 2-propanol, with stirring. After 5 hr, the solid was collected, washed thoroughly with ether, and dried over P_2O_5 . During ether washing, the solid, some of which was initially somewhat orange, was converted to a uniform yellow color. The product did not contain 2-propanol and did not undergo appreciable loss in weight on heating to 110° , or to 75° in vacuo. Anal. Calcd for $[\text{Co}(\text{en})_2\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{SO}_2\}]\text{ClO}_4$: C, 19.57; H, 4.93; N, 16.30; S, 7.46. Found: C, 19.72; H, 4.82; N, 16.50; S, 7.47.

Characterization of the Complexes. Infrared spectra were obtained from Nujol mulls of the samples using a Perkin-Elmer Model 180 spectrophotometer. Since perchlorate absorbs strongly in the range $1050\text{--}1150\text{ cm}^{-1}$, ir spectra were obtained on the iodide complexes. Each iodide complex was prepared by dissolution of the corresponding perchlorate in a minimum of water, addition of a fourfold excess of sodium iodide, and precipitation of the solid by addition of two volumes of ethanol. The products were recrystallized and dried over P_2O_5 before use. Finely powdered samples of the iodide complexes were protonated by exposure to an atmosphere of dry gaseous HCl for 2 hr (except 20 min for the sulfinato complex, which reacts to form a brown solid on longer exposure).

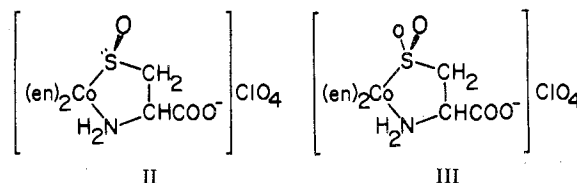
Proton NMR spectra of the complexes in 99.8% D_2O solution were obtained using a Varian Model HA 100 spectrometer. In these solutions the residual H_2O signal occurs at $\delta 5.1$, relative to external TMS. Chemical shifts are reported as ppm upfield of the H_2O peak. Spectra in base solution were obtained by addition of 0.1 ml of 0.2 M NaOH to 1.0 ml of a ~ 0.07 M solution of the complex and allowing 1 hr for reaction. This treatment was repeated twice with additional 0.1-ml volumes of 0.2 M NaOH . Partial decomposition of the complex resulted in formation of a small amount of solid which was removed prior to running the spectrum.

Uv-visible spectra were obtained on a Cary Model 16K spectrophotometer.

Stoichiometric analysis of the reaction of bromine with II was carried out by permitting the reaction to proceed to completion in the presence of excess Br_2 in 0.1 M Br^- . Unreacted bromine was analyzed by addition of excess iodide and spectrophotometric determination of I_3^- at 350 nm. Control runs were also carried out to estimate the extent of bromine loss due to reducing impurities and volatilization. Complex III was analyzed for cysteinesulfinate by treatment with N_2 -purged NaOH solutions for various times, followed by neutralization to give a pink solution and solid cobalt(II) hydroxide. The CySO_2^- released was determined by reaction with triiodide at pH 7, followed by estimation of the remaining iodine with thiosulfate.

Results

Oxidation of $[\text{Co}(\text{en})_2(\text{CyS})]\text{ClO}_4$ (I) with H_2O_2 in a 1:1 mole ratio yielded an orange solid, formulated as II, with a composition corresponding to that expected of a sulfenato complex. Treatment of I with excess H_2O_2 afforded the yellow sulfinato complex III.



Cation-Exchange Chromatography. Elution of each product, and of complex I, with 0.5 M $\text{NaClO}_4\text{--}0.01$ M $\text{NaC}_2\text{H}_3\text{O}_2$ on a Dowex 50W-X4 (100–200 mesh) column revealed in each case a single band with elution characteristics consistent with a species having a 1+ charge. During elution, if the eluent was changed to 0.5 M $\text{NaClO}_4\text{--}0.1$ M HClO_4 , the bands were greatly retarded. Further changing the eluent to 3 M $\text{NaClO}_4\text{--}0.1$ M HClO_4 resulted in movement of the bands with characteristics expected of a 2+ species. These observations are consistent with the presence of an uncoordinated carboxylate group as in structures II and III.

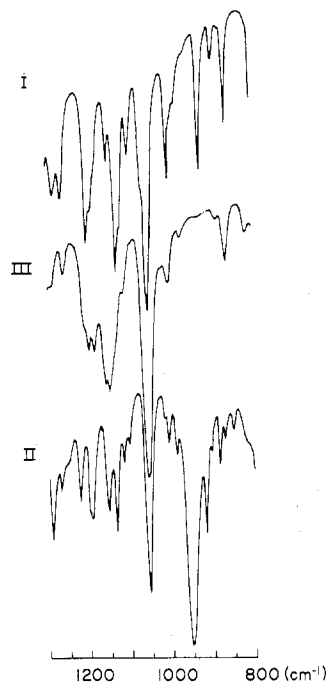


Figure 1. Infrared spectra of iodide salts of (I) $\text{Co(en)}_2(\text{CyS})^+$, (II) $\text{Co(en)}_2(\text{CySO})^+$, and (III) $\text{Co(en)}_2(\text{CySO}_2)^+$ in Nujol.

Infrared Spectra. Ir spectra of the complexes (as iodide salts) contain broad doublets centered at 3150 cm^{-1} , arising from stretching of coordinated $-\text{NH}_2$ groups, and strong absorptions at 1610 , 1630 , and 1635 cm^{-1} for complexes I, II, and III, respectively, arising from an uncoordinated carboxylate group.⁹ Upon protonation of the complexes the latter absorptions are shifted to 1715 , 1700 , and 1720 cm^{-1} , respectively, consistent with conversion of a free carboxylate group to $-\text{COOH}$.^{1,9} Figure 1 shows the region in which sulfur-oxygen stretching frequencies are expected. The strong, sharp absorption at 953 cm^{-1} in the spectrum of II, absent in the spectrum of I, is assigned as the $\text{S}=\text{O}$ stretch arising from a sulfenato ligand bound to cobalt through sulfur. This assignment is supported by the results of George and Watkins, who found sulfur-oxygen stretching frequencies near 1000 cm^{-1} in (sulfenato)-*S*-iridium(III) complexes.⁷ An O-bonded sulfenato is expected to exhibit a considerably lower frequency.⁷

O-Bonded sulfinato complexes exhibit sulfur-oxygen stretching at 1050 and $950\text{--}830\text{ cm}^{-1}$;^{5,10} sulfinate-*S*- $\text{S}(\text{O})_2$ -absorptions occur in the ranges $1250\text{--}1100\text{ cm}^{-1}$ (ν_{asym}) and $1050 \pm 50\text{ cm}^{-1}$ (ν_{sym}).^{5,10,11} A strong C-C or C-N vibration at 1055 cm^{-1} ,¹² common to all the spectra in Figure 1, precludes the identification of a sulfur-oxygen band in this region.¹³ Comparing III with I, there is no gain in intensity in the $950\text{--}830\text{ cm}^{-1}$ region as required for an O-bonded sulfinate.¹⁴ There is, however, a substantial gain in intensity in III, relative to I, around 1150 cm^{-1} which may correspond to ν_{asym} for $\text{Co-S}(\text{O})_2\text{CH}_2^-$. Thus, the infrared data favor the sulfinate-*S* structure for III.

NMR Spectra. Proton NMR spectra, obtained for complexes I-III in D_2O , are shown in Figure 2. As a consequence of exchange with the solvent, no NH_2 resonances or couplings to other protons are observed in these spectra. In the spectrum of I, triplet Ia ($\delta\ 1.10$, 1.0 H)¹⁵ is assigned to the methine proton in the cysteinato ligand. Id ($\delta\ 2.28$, 1.8 H) arises predominantly from the adjacent methylene protons, with possible overlap from Ic. Results of spin decoupling experiments support these assignments. Irradiation of Ia altered the Id absorption; irradiation at any of several frequencies within Id caused complete collapse of Ia to a singlet. The methylene protons in ethylenediamine occur as two overlapping

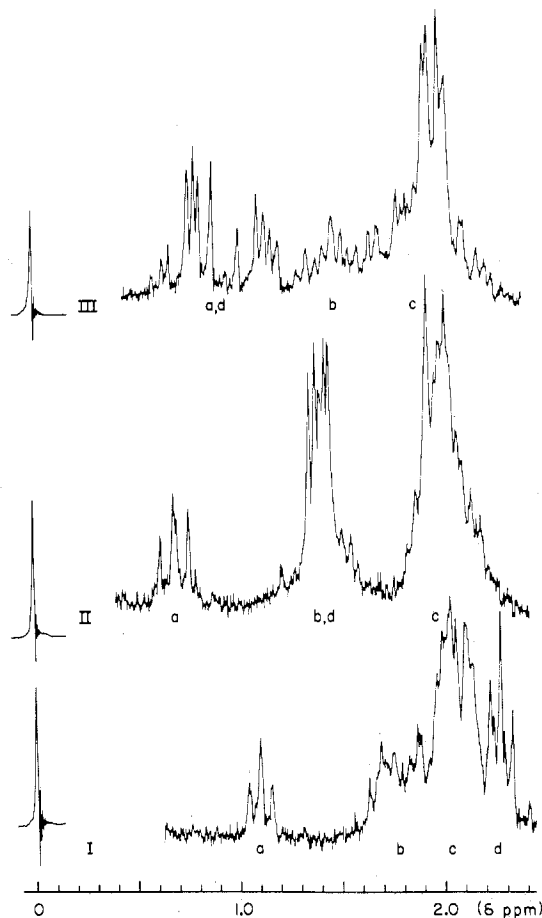


Figure 2. The 100-MHz proton NMR spectra of (I) $\text{Co(en)}_2(\text{CyS})^+$, (II) $\text{Co(en)}_2(\text{CySO})^+$, and (III) $\text{Co(en)}_2(\text{CySO}_2)^+$ in D_2O . Chemical shifts are in ppm upfield of internal H_2O .

resonances, Ib and Ic (8.0 H , combined), from which it appears that one set of two ethylenediamine CH_2 protons occurs downfield of the remaining six protons. Because of the trans influence of sulfur donor groups,¹⁶ it seems likely that Ib corresponds to CH_2 adjacent to the amine group trans to the sulfur-containing group, denoted as $(\text{en}-\text{CH}_2)_t$. Note that with oxidation of sulfur this resonance is significantly shifted to a lower field in II.

In the spectrum for complex II, feature IIb,d ($\delta\ 1.43$, 4.0 H) appears to consist of a sharp four-line multiplet from CH_2 adjacent to sulfur (IIId) which coincidentally overlies the broader $(\text{en}-\text{CH}_2)_t$ resonance, with IIc ($\delta\ 2.1$, 6.0 H) attributable to the remaining ethylenediamine protons. The occurrence of the cysteinesulfenato CH_2 in IIb,d and the assignment of IIa ($\delta\ 0.72$, 1.0 H) to the methine proton were confirmed by the expected collapse of the multiplet structures upon double irradiation. The methine proton gives rise to a four-line pattern with coupling constants of 8 and 7 Hz . (The central peak exhibits a reproducible splitting of 2 Hz .) The two four-line multiplets produced by coupling in the $\text{CH}-\text{CH}_2$ spin system closely resemble those expected for an XA_2 system with some BA_2 character;¹⁷ i.e., in complex II, the CH_2 resonance has moved sufficiently close to that of CH that some departure from first-order coupling occurs. The multiplets observed may also correspond to an XAB system in which the methylene protons are nonequivalent. Because of interference by $(\text{en}-\text{CH}_2)_t$ in the IIb,d region, an attempt to make a more complete assignment of the $\text{CH}-\text{CH}_2$ system seems inadvisable.¹⁸

In spectrum III, absorptions attributable to the methylene group in the cysteinesulfinato ligand have moved downfield of the ethylenediamine protons, which absorb in regions IIIb

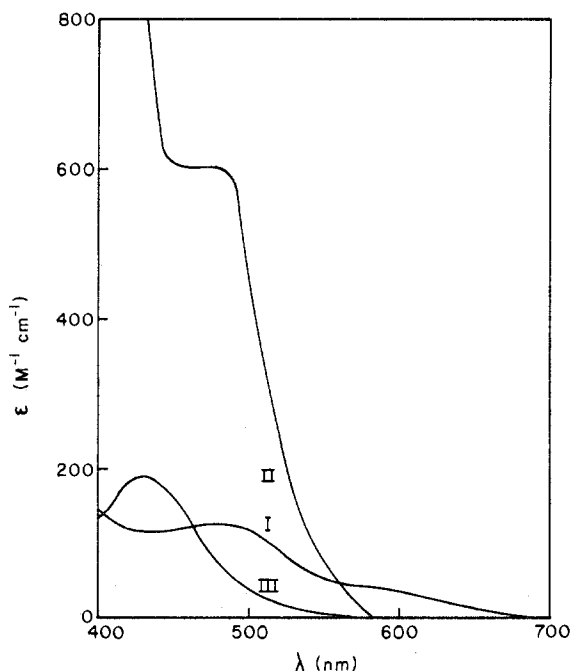


Figure 3. Visible spectra of (I) $\text{Co}(\text{en})_2(\text{CyS})^+$, (II) $\text{Co}(\text{en})_2(\text{CySO})^+$, and (III) $\text{Co}(\text{en})_2(\text{CySO}_2)^+$ in water.

(δ 1.6, 2.1 H) and IIIc (δ 2.0, 6.0 H). The CH-CH₂ system exhibits resonances throughout the IIIa,d region (δ 0.72–1.25, 2.7 H), in what appears to be a 12-line ABC pattern.

As evidenced by the degree of coupling exhibited in their spectra, the proton NMR results are in accord with the assigned N,S binding in the three complexes and the concomitant restriction to a single N-CH-CH₂-S configuration, or perhaps rapid interchange between two conformations.

The spectra of complexes I-III were obtained in the presence of sodium hydroxide added to promote the exchange of potentially acidic protons. The methine resonance for II disappeared entirely and apparently the methylene protons were exchanged as well since both the area and fine structure in peak IIb,d were diminished considerably. Some broadening of the residual ethylenediamine peaks was noted, probably due to cobalt(II) formed in base decomposition. In the spectrum of III all peaks attributable to the CH-CH₂ system disappeared entirely. The exchange of CH and CH₂ in I, however, was much slower than in II or III. Thus, susceptibility of both CH₂ and CH protons to exchange is strongly influenced by the presence of a sulfur group containing one or more polar sulfur-oxygen bonds.¹⁹

UV-Visible Spectra. The electronic spectra of I-III, shown in Figure 3, remain unchanged throughout the pH region 2–10. Molar absorption coefficients ($M^{-1} \text{ cm}^{-1}$) at the various maxima are as follows, in parentheses: I, 600 nm (37, sh), 483 nm (126), 283 nm (11,700); II, 480 nm (600, sh), 371 nm (5910), 287 nm (3750); III, 430 nm (190), 287 nm (11,900). Approximating complex I as possessing C_{4v} symmetry with respect to donor atoms, the 600- and 480-nm absorbances in I are assigned as ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow {}^1A_2$ transitions, respectively.^{1,20} The splitting of the 1T_1 state occurs because thiolate occupies a much lower position in the spectrochemical series than does NH_2 .²⁰ The single transition in II at 480 nm probably corresponds to ${}^1A_1 \rightarrow {}^1T_1$,²¹ suggesting that S-bonded sulfenate occupies a higher position, near NH_2 , in the spectrochemical series. This transition appears in III at a higher energy. The position of this 430-nm band in III is comparable with those observed for $\text{Co}(\text{NH}_3)_5\text{SO}_3^+$ at 456 nm^{16d} and $\text{Co}(\text{CySO}_2)_3^{3-}$ at 406 nm.⁴

Stability and Oxidation of the Complexes. Complexes II and III are potentially subject to aquation and to oxidation.

The uv-visible spectra of solutions of II were unchanged in 4 hr in the pH region 4–10. Some aquation occurred over a period of several days as evidenced by the appearance of peaks near 500 and 360 nm, typical of aquoammine- and diaquo-cobalt(III) complexes. There was no evidence for air oxidation of II to III. Aquation of II was accelerated by acid (pH < 2), presumably owing to protonation of the sulfenate group. Rapid decomposition took place in strongly basic media. Complex III also reacted rapidly at pH > 11 but was stable for days in neutral solution and in 1 M HClO_4 . The difference in susceptibility to acid-catalyzed aquation of II and III is in accord with the difference in basicities of the uncoordinated ligands, $\text{p}K_a \approx 2.8$ for CySO_2H and 8 as a rough approximation for CySOH .

The structures proposed for II and III suggest that II should undergo oxidation since there is a lone pair on sulfur but that III should resist oxidation under conditions where aquation is negligible. Complex II reacted readily with aqueous bromine, iodine, and hydrogen peroxide. Stoichiometric analysis of the bromine reaction yielded a value of 1.03 ± 0.03 (six determinations) for the ratio moles of Br_2 consumed/mol of $\text{Co}(\text{en})_2(\text{CySO})^+$. UV-visible spectra of the product solutions were consistent with formation of III. $[\text{Co}(\text{en})_2(\text{CySO}_2)]\text{ClO}_4$ was unreactive toward iodine and hydrogen peroxide but slowly consumed bromine. An attempt was made to release quantitatively cysteinesulfinate by base-catalyzed hydrolysis. Solutions of III were treated with either 0.04 or 0.4 M NaOH for periods ranging from 10 min to 18 hr and analyzed iodometrically for CySO_2^- . Values of moles of CySO_2^- /mol of III in the range 0.20–0.65 were obtained for seven analyses. Independent experiments with cysteinesulfinate showed it to be unstable in the highly basic media required for hydrolysis of the ligand, accounting for the failure to observe 100% release of CySO_2^- from III. It is clear, however, that III does contain a reducing ligand with properties consistent with those expected for a sulfinate, eliminating the possibility that III might be a cysteinesulfonate complex.

Discussion

The formation of $[\text{Co}(\text{en})_2(\text{CySO})]\text{ClO}_4$ is significant in that it provides a means of stabilizing the highly reactive cysteinesulfenate anion which has not previously been isolated.^{22,23} Oxidation of free cysteine normally leads to cystine via nucleophilic substitution at sulfenyl sulfur by unreacted thiol.²⁴ By contrast, coordination of cysteine clearly promotes formation of sulfur-oxy anions under mild, oxidizing conditions. The susceptibility of the sulfenate complex to attack, either by an unoxidized cysteinato complex to form a disulfide or by another sulfenate species, resulting in disproportionation, is greatly reduced by steric hindrance and the adverse effect of reaction between species of like charge.

The visible spectra obtained reveal an increase in ligand field strength in the series $\text{Co}-\ddot{\text{S}}-\text{R}$, $\text{Co}-\ddot{\text{S}}(\text{O})-\text{R}$, $\text{Co}-\text{S}(\text{O})_2-\text{R}$. This increase is associated with an increase in oxidation state and a corresponding decrease in the number of lone pairs on sulfur. Jorgensen has pointed out that for a variety of sulfur donor groups, a decrease in the number of lone pairs on sulfur is correlated with an increase in position in the spectrochemical series.²⁵

As expected, increasing electron-withdrawing character of the sulfur group in the series above results in pronounced deshielding of the adjacent methylene protons. In comparing features Ib and IIb in the NMR spectra, the inductive effect associated with increased oxidation state also appears to be transmitted to the $(\text{en}-\text{CH}_2)_t$ protons in the position trans to sulfur.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. I⁺ClO₄⁻, 54713-70-1; II⁺ClO₄⁻, 54713-72-3; III⁺ClO₄⁻, 54750-89-9; I⁺I⁻, 25749-39-7; II⁺I⁻, 54713-73-4; III⁺I⁻, 54750-90-2.

References and Notes

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Site of Deprotonation in the Base Hydrolysis of Chloropentaaminecobalt(III) Ions

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Received September 4, 1974

AIC406275

Proton-exchange studies at the amine centers, base hydrolysis studies, and steric strain calculations on the two isomers of [Co(tren)NH₃Cl]²⁺ (tren = tris(2-aminoethyl)amine) are reported. The results indicate that deprotonation at the N center trans to bound Cl⁻ leads to the most reactive intermediate for loss of Cl⁻ and the stereochemistry of the two reaction paths is discussed in relation to likely structures for the intermediates.

Introduction

Much evidence has now appeared to support a dissociative mechanism for hydrolysis of cobalt(III)-amine complexes in basic media.¹⁻⁷ The proposed mechanism, Figure 1, requires a preliminary deprotonation at a primary or secondary N center which is usually a preequilibrium but may be rate determining.^{1,2,6} This is followed by dissociation of the leaving group X, usually rate determining, to give an intermediate of reduced coordination number.^{4,7} The intermediate then rapidly captures nucleophiles in solution to give the products.⁸ The evidence which supports the proposal involves studies of H exchange,^{1,2} capture of the intermediate by competing species to give common products^{4,6} and stereochemistry⁷ independent of the leaving group and gross accelerations in rates when steric compression is introduced in the parent ions.⁹ At least two points of uncertainty in the mechanistic proposals are the position of deprotonation in the parent ion which leads to hydrolysis¹⁰⁻¹² and the stereochemistry of the intermediate of reduced coordination number. The present work was designed to examine both these aspects.

It is conceivable that the two isomers¹³ or [Co(tren)-NH₃Cl]²⁺ depicted in Figure 2 could be revealing in the context of the deprotonation problem since there is no N proton trans to Cl⁻ in one instance, while there is in the other. Superficially the complexes appear to be electronically

equivalent and strain free or at least equally strained and no undue influence should arise from these sources. It seemed therefore that an analysis of base hydrolysis and proton exchange rates along with some quantitation of the strain problem might allow an evaluation of which deprotonated reactant leads on to hydrolysis.

Experimental Section

Synthesis of [Co(tren)NH₃Cl]Cl₂, Purple Isomer. tren·3HCl (25.6 g) and NaOH (12 g) were dissolved in water (200 ml) and NaClO₄·H₂O (50 g) was added after a clear solution had formed. Co(ClO₄)₂·6H₂O (36.7 g) in water (100 ml) was added, followed immediately by NaNO₂ (10 g) in water (100 ml). A brown solution containing some greenish precipitate was formed, but on vigorous passage of air for 45 min the precipitate dissolved and a crystalline, khaki-colored solid was deposited. This was washed on the filter with a little ice water and then with CH₃OH and H₂O; yield 35 g (95%) presuming a constitution of [Co₂(tren)(NO₂)₂O₂](ClO₄)₂.

Peroxo dimer (35 g) was added in portions to hot concentrated HCl (200 ml) and heating (steam bath) was continued for 10 min after the final addition. Ethanol (300 ml) was mixed into the deep blue solution and, on cooling, a nearly quantitative yield of flaky blue crystals was obtained (31 g).

[Co(tren)Cl₂]Cl (1.0 g) was suspended in a saturated solution of ammonia in methanol (50 ml) and warmed to 30-40° for 30 min, during which time the suspension changed from blue to pink. The mixture was cooled and anhydrous ether (100 ml) added. The solids