by column chromatography, showed a large optical rotation.[15] The optical purity of Va was determined by the use of chiral shift reagents.[16] Figure 1, shows the portion of the shifted spectrum resulting from *one* of the methylene protons adjacent to the ether oxygen. As can be seen (spectrum a) the doublet in the unshifted spectrum from this proton splits into four lines. When the opposite enantiomers of the complex were used different pairs of these lines decrease in intensity (spectra b, c). Although an exact integration was difficult, the optical purity (31 ± 2%) of the product appears to be the same as the starting complex.

Thus, the product Vb results from trapping of an intermediate cyclobutadienoid while it is still under the chiral influence of the metal. This suggests that in the earlier[3,4] intermolecular trapping experiments, optically active products would have resulted if the cyclobutadiene ligand was not free from the metal at the time of reaction.

References and Notes

(1) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 623 (1966); P. Reeves, J. Henery, and R. Pettit, *ibid.*, **91**, 5890 (1969); E. K. G. Schmidt, L. Brener, and R. Pettit, *ibid.*, **92**, 3240 (1970), and references therein.

(2) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); O. L. Chapman, D. DeLaCruz, R. Roth, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 1337 (1973); G. Maier, *Angew. Chem.*, **86**, 491 (1974); F. R. Wright, *Tetrahedron Lett.*, **41**, 3691 (1970).

(3) R. H. Grubbs and R. A. Grey, *J. Am. Chem. Soc.*, **95**, 5765 (1973).

(4) E. K. G. Schmidt, *Chem. Ber.*, **108**, 1609, 1599 (1975); *Angew. Chem.*, **85**, 820 (1973).

(5) J. Rebek and F. Gaviña, *J. Am. Chem. Soc.*, **96**, 7113 (1974).

(6) R. H. Grubbs, T. A. Pancoast, and R. A. Grey, *Tetrahedron Lett.*, **28**, 2425 (1974).

(7) Identified by NMR and molecular weight and comparison to analogous compounds.

(8) The spectral properties of compound Va are: ^{1}H NMR, δ (Me_4Si): 6.60 (doublet $J_{7,8}$ = 2.7 Hz, 1 H) (7), 6.33 (doublet of doublets, $J_{7,8}$ = 2.7, $J_{8,9}$ = 1.5 Hz, 1 H) (8), 4.47 (multiplet, 2 H) (4), 4.12 (doublet, J = 9 Hz, 1 H) (5), 3.72 (doublet, J = 9 Hz, 1 H) (5), 3.47 (doublet, $J_{8,9}$ = 1.5 Hz, 1 H), 1.70 (triplet, $J_{4,10}$ = 1.5 Hz, 3 H (10); ^{13}C: 191.7 (1), 171.1 (3), 145.3 (7), 136.0 (8), 131.6 (2), 69.0 (4), 64.6 (5), 62.5 (6), 56.4 (9), 9.45 (10); MS *m/e* 162.

(9) A. Bond and M. Green, *J. Chem. Soc., Dalton Trans.*,. 763 (1972).

(10) Compound IIIb was prepared from 1,2-dicarbomethoxycyclobutadienyliron tricarbonyl (IX).[11] IX was converted to the half acid, reduced with BH_3/THF–$BF_3 \cdot Et_2O$ to 1-carbomethoxy-2-methylcyclobutadienyliron tricarbonyl and then with diisobutylaluminum hydride to 1-hydroxymethyl-2-methylcyclobutadieneiron tricarbonyl. The alcohol was converted to the bromide and resolved as before.[12]

(11) G. Berens, F. Kaplan, R. Rimerman, B. W. Roberts, and A. Wissner, *J. Am. Chem. Soc.*, **97**, 7076 (1975).

(12) R. Grubbs and R. A. Grey, *J. Chem. Soc., Chem. Commun.*, 76 (1973).

(13) The spectra of Vb are: ^{1}H NMR, δ (Me_4Si) 5.93 (multiplet, 1 H) (8), 4.47 (multiplet, 2 H) (4), 4.12 (doublet, J = 9 Hz, 1 H) (5), 3.72 (doublet, J = 9 Hz, 1 H) (5), 3.27 (multiplet, 1 H) (9), 1.80 (multiplet, 3 H) (11), 1.70 (triplet, $J_{4,10}$ = 1.5 Hz, 3 H) (10); ^{13}C: 201.7 (1), 171.9 (3), 155.3 (7), 131.3 (2), 126.5 (8), 67.5 (4), 64.4 (5), 63.1 (6), 52.8 (9), 13.6 (11), 9.3 (10); MS *m/e* 176.

(14) These yields were obtained when the reaction was carried out under 1 atm of carbon monoxide. Lower yields were obtained under nitrogen.

(15) Calculated $[\alpha]^{25}{}_{578}$ 280 ± 20° (0.015 g in ether).

(16) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Am. Chem. Soc.*, **93**, 5913 (1971). Tris[3-(heptafluorobutyryl)-*d*-camphorato]europium(III) was used.

(17) Sloan Foundation Fellow and Camille and Henry Dreyfus Teacher–Scholar Grantee.

Robert H. Grubbs,* [17] **Taylor A. Pancoast**

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Received November 18, 1976

Stereospecific Synthesis of a Sulfenamide Cobalt(III) Complex Derived from (*R*)-Cysteine

Sir:

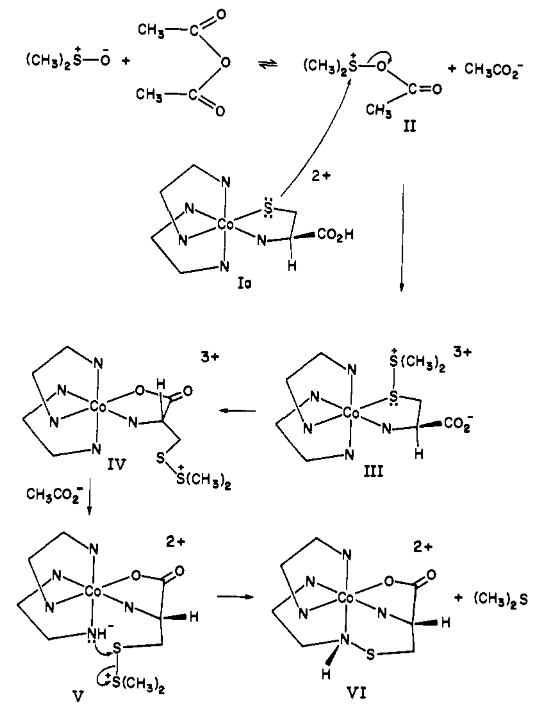

Figure 1. Mechanism for sulfenamide formation.

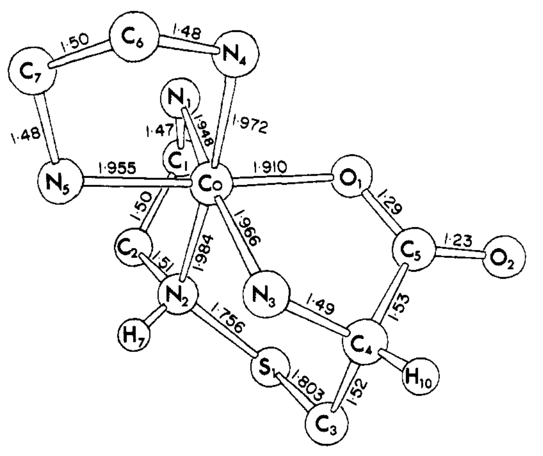

Figure 2. The crystal structure of Δ-(*S*)-(ethylenediamine-(*R*)-cysteinesulf*e*namide)(ethylenediamine)cobalt(III) tetrachlorozincate.

[$Co(en)_2$-(*R*)-cysteinato]$(ClO_4)_2 \cdot H_2O$ was prepared from (R,R)-cystine, ethylenediamine and cobalt(II) perchlorate and separated into two brown diastereoisomers (Ia, Ib). The proposed structure of one of these isomers (Ia, $[M]^{483}{}_{20}$ +9015 deg M^{-1} m^{-1}, 10^{-2} M $HClO_4$) is depicted in Figure 1. Two components are observed for the first ligand field band consistent with the C_{4v} symmetry of the bonding atoms ($\epsilon^{484}{}_{max}$ = 133, $\epsilon^{\sim 580}{}_{sh}$ 50 M^{-1} cm^{-1}, 10^{-2} M $HClO_4$) but a strong charge transfer absorption ($\epsilon^{281}{}_{max}$ 12 450) obscures the second ligand field band region ($\epsilon^{\sim 360}{}_{sh}$ 324). This spectral property is characteristic of S bound to Co(III).[1,2] For N,O amino acid chelates in general, both ligand field bands are observed (~485 and 345 nm). Comparison of the ^{1}H NMR and visible spectra of Ia with [$Co(en)_2S(CH_2)_2NH_2$]-$(ClO_4)_2$($\epsilon^{481}{}_{max}$ 126, $\epsilon^{\sim 580}{}_{sh}$ 48, $\epsilon^{\sim 360}{}_{sh}$ 318, $\epsilon^{281}{}_{max}$ 13 400)[2] and [$Co(en)_2SCH_2OCO$]ClO_4 ($\epsilon^{514}{}_{max}$ 153, $\epsilon^{360}{}_{sh}$ 367, $\epsilon^{280}{}_{max}$ 11 300) eliminated the third possibility of S,O chelation. The other feature consistent with N,S bonding is the pK_a of the ionizable proton which is ~4, characteristic of a free carboxylic acid group in this type of complex.[3] Further, ion-exchange chromatography (pH 2 and 7) reflects the two possible cation charges, 2+ and +, and both mono- and diperchlorate salts of I have been isolated. Note that (uncoordinated) -NH_3^+ (pK_a ~ 9) or -SH (pK_a ~ 10) is expected to be significantly less acidic than -COOH.

The cysteinato isomers show a capacity for oxidation at S by a variety of oxidizing agents. In particular, a dimethyl

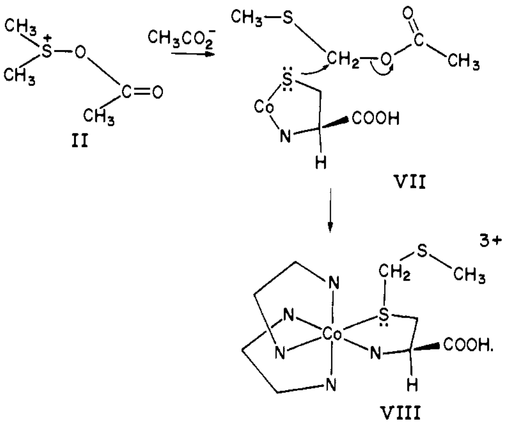

Figure 3. Alkylation of N,S chelated cysteine via the Pummerer rearrangement.

sulfoxide/acetic anhydride mixture yielded a single isomer of a red complex(VI) in >90% yield. This product had essentially the same analysis as the reactant but exhibited widely different ^{1}H NMR and visible spectra from Ia or Ib and from the S-bound sulf*e*nato and sulf*i*nato complex products derived from other oxidants.[4] Charge transfer absorption obscured the second ligand field band, suggesting S bound to Co(III). However, no sensible structural assignment could be made with all these data and a crystal of the $ZnCl_4^{2-}$ salt was therefore examined by x-ray crystallography. Anal. Calcd for $CoC_7H_{20}N_5SO_2ZnCl_4$: C, 16.7; H, 4.0; N, 13.9; S, 6.4; Cl, 28.1. Found: C, 16.7; H, 4.2; N, 13.4; S, 6.4; Cl, 27.8.

Crystal data: $CoZnCl_4SO_2N_5C_7H_{20}$; orthorhombic with $a = 16.455$ (2), $b = 16.646$ (2), $c = 6.315$ (7) Å; space group $P2_12_12_1$, M = 504.4 amu; $d_m = 1.9$, $d_c = 1.94$ g cm^{-3} for $Z = 4$. For 1905 independent data with $F_o^2 > 3(F_o^2)$ the R index is 0.035. Coordination about Co(III) is octahedral (normal), and there are no significant distortions in the chelates. (N2-S1-C3, 99.0 (3)°; Co-N2-C2, 107.6 (4)°; S1-C3-C4, 114.4 (5)°).

The structure (Figure 2) points to two remarkable features for the mild conditions (20 °C, ~12 h) of the synthesis. A shift from the N,S to the N,O bonded chelate has occurred and the freed S atom has then condensed with one of the N atoms of one ethylenediamine chelate to generate an unusual heterocyclic six membered (chair) ring containing a sulf*e*namide linkage. Overall a new quadridentate has been formed from a *tris* chelate.

The ^{1}H NMR of VI (10^{-3} M DCl and D_2O) was complex. In addition to the characteristic CH_2 (τ 7.26, m, br, 6 H) and NH_2 (τ 4.7, 4.95, 5.59, s, br, 6 H) signals of en, resonances were observed at τ 4.04 (s, br, 2 H, NH_2 of amino acid), τ 6.88-7.20 (m, br, 2 H, CH_2 of en α to N-bound sulf*e*namide linkage), and, as a complex pattern of sharp lines, at τ 6.48-6.95 (m), 6.26 (d), 6.13 (d), 5.96 (s), and 5.92 (d, br) (S-CH_2 and -CH-, ABX pattern). The NH sulf*e*namide proton was exchanged instantly even in 1 M DCl but was clearly observed in Me_2SO-d_6 at τ 2.48 (s, br, 1 H). The proton decoupled ^{13}C NMR (D_2O) showed all seven C atoms as separate sharp singlets, confirming the presence of a single isomer (vide infra). The first ligand field band ($\epsilon^{486}{}_{max}$ 135; 10^{-2} M $HClO_4$) in the visible spectrum is consistent with a CoN_5O chromophore. The intense charge transfer band ($\epsilon^{345}{}_{max}$ 2590) which obscures the second ligand field band is ascribed to the chromophore of the sulf*e*namide, although bonded through the N atom rather than the S atom. The band is reduced in intensity and shifted to lower energies relative to the S bonded complexes I. Complex VI shows a pK_a of ~10 (NH of sulf*e*namide), and crystals of a deep wine red deprotonated form have been isolated.

The extraordinary rearrangement (Figure 1) has a rational interpretation if the properties of the Me_2SO/acetic anhydride mixture are exercised. Acetylation of the $(CH_3)_2SO$ oxygen[5] yields the sulfoxonium ion II and allows a nucleophilic displacement by the coordinated mercaptide ion of the cysteinato complex Ia to generate a disulfide linkage III and acetate ion. This immediately renders the coordinated cysteine S^- positive and thence a good leaving group. Capture of the free carboxyl group gives the N,O bound ion IV. The alkylated disulfide residue is now susceptible to nucleophilic attack and removal of a proton from an ethylenediamine nitrogen by acetate provides this opportunity. Finally the coordinated amide ion of V cleaves the disulfide link to generate the complex product VI and $(CH_3)_2S$.

In larger scale preparations of the sulf*e*namide VI a small quantity (~2%) of an orange 3+ product (VIII) was isolated and characterized (anal., ^{1}H NMR, visible, and ORD spectra) as $\Delta Co(en)_2$-(R)-$(NH_2CH(CH_2SCH_2SCH_3)COOH)^{3+}$ (Figure 3). This arises from the Pummerer rearrangement of the sulfoxonium ion II to the thioether VII[5] followed by nucleophilic attack of the bound mercaptide ion of I. Similar rearrangements have been observed with the Me_2SO/$(CF_3CO)_2O$ reagent.[5,6]

The remarkable stereospecificity of the sulf*e*namide reaction prompts comment. The chirality of the amino acid directs the condensation to one N atom (Figure 1). However two other isomeric products are possible, one inverted about the cobalt center and the other inverted about the chiral sulf*e*namide N center (Figure 2). We have shown that Λ-N,S-Co(en)$_2$-(R)-cysteinato^{2+} ion undergoes the same type of oxidation to give the same Δ sulf*e*namide isomer described here. These stereochemical aspects and the equilibration and structures of both the Λ and Δ sulf*e*namide isomers will be described in a subsequent publication.

References and Notes

(1) L. E. Asher and E. Deutsch, *Inorg. Chem.*, **12**, 1774 (1973).
(2) R. H. Lane and L. E. Bennett, *J. Am. Chem. Soc.*, **92**, 1089 (1970).
(3) V. M. Kothari and D. H. Busch, *Inorg. Chem.*, **8**, 2276 (1969).
(4) W. G. Jackson, A. M. Sargeson, and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 1934 (1976).
(5) A. K. Sharma, T. Ku, A. D. Dawson, and D. Swern, *J. Org. Chem.*, **40**, 2758 (1975).
(6) W. G. Jackson and A. M. Sargeson, unpublished results.

G. J. Gainsford
Chemistry Division, D.S.I.R. Bag, Private Bag
Petone, New Zealand

W. G. Jackson, A. M. Sargeson*
Research School of Chemistry
Australian National University
Canberra, A.C.T. 2600, Australia

Received November 8, 1976

Disproportionation at the Ligand in Nitro Complexes of Ruthenium(III)

Sir:

Complexes of Ru(II) and Ru(III) are usually substitution inert and stable, and Ru(III)/Ru(II) couples have been used extensively in the study of one-electron transfer processes.[1] This is certainly true for *cis*-bis-2,2′-bipyridine (bpy) complexes where more than 100 reversible Ru(III)/Ru(II) couples are known.[2] However, oxidation to Ru(III) can lead to chemical instability because of oxidation of a bound ligand (reactions 1, 2).

$$[Ru^{III}(bpy)_2(N_3)_2]^+ + CH_3CN \rightarrow [Ru^{II}(bpy)_2(CH_3CN)N_3]^+ \ {}^3\!/\!_2N_2 \quad (1)^3$$