carbon monoxide toward migratory insertion,[2-4,14] both kinetically and thermodynamically.

Decomposition of the acetyl cation radicals, **5a-c**, was found to be first order for three half-lives in AN at 20 °C (monitoring the decrease in the low-energy absorption maximum, with [Fe] $\sim 3 \times 10^{-3}$ M and [oxidant] $\sim 1 \times 10^{-3}$ M). This contrasts with the second-order decomposition in cation radical observed for alkyl cobaloxime(IV) complexes, for which a disproportionative mechanism has been proposed.[15] The evidence suggests that acyl cation radicals are the immediate precursors to one-electron oxidative decomposition products previously reported for $Cp(CO)_2FeR$ systems.[2-7] The possibility cannot be dismissed that organic products arise from nucleophilic attack at the acyl carbonyl (esters, amides, etc.), nucleophilic displacement at the α carbon of the acyl (ethers, alkyl halides), or homolytic scission of the acyl carbonyl-α carbon bond (organic dimers). In support of this, $PhCH_2CO_2CH_3$, $PhCH_2OCH_3$, and $PhCH_2CH_2Ph$ all resulted from the Ce(IV) oxidation of $Cp(CO)_2Fe(COCH_2Ph)$ in methanol.

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Photochemical Preparation of an *O*-Sulfinato Complex of Cobalt(III)

Sir:

The ability of sulfinic acids, RSO_2H, to coordinate to main group and to transition-metal ions is well-known, and the structure and bonding have been studied in some detail.[1,2] The bonding may be via one or both oxygen atoms, sulfur, or a sulfur-oxygen π system. To our knowledge, however, all reported Co(III) complexes containing sulfito, sulfinato, or sulfenato ligands show only Co-S bonding.[3] The only indication otherwise is a recent observation[4] of a transient in the reaction of SO_2 with $Co(NH_3)_5(OH)^{2+}$, tentatively assigned as $Co(NH_3)_5(OSO_2)^{2+}$. We report here the synthesis and characterization of what appears to be the first example of a *robust* Co(III) complex containing an O-bonded sulfinato ligand.

The observations are a sequel to an earlier photochemical study of Co(III) chelate complexes containing a Co-S bond,[5] of the type $Co(en)_2L^{n+}$, where L is a bidentate ligand containing sulfur, and en denotes ethylenediamine. Upon extension of the photochemical investigations to the complex $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$, here designated as CoSOON, an unusually clean photochemistry was observed. On photolysis at various wavelengths in the 350-450-nm region, the spectral changes that occur with an aqueous solution of the perchlorate salt maintain very good isosbestics up to essentially complete conversion to product, accompanied by a color change from yellow to red. Ion-exchange chromatography with Sephadex SP-25 confirmed that a single product was present. The electronic absorption spectra of aqueous CoSOON and of the photoproduct are shown in Figure 1, with details included in Table I. Quantum yields decreased from 0.1 to 0.01 over the wavelength range 313-460 nm; details on this aspect are to be included in a later report.

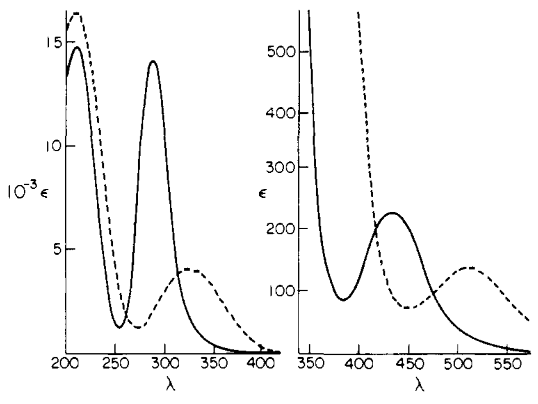

Figure 1. Absorption spectrum of aqueous CoSOON (—) and CoOSON (----).

Table I. Spectral Data for $Co(en)_2[S(O)_2CH_2CH_2NH_2]^{2+}$ and $Co(en)_2[OS(O)CH_2CH_2NH_2]^{2+}$

A. Electronic Absorption (H_2O, 25 °C)

complex	λ_{max} (ϵ)	λ_{max} (ϵ)
$Co(en)_2(S(O)_2CH_2CH_2NH_2)(ClO_4)_2$	432 (220)	288 (14 200)
$Co(en)_2(OS(O)CH_2CH_2NH_2)(ClO_4)_2$	512 (134)	326 (4100)

B. 100-MHz ^{1}H NMR (D_2O, 25 °C, HDO internal reference)

complex	τ from HDO (shape, assignment)
$Co(en)_2(OS(O)CH_2CH_2NH_2)(ClO_4)_2$	−2.0 (br, en CH_2) −1.5 to −1.9 (complex m, NCH_2RSO_2-) −1.24 (m, $NRCH_2S$) −0.6 (v br, NH_2) +0.4 (br, NH_2)
$Co(en)_2(OS(O)CH_2CH_2NH_2)(ClO_4)_2$	−2.3 to −1.9 (complex m, $NCH_2RSO_2^-$) −2.0 (br, en CH_2) −1.55 (m, $NRCH_2S$)

C. Vibrational[a] Data (IR; KBr pellet; Raman, H_2O, 647.1 nm)

complex	IR,[b] cm^{-1}	Raman,[c] cm^{-1}
$Co(en)_2(S(O)_2CH_2CH_2NH_2)^{2+}$	1190 (s)	1204 (w)
$Co(en)_2(OS(O)CH_2CH_2NH_2)^{2+}$	950 (m)	950 (w sh on ClO_4^- peak)
	1030-1037 (s)	1038 (w)

[a] Only frequencies not common to both complexes are listed. [b] Halide salts. [c] ClO_4^- salts.

The photoproduct was isolated on a preparative scale by nearly complete photolysis of a stirred, nearly saturated aqueous solution of the perchlorate salt of CoSOON, using white light (λ > 400 nm), followed by evaporation to dryness to obtain the product as an essentially pure red solid. Elemental analyses of the product were consistent with the formulation, $Co(en)_2(SO_2CH_2CH_2NH_2)(ClO_4)_2 \cdot H_2O$.[6] As a check, further purification was accomplished by dissolving the material in minimal wet methanol, filtering the solution, and then precipitating the product by the addition of acetone and ether, with no change in properties except that a methanol solvate was obtained.[6] The

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thiocyanate salt could be precipitated out by the addition of sodium thiocyanate to a concentrated solution of the product in wet methanol.[7] Preparation of macrocrystalline material was difficult because of the hygroscopic nature of the various salts tried.

This photoproduct is evidently the O-bonded isomer, $Co(en)_2[OS(O)CH_2CH_2NH_2]^{2+}$, designated as CoOSON. The chromatographic elution rate is that for a divalent ion, and is independent of pH over the range 2–8.7. Further, the visible–UV absorption spectrum of an irradiated solution of CoSOON is also independent of pH in this range. Thus, neither complete aquation to give free ligand $NH_2CH_2CH_2SO_2^-$, nor partial aquation to give $Co(en)_2(NH_2CH_2CH_2SO_2)(H_2O)^{2+}$ could have occurred. Confirmation that the photoproduct is the O-bonded isomer comes from the absorption spectrum. The position of the first ligand field absorption band of CoOSON is characteristic of a Co(III) complex having one oxygen and five nitrogens coordinated.[8] The lack of the characteristic intense charge-transfer (CT) band at ~285 nm confirms that sulfur is not coordinated,[9] but the new CT band at 326 nm indicates that the sulfinate moiety can still interact with the Co(III) center. This would be true for the O-bonded isomer, but not if the group were detached. Further, the 326-nm band (ϵ 4100 $M^{-1}\ cm^{-1}$) is analogous to an absorption feature present in the transient spectrum observed by Harris and co-workers [333 nm (ϵ ~2100 $M^{-1}\ cm^{-1}$)].[4] A similar CT band is present in the spectra of other Co(III) complexes in which sulfur is separated from cobalt by one ligating atom,[10] as in a Co(III)–sulfenamide complex.[10a] We thus assign our 326-nm absorption to CT from the sulfinic acid chromophore to Co(III).

Other spectral aspects are summarized in Table I. The 100-MHz NMR spectrum of CoOSON is very similar to that of CoSOON, except that the resonance attributable to the $S-CH_2$ protons occurs significantly further upfield in the former. Interestingly, the lack of an NH_2 proton signal for CoOSON indicates that these protons are much more easily exchanged than they are in the starting complex. The latter showed NH_2 proton resonance even after several days in D_2O solution.

The vibrational data obtained from the infrared and Raman spectra of the two complexes were complicated by the large number of ligand vibrations present. Also, both complexes are poor Raman scatterers. However, the observed vibrational features not common to both product and starting complex are given in Table I. It can be seen that the strong vibration at 1190 cm^{-1}, likely due to the asymmetric O=S=O stretch,[1,3,9a] is not present in the product. In the product, two new vibrations appear, at ~1035 and 950 cm^{-1}, attributable, respectively, to the S=O stretching mode and to the asymmetric Co–O–S stretching mode of an *O*-sulfinato ligand.[1,3] Due to the overlapping C–C and C–N vibrations in the 1000–1100-cm^{-1} region, it was not possible to confirm the absence of a symmetric O=S=O stretching mode in the product spectrum. This mode occurs at 1080 cm^{-1} in CoSOON.[9a]

Chemical properties of CoOSON include the following. The aqueous (or methanolic) solution is not photosensitive in the 350–450-nm region. It does, however, revert thermally to CoSOON. The reaction is very clean and is first order. Kinetic studies over the temperature range 28–67 °C give $\Delta H^{\circ\ddagger} = 22.6$ kcal mol^{-1} and $\Delta S^{\circ\ddagger} = -15.6$ eu (corresponding to a half-life of about 600 h at room temperature). While CoOSON shows no weak acid or base properties, major spectral change does occur to the CT band in 1–8 M perchloric acid solution. There is a large blue shift, leaving a shoulder at about 270 nm. The first ligand field band maximum changes only slightly, however, from 512 to 508 nm. These spectral changes were reversible even after several days, and an acid–base equilibrium is indicated. Spectrophotometric titration with solutions buffered to ionic strength 8 M by means of sodium perchlorate gave a pK_a of −0.7 (uncorrected for H^+ activity coefficient changes). Possible protonation sites would be (a) the Co-bonded oxygen, (b) the sulfur, and (c) the S=O oxygen; case (a) seems the least likely in view of the minimal change in the ligand field band.

The photochemical generation of CoOSON, a thermodynamically unstable and perhaps otherwise unobtainable linkage isomer of CoSOON, is somewhat analogous to the nitro to nitrito linkage isomerization observed in the photolysis of $Co(NH_3)_5(NO_2)^{2+}$.[11] The mechanism may be similar, in that photochemical homolytic bond fission may occur to break the Co–S bond of CoSOON, followed by rapid cage recoordination to yield CoOSON. Unlike the case with the nitro complex, however, there is negligible redox decomposition so that the photochemical reaction is unusually clean. Current efforts are directed toward obtaining crystals of a salt of CoOSON suitable for X-ray structure determination. Finally, preliminary observations are that the behavior of the corresponding cysteinesulfinato complex on irradiation is very similar to that of CoSOON; details will be reported later.

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(7) Too slow a crystallization leads to a different red salt, which analyzes for $[Co(en)_2(NCS)_2]NCS$. Anal. Calcd: C, 23.79; N, 27.75; H, 4.56. Found: C, 23.92; N, 27.64; H, 4.52.

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Claisen Rearrangements of Lactonic (Silyl) Enolates: A New Route of Functionalized Cycloalkenes

Sir:

The Claisen rearrangement, in both its aromatic and aliphatic modes,[1,2] has been of considerable value in organic synthesis. Büchi[3] demonstrated the rearrangement of dihydropyran (**1**) to cyclohexene (**2**) under forcing conditions (ca. 400–425 °C in a flow system or 240 °C in a sealed tube). In the Ireland[4] rearrangement, **3** → **4**, a relatively accessible acyl oxygen bond is used to furnish a more difficultly available carbon–carbon bond. Moreover, the ability to generate systems such as **3** with high *E* or *Z* stereoselectivity,[4b,c] in conjunction with the chairlike geometry of the Claisen rearrangement, allows for erythro:threo stereospecificity in the formation of **4**.

We have investigated the feasibility of using vinyl lactones such as **5** as precursors of cycloalkenes (cf. **8**). Below, we report (i) that the reorganization reaction, **6** → **7**, is eminently feasible provided that $n > 1$, (ii) that an unusual, stereospecific [1,3] rearrangement occurs in constrained versions of system **6** (cf. **5k–m** → **16k–m**), (iii) that relative to the reaction **1** → **2**, the **6** → **7** rearrangement occurs under remarkably mild conditions, and (iv) that its stereochemical outcome is indicative of a boatlike transition state. See Scheme I.

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