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Three-Membered $-\overline{\mathrm{SCoC}}\mathrm{H}_2$ Chelate Ring Complex Formed by Photodecarboxylation Reaction of Optically Active *trans*(*O*)-[Co(edtda)(en)]Cl (edtda = Ethylenedithiodiacetate)

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Introduction

Many cobalt(III)−sulfide complexes have been extensively investigated in view of their stereochemistries, kinetics of ligand substitution, and electron-transfer reactions.[2,3] Recent reports have revealed that the thioether sulfur atom to the coordinated cobalt(III) ion induces remarkable effects upon the reversible rearrangement from a S- to a C-bonded complex in basic solutions and deuteration of the methylene protons adjacent to the coordinated thioether group in D_2O solutions.[4,5] Further, the methylcobalamin-dependent enzyme catalyzes the reaction converting homocysteine to methionine.[6] Reactions of analogous model systems have been used to address various aspects of thiolate organocobalt(III) vitamin B_{12} chemistry.[7] The major part of organocobalt(III) chemistry has been confined to organic solvents, and many thiolate organocobalt(III) compounds are air-sensitive, thus preventing the investigation in aqueous solution. However, the chemistries of this type of organocobalt(III) complex have led us to some interesting results concerning the coordinated thioether sulfur and methylene carbon atoms. Hence, to study the formation of the unique $-\overline{\mathrm{SCoC}}\mathrm{H}_2$ three-membered ring in an aqueous solution and reveal the properties of the photoproduct, we have undertaken the preparation of the (dithiodicarboxylato)cobalt(III) complex with the tetradentate-*O,S,S,O* ligand and the investigation of its photochemical reaction.

The present paper deals with the synthesis and some properties of a novel (dithiodicarboxylato)cobalt(III) complex, *trans*(*O*)-$[Co(edtda)(en)]^+$, together with the crystal structure of its spontaneously resolved isomer. In addition, the photoreaction of the *trans*(*O*)-$[Co(edtda)(en)]^+$ and the characterization of the photoproduct, *trans*(*C*,*O*)-$[Co(CH_2S(CH_2)_2SCH_2COO)(en)]^+$, and its interesting and unique properties are also discussed by comparison with the starting dithiodicarboxylato complex.

Experimental Section

Caution: Generally, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. The present complexes are not hazardous in solutions and upon normal treatment of the solid.

Synthesis of *trans*(*O*)-[Co(edtda)(en)]Cl·H_2O (1Cl·H_2O). A solution of H_2edtda[8] (4.20 g, 20 mmol) in 50 mL of water was added to a solution containing $Co(NO_3)_2\cdot 6H_2O$ (5.82 g, 20 mmol) in 150 mL of water. After the pH of the mixed solution was adjusted to 7, a solution containing ethylenediamine (1.12 g, 20 mmol) in 10 mL of water was added. While maintaining the pH constant at 7 with 2 M KOH solution, PbO_2 (5 g) was added to the solution and the mixture was then stirred at 40 °C for 1 h. The reddish purple solution was poured onto an SP-Sephadex C-25 column (K^+ form, 4.7 cm × 90 cm). The adsorbed band was developed with a 0.2 M KCl aqueous solution. The eluate of the purple band was concentrated to a small volume with a rotary evaporator below 30 °C. The resulting purple crystals, which were spontaneously resolved, were collected by filtration and dried over silica gel in a desiccator. Yield: 3.9 g (51%). UV/vis (λ_{max}/nm (water) (ϵ/(dm^3 mol^{-1} cm^{-1})): 550 (178), 470 (sh), 395 (sh), 278 (sh), 254 (12 600). CD of $(+)_{563}$ enantiomer (λ_{max}/nm (water) ($\Delta\epsilon$/(dm^3 mol^{-1} cm^{-1})): 563 (+3.69), 470 (−3.40), 401 (+1.22), 360 (−0.46), 306 (+9.97), 266 (−25.20). ^{13}C NMR (ppm (D_2O)): 37.2, 38.7, 46.5, 182.9. IR (ν_{max}/cm^{-1} (KBr)): 1616 vs (C=O), 1575 s (N−H). Anal. Calcd for *trans*(*O*)-[Co(edtda)(en)]Cl·H_2O = $C_8H_{16}N_2O_4S_2ClCo\cdot H_2O$: C, 25.24; H, 4.76; N, 7.36. Found: C, 25.09; H, 4.78; N, 7.24.

Photoreaction and Isolation of *trans*(*C*,*O*)-[Co($CH_2S(CH_2)_2SCH_2COO$)(en)]ClO_4 (2ClO_4). A solution of *trans*(*O*)-[Co(edtda)(en)]Cl·H_2O (**1**Cl·H_2O) (0.30 g) in 300 mL of water was bubbled with nitrogen gas for 15 min in an ice−NaCl bath prior to photoirradiation. The solution was irradiated by a 400 W high-pressure mercury lamp (internal irradiating type) at ca. 5 °C for 7 min with bubbling N_2 gas through the solution. The color of the solution turned from purple to violet. The resulting solution was poured onto an SP-Sephadex C-25 column (Na^+ form, 2.7 cm × 25 cm). The adsorbed band was developed with a 0.2 M $NaClO_4$ aqueous solution. A major violet band (**2**) and a minor purple (starting material **1**) band were separated from the

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Table 1. Crystallographic Data for $(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O and **2**ClO_4

	$(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O	**2**ClO_4
empirical formula	$CoC_8H_{18}O_5N_2S_2Cl$	$CoC_7H_{16}O_6N_2S_2Cl$
fw	380.76	382.73
space group	$P2_12_12_1$ (No. 19)	*Pbca* (No. 61)
a/Å	6.788(1)	12.4010(5)
b/Å	12.799(1)	14.7820(6)
c/Å	16.999(2)	15.1599(7)
V/Å^3	1477.0(3)	2779.0(2)
Z	4	8
ρ_{calcd}/(g cm^{-3})	1.71	1.83
μ(Mo Kα)/cm^{-1}	16.3	17.4
R^a	0.035	0.049
$R_w{}^b$	0.050	0.065

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o{}^2)]^{1/2}$.

adsorbed band in the order of elution. To obtain a sufficient amount of the violet eluate, the procedure described above was repeated eight times. The combined eluate was concentrated to a small volume with a rotary evaporator below 25 °C. The violet crystals were collected by filtration and dried over silica gel in a desiccator. Yield: 2.2 g (91%). UV/vis (λ_{max}/nm (water) (ϵ/dm^3 mol^{-1} cm^{-1})): 555 (204), 445 (sh), 356 (603), 325 (sh), 240 (9550). ^{13}C NMR (ppm (D_2O)): 16.7 (Co−*C*H_2), 29.1, 34.7, 44.8, 45.2, 183.0. IR (ν_{max}/cm^{-1} (KBr)): 1589 vs (C=O). Anal. Calcd for *trans*(*C*,*O*)-[Co($CH_2S(CH_2)_2SCH_2COO$)(en)]-ClO_4 = $C_7H_{16}N_{12}O_6S_2ClCo$: C, 21.96; H, 4.21; N, 7.31. Found: C, 21.79; H, 4.23; N, 7.18.

Measurements. The UV/vis absorption spectra were recorded on a JASCO UVIDEC-670 spectrophotometer and the CD spectra on a JASCO J-720 spectropolarimeter. All the measurements were carried out in aqueous solutions at room temperature. The infrared spectra were recorded with a JASCO FT/IR-5300 infrared spectrophotometer using the KBr method. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Hitachi R-90H NMR spectrometer at the probe temperature in D_2O. Sodium 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid (0 ppm) for ^{1}H NMR and 1,4-dioxane (67.4 ppm) for ^{13}C NMR were used as internal references. The rotating disk electrode voltammetry (RDE) measurements were recorded with a Yanaco P-900 apparatus using a glassy-carbon rotating-disk working electrode (Yanaco, GC-P2; 2000 rev min^{-1}) attached to a Yanaco P-10-RE Mark II head. An aqueous Ag/AgCl/NaCl (3 mol·dm^{-3}) electrode (Bioanalytical Systems, Inc., RE-1B) and platinum wire were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted at 22 ± 1 °C in a 0.1 mol·dm^{-3} aqueous solution of $NaNO_3$ as the supporting electrolyte and 1.0 mmol·dm^{-3} complex concentrations.

X-ray Crystal Structure Analysis. Single-crystal X-ray diffraction experiments were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The crystal data and experimental details are given in Table 1. Unit cell parameters were determined by a least-squares refinement, using the setting angles 25 reflections in the range of $16 < 2\theta < 20$ ($(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O) and $22 < 2\theta < 42$ (**2**ClO_4). The intensity data were collected by the $\omega - 2\theta$ scan mode up to $2\theta = 60°$ with scan rate of 1−5 ($(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O) and 2−20°/min (in ω) (**2**ClO_4) and scan width $(0.4 + 0.350 \tan \theta)°$ for $(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O and $(0.7 + 0.450 \tan \theta)°$ for **2**ClO_4. The 1502 ($(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O) and 3058 (**2**ClO_4) independent reflections with $F_o > 3\sigma(F_o)$ of the measured 1538 ($(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O) and 4519 (**2**ClO_4) reflections were considered as "observed" and used for structure determinations of $(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O and **2**ClO_4, respectively.

The position of the cobalt atom was determined by the heavy atom method. The successive difference Fourier maps based on the Co atom position revealed the other non-hydrogen atom positions. The structures of $(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O and **2**ClO_4 were refined by a full-matrix least-squares treatment on F with anisotropic thermal parameters for the non-hydrogen atoms. All the calculations were performed on a VAX computer using the crystallographic package MOLEN.[9]

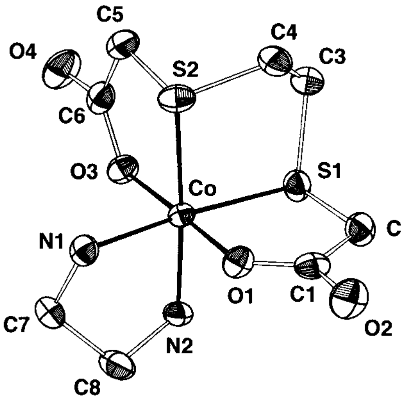

Figure 1. Perspective view of Λ-$(+)^{\mathrm{CD}}_{563}$-*trans*(*O*)-[Co(edtda)(en)]$^+$ ($(+)^{\mathrm{CD}}_{563}$-**1**) with the atom labeling scheme.

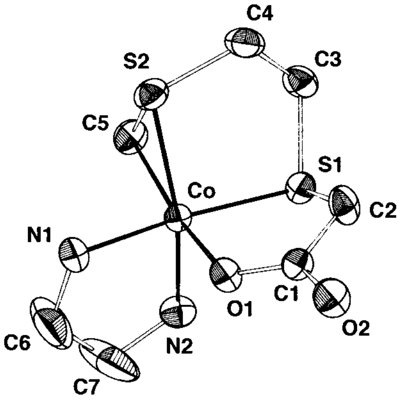

Figure 2. Perspective view of *trans*(*C*,*O*)-[Co($CH_2S(CH_2)_2SCH_2COO$)-(en)]$^+$ (**2**) with the atom labeling scheme.

A crystal, which was selected from the bulk, was analyzed by X-ray diffraction and then used for the UV/vis absorption and CD spectra in an aqueous solution. For $(+)^{\mathrm{CD}}_{563}$-*trans*(*O*)-[Co(edtda)(en)]Cl·H_2O ($(+)^{\mathrm{CD}}_{563}$-**1**Cl·H_2O), the refinements were carried out using a set of the non-H atomic parameters containing the Λ configuration of the complex cation; the residual values converged to R = 0.035, R_w = 0.050. Refinement with the enantiomeric atomic parameters (the Δ configuration) resulted in residual values of R = 0.046, R_w = 0.057. It was thus assumed that the former is most likely to be the correct choice, namely, the $(+)^{\mathrm{CD}}_{563}$ complex cation with the Λ configuration.

Results and Discussion

Crystal Structures. Perspective drawings of the complex cations $(+)^{\mathrm{CD}}_{563}$-**1** and **2** are given in Figures 1 and 2, together with a numbering scheme. The selected bond distances and angles in the complex cations are summarized in Table 2. In the $(+)^{\mathrm{CD}}_{563}$-**1** cation, the edtda ligand coordinates to the cobalt atom through two oxygen and two sulfur atoms to form three five-membered rings. The two coordinated O atoms are almost on a straight line with Co atom (O(1)−Co−O(3), 178.8(2)°). Of the two geometrical isomers, trans(O) and cis(O), possible for the [Co(edtda)(en)]$^+$ complex, it turns out that the $(+)^{\mathrm{CD}}_{563}$-**1** takes the trans(O) configuration. The bond distances of Co−S(thioether), 2.252(2) and 2.253(2) Å, are within the range normally observed for thioether complexes.[10] This indicates that the coordinated thioether sulfur atoms of the edtda ligand do not appear to exert a remarkable trans influence, which is distinct

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $(+)^{CD}_{563}$-**1**Cl·H$_2$O and **2**ClO$_4$

	$(+)^{CD}_{563}$-**1**Cl·H$_2$O	**2**ClO$_4$
	(a) Bond Distances (Å)	
Co−S(1)	2.252(2)	2.219(1)
Co−S(2)	2.253(2)	2.207(2)
Co−O(1)	1.901(4)	1.997(4)
Co−O(3)	1.895(4)	
Co−C(5)		1.957(6)
Co−N(1)	1.964(6)	1.965(5)
Co−N(2)	1.950(5)	1.979(5)
S(1)−C(2)	1.816(7)	1.791(6)
S(1)−C(3)	1.814(7)	1.815(6)
S(2)−C(4)	1.817(8)	1.824(7)
S(2)−C(5)	1.812(7)	1.777(6)
	(b) Bond Angles (deg)	
S(1)−Co−S(2)	91.76(7)	91.31(6)
S(1)−Co−O(1)	87.8(1)	86.0(1)
S(1)−Co−O(3)	93.4(1)	
S(1)−Co−C(5)		94.0(2)
S(1)−Co−N(1)	174.6(2)	173.7(2)
S(1)−Co−N(2)	90.8(2)	92.0(2)
S(2)−Co−O(1)	92.5(1)	113.0(1)
S(2)−Co−O(3)	87.6(1)	
S(2)−Co−C(5)		50.1(2)
S(2)−Co−N(1)	92.5(2)	93.6(2)
S(2)−Co−N(2)	175.2(2)	154.0(1)
O(1)−Co−O(3)	178.8(2)	
O(1)−Co−C(5)		163.0(2)
O(1)−Co−N(1)	88.7(2)	88.4(2)
O(1)−Co−N(2)	91.6(2)	93.0(2)
O(3)−Co−N(1)	90.0(2)	
C(5)−Co−N(1)		92.2(2)
O(3)−Co−N(2)	88.3(2)	
C(5)−Co−N(2)		103.9(2)
N(1)−Co−N(2)	85.1(2)	85.3(2)
Co−S(2)−C(4)	101.9(2)	105.3(2)
Co−S(2)−C(5)	97.2(2)	57.6(2)

from the coordinated thiolato sulfur ones.[11] For *trans*(*O*)-[Co(edtda)(en)]$^+$, two configurational isomers, Δ and Λ, are possible. The **1**Cl·H$_2$O was spontaneously resolved, and the $(+)^{CD}_{563}$ isomer takes the Λ configuration (Figure 1). The chiralities at the two asymmetric thioether S atoms were found to be *R*, *R*.

In complex **2**, the cobalt atom is coordinated to a carbon, oxygen, two sulfur, and two nitrogen atoms to form an octahedral arrangement. The −CH$_2$S− moiety of the $^-$CH$_2$S(CH$_2$)$_2$SCH$_2$COO$^-$ ligand coordinates to the cobalt atom through a carbon atom (C(5)) and sulfur atom (S(2)) to form the three membered $-\overline{SCoCH_2}$ ring. The $^-$CH$_2$S(CH$_2$)$_2$SCH$_2$COO$^-$ coordinating as a tetradentate ligand takes the trans(C,O) form. The formation of the three-membered $-\overline{SCoCH_2}$ ring introduces significant distortions into the octahedral coordination around the Co atom as is evident by the S(2)−Co−C(5) bond angle (50.1(2)°). The bond distances Co−S (2.219(1), 2.207(2) Å) are slightly shortened due to this distortion compared with the starting complex **1**. On the other hand, the Co−O bond distance (1.997(4) Å) is much longer than the value of the corresponding distances in $(+)^{CD}_{563}$-**1** (average 1.897 Å). This indicates that there is a significant trans influence by the ligating CH$_2$ group. The similar trans influence is observed in a number of Co(III) complexes containing Co−C bonds.[12]

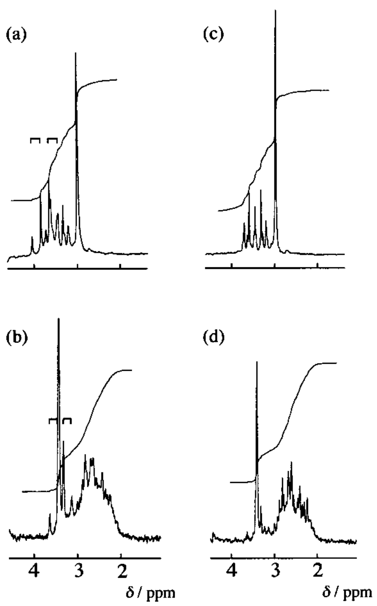

Figure 3. Proton NMR spectra in D$_2$O: (a) undeuterated complex **1** (at 0 min), (b) undeuterated complex **2** (at 0 min), (c) deuterated complex **1** (after 30 min), and (d) deuterated complex **2** (after 180 min).

Properties. The UV/vis absorption spectrum of complex **1** exhibits the intense broad band, which is composed of two components, in the region (35−40) × 10^3 cm^{-1} due to the sulfur(thioether)-to-cobalt charge-transfer (SCCT) transition. The result suggests that the characteristic SCCT bands of cis(S)-Co(III) complexes appear in the region of (35−40) × 10^3 cm^{-1} and that the bands have two or more components. Complex **1** provides the first X-ray structural evidence demonstrating such characteristic spectral behavior of a cis(S)-Co(III) thioether complex. Further, the complex shows the d−d absorption band at 18.18 × 10^3 cm^{-1} with a shoulder at a higher energy side (21.3 × 10^3 cm^{-1}). This absorption splitting pattern in the first absorption region is also quite similar to those of cis(S)trans-(O)-[Co(aeta)$_2$]$^+$ (aeta = (2-aminoethylthio)acetate) and [Co(aetp)$_2$]$^+$ (aetp = (2-aminoethylthio)propionate).[2e] Thus, the geometry of this Co(III) thioether complex is predictable from the UV/vis absorption spectrum on the basis of the Yamatera's rule for cobalt(III)−aminocarboxylato complexes and spectrochemical series (N > S > O).[13] The result shows that the rule can be applied to the assignment of the geometry of complexes having coordinated thioether sulfur atoms. In the first absorption band region of the CD spectrum, $(+)^{CD}_{563}$-**1** has two CD components, (+) and (−) from the low-energy side. This spectral pattern is almost enantiomeric to that of the ΔΔΛ-$(-)_{589}$-*trans*(*O*)-[Co(aeta)$_2$]$^+$ (net Δ).[2e] Therefore, the absolute configuration of $(+)^{CD}_{563}$-**1** is assignable to Λ consistent with the X-ray result. The violet complex **2**, which was obtained in strikingly high yield by the photodecarboxylation reaction of **1**, showed the first absorption band in ca. 18 × 10^3 cm^{-1}. The UV/vis absorption spectra of **1** and **2** do not exhibit a remarkable difference in the first absorption band region. In the SCCT band region, while complex **1** exhibited a strong broad band in the (35−40) × 10^3 cm^{-1} region, complex **2** shows only an intense

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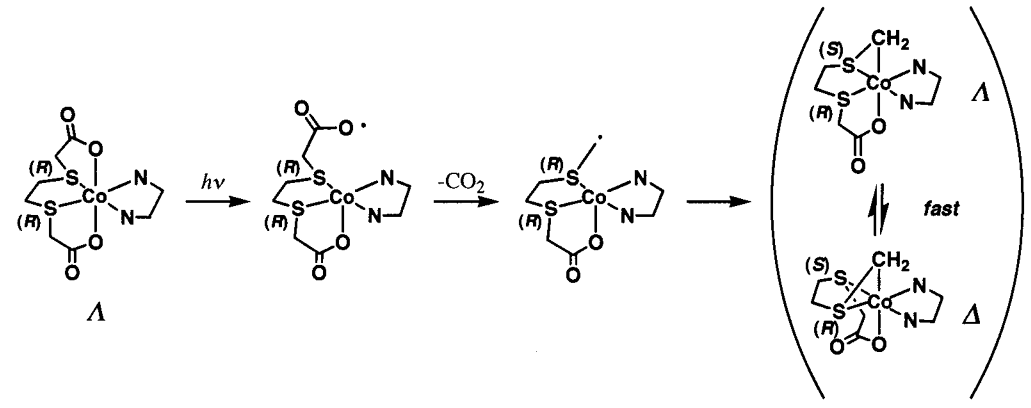
Scheme 1



$(+)^{\mathrm{CD}}_{563}$-**1**

rac-**2**

band in the 40 × 10^3 $\mathrm{cm^{-1}}$ region and a relatively weak one at ca. 28 × 10^3 $\mathrm{cm^{-1}}$. Interestingly, the characteristic SCCT bands in the thiolato or thioether complex have disappeared in the three-membered $-\overline{\mathrm{SCoC}}\mathrm{H_2}$ ring complex **2**.

Only one reduction potential value ($E_{1/2} = -0.08$ V vs Ag−Ag$^+$) was obtained in the potential region of +1.0 to −1.0 V (vs Ag−Ag$^+$). As this $E_{1/2}$ value is more positive than those of the other cobalt(III) thiolate or sulfide complexes,[14] the central cobalt(III) ion of **1** can easily be reduced electrochemically. On the other hand, the RDE for **2** did not show any obvious redox couple in the same potential region. It is thought that the above result, the weak SCCT band in the UV/vis absorption spectra, and the covalency of Co−$\mathrm{CH_2}$ bonding reflect the difference of the electronic state on the central $\mathrm{Co^{III}}$ ion among **1** (Werner-type complex) and **2** (Co−Cσ organometallic complex).

The ^{1}H NMR spectra of complexes **1** and **2** are given in Figure 3. The spectrum of **1** shows one singlet peak ($\delta = 2.99$) assignable to the methylene protons of the en ligand and the multiplet (symmetrical five lines) peaks of $\mathrm{A_2B_2}$ pattern due to the $-\mathrm{SCH_2CH_2S}-$ ring protons of the edtda ligand. Further, the two inequivalent protons of the two $-\mathrm{SCH_2COO}-$ (thioglycolato) arms in the coordinated edtda appear as an AB quartet ($\delta = 3.57$ and 3.92, $J = 12$ Hz). The methylene protons on facially coordinated thioglycolate rings are rapidly deuterated in neutral $\mathrm{D_2O}$ solution, as shown in Figure 3a,b. Finally (after 30 min), this AB quartet disappeared completely to form the $-\mathrm{SCD_2COO}-$, and only the $\mathrm{A_2B_2}$ pattern signal remained. Although similar ^{1}H NMR spectral changes were also observed for the *t*-$[\mathrm{Co(CH_3SCH_2COO)(tren)}]^{2+}$ (tren = tris(2-aminoethyl)amine)[5a,15] and $[\mathrm{Co(edma)_2}]^+$ (edma = ethylenediamine-*N*-acetate)[16] complexes, such a rapid H−D exchange reaction is peculiar. In complex **2**, the two inequivalent $-\mathrm{SCH_2COO^-}$ protons appear at $\delta = 3.27$ and 3.50 ($J = 12$ Hz) as an AB quartet. The spectra of **2** indicated that the H−D exchange reaction in the facially coordinated $-\mathrm{CH_2S(CH_2)_2SCH_2COO^-}$ also occurred, but the deuteration rate was much slower than **1** and other thiocarboxylato complexes (Figure 3c,d).[5] It is thought that the less activation in the deuteration of the methylene protons in **2** is attributable to the long Co−O bond distance, which is due to the trans influence from the coordinated $\mathrm{CH_2}$ group (vide supra). The singlet peak at 3.42 ppm (overlapping the AB system) is assignable to the protons of the coordinated methylene by considering the integrated intensity ratio.

Whereas the remaining **1** maintained the optical activity on the photoreaction of $(+)^{\mathrm{CD}}_{563}$-**1**, complex **2** was obtained as a racemate. Such racemization accompanied with the chiral inversion in the process of the photodecarboxylation reaction has not before been observed for the (aminocarboxylato)cobalt(III) complexes. This racemization reaction can be presumed to be the result of the rapid chiral inversion on the coordinated two chiral thioether S atoms (Scheme 1). As the attempted optical resolution of **2** was unsuccessful using the method of a column chromatographic technique and/or using the optically active anion, further, it is clear that the chiral inversion of S atoms of **2** is rapid even in the acidic solution. Though epimerization of the coordinated chiral thioether S atoms has been previously reported for *p*-$[\mathrm{Co(CH_3S(CH_2)_2NH_2)(tren)}]^{3+}$ [2f,15] and *t*-$[\mathrm{Co(CH_3SCH_2COO)(tren)}]^{2+}$,[5a,11c,15] there is no example such chiral inversion on the tertiary S atoms in the three-membered $-\overline{\mathrm{SCoC}}\mathrm{H_2}$ ring. However, it is difficult to define whether the racemization of **2** occurred during the course of the photoreaction or after that. Further study concerning the process of the rapid epimerization of the other cobalt(III)−sulfide complexes is now in progress.

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles and figures showing UV/vis absorption, CD, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The *t* and *p* nomenclature using the earlier convention for $[\mathrm{Co(aet)(tren)}]^{2+}$ (aet = 2-aminoethanethiolate) in ref 2f.

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