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Photochemistry of Cobalt(III) Complexes. II.

Cobalt(III) Complex with a $\overline{\mathrm{Co{-}C{-}S}}$ Three-Membered Ring Prepared by Photodecarboxylation of 2,2′-Thiodiacetato Complex. Crystal Structure of $(-)^{\mathrm{CD}}_{537}$-*fac-trans*(NH,O)-[Co(CH_2SCH_2COO)(dien)]ClO_4

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The diethylenetriamine (dien) cobalt(III) complex with a $\overline{\mathrm{Co{-}C{-}S}}$ three-membered ring, *fac-trans*-(NH, O)-[Co(CH_2SCH_2COO)(dien)]$^+$ (**1**), has been prepared in an aqueous solution by the photodecarboxylation of *u-fac*- (**2**) or *s-fac*-[Co(2,2′-thiodiacetato)(dien)]$^+$ (**3**). Perchlorate salt of **1** was subject to spontaneous resolution, and the crystal structure and absolute configuration for the $(-)^{\mathrm{CD}}_{537}$ isomer were determined by X-ray diffraction. The crystal is monoclinic, space group $P2_1$, $a=6.962(1)$, $b=13.411(1)$, $c=7.663(1)$ Å, $\beta=101.921(8)°$, $V=700.1(2)$ Å^3, $Z=2$, and $R=0.032$. The formation of the $\overline{\mathrm{Co{-}C{-}S}}$ three-membered ring introduces a significant distortion into the octahedral coordination around the Co atom ($\angle$C–Co–S=49.4(1)°), although the bond lengths in the $\overline{\mathrm{Co{-}C{-}S}}$ ring are within the range normally observed for other complexes. For the $(-)^{\mathrm{CD}}_{537}$ isomer the chiral configuration is regulated to $\Delta\Lambda\Delta$ and R for the sulfur atom. The racemization rate of **1** is very fast in water and DMSO. The position of the first d–d band of **1** is red-shifted by 1600—1100 cm^{-1} relative to those of **2** and **3**. The photolysis of *mer*-[Co(3,3′-thiodipropionato)(dien)]$^+$ did not give a similar product to **1**.

During the last decade many cobalt(III) complexes containing the Co–C bond were prepared by the photodecarboxylation reaction of the (amino carboxylato)cobalt(III) complexes.[1)] We have also reported on the preparation and stereochemistry of optically active cobalt(III) complexes with a Co–C bond.[2—6)] Recently, it was also reported that some amino sulfide complexes of cobalt(III) exhibit an interesting behavior: The Co–S bond reversibly transforms to the Co–C bond upon the addition of a base.[7—9)] However, few papers have been published concerning the photolysis of a complex containing an S–$(CH_2)_n$–COO^- chelate ring.

In this paper the photolysis reactions of *u-fac* (**2**) and *s-fac* (**3**) isomers of [Co(2,2′-thiodiacetato)(dien)]$^+$ (2,2′-thiodiacetate, $S(CH_2COO^-)_2$; dien, $NH(CH_2CH_2NH_2)_2$) and the characterization of those products are described. In addition, the photolysis of *mer*-[Co(3,3′-thiodipropionato)(dien)]$^+$ (3,3′-thiodipropionate, $S(CH_2CH_2COO^-)_2$) (**4**) is briefly reported.

Experimental

Preparation of Complexes. *u-fac*- (**2**) and *s-fac*-[Co(2,2′-thiodiacetato)(dien)]$^+$ (**3**): To an aqueous solution (40 cm^3) containing $CoSO_4{\cdot}7H_2O$ (22.48 g) were added 2, 2′-thiodiacetic acid (12.0 g in 40 cm^3 of water) and diethylenetriamine (8.24 g in 320 cm^3 of water). The pH of the mixed solution was then adjusted to 7.0 with 1 M HCl (M=mol dm^{-3}). After the addition of PbO_2 (40 g), the mixture was stirred at room temperature for 1.5 h. The reaction mixture was filtered in order to remove any insoluble materials. The filtrate was diluted by about 100 times with water, and poured onto an SP-Sephadex C-25 column (4.7 cm×90 cm, K$^+$ form). By development with a 0.1 M K_2SO_4 solution, a reddish band was separated out from the band adsorbed on the top of the column. The reddish band was further separated into two bands, red (**3**) and red-purple (**2**), in the order of elution by recyclic development. The eluates from the two bands were separately desalted and treated with a Dowex 1X8 (Cl^- form) column in order to isolate **2** and **3** as Cl^- salt. These complexes were recrystallized from the water–ethanol system. Found for **2**: C, 25.71; H, 5.60; N, 11.41%. Calcd for $C_8H_{17}ClCoN_3O_4S\cdot1.5H_2O$: C, 25.78; H, 5.40; N, 11.27%. Found for **3**: C, 25.09; H, 5.24; N, 10.81%. Calcd for $C_8H_{17}ClCoN_3O_4S\cdot2H_2O$: C, 25.17; H, 5.54; N, 11.00%.

The racemate of **2** was resolved into optically active isomers by such a chromatographic method, as described in our previous paper.[10)] CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/$mol^{-1}\,dm^3\,cm^{-1}$): 18.4 (+2.17), 20.8 (−1.07), 24.7 (+0.22), 28.3 (+0.30), 34.7 (−3.17), 41.9 (−7.57), 47.9 (+7.81).

***mer*-[Co(3,3′-thiodipropionato)(dien)]$^+$ (4):** This complex was prepared according to a method described in the literature.[11)] Found: C, 29.94; H, 6.29; N, 10.66%. Calcd for $C_{10}H_{21}ClCoN_3O_4S\cdot1.5H_2O$: C, 29.97; H, 6.03; N, 10.48%.

Photolysis and Isolation of Products. An aqueous solution containing 0.3 g of **2** chloride in 300 cm^3 of water was irradiated with a 400-W high-pressure mercury lamp (internal irradiating type) at ca. 5 °C for 5 min with bubbling N_2 gas through the solution. The resulting solution was chromatographed on an SP-Sephadex C-25 column (2.7 cm×60 cm, Na^+ form) using 0.2 M NaCl as an eluent. The band adsorbed on the column was separated into two bands by a recyclic development: purple (photolysis product, **1**) and red-purple (starting material) bands in the order of elution. After the eluate from the purple band was concentrated, it was then desalted by adding a methanol–ethanol mixture. The purple complex (Cl^- salt) was deposited as a crystalline powder from the desalted solution upon the addition of ethanol. The ClO_4^- salt of the purple complex (**1**), which was converted from Cl^- salt using a Dowex 1X8 column (ClO_4^- form), was crystallized from its concentrated aqueous solution upon standing in a refrigerator for a few days. The crystals, which were spontaneously resolved, were used for absorption, CD, and X-ray diffraction measurements. Found: C, 23.01; H, 4.80; N, 11.42%. Calcd for $[Co(CH_2SCH_2COO)(dien)]ClO_4=C_7H_{17}ClCoN_3O_6S$: C, 22.99; H, 4.68; N, 11.49%.

The photolysis of **3** was also performed under the same conditions as those described above. In this case, the starting material disappeared upon irradiation of a mercury lamp for 5 min; only a purple band of the photolysis product (**1**) was eluted out in the chromatographic separation.

Measurements. The absorption and CD spectra were measured by a JASCO UVIDEC-670 spectrophotometer and a JASCO J-720 spectropolarimeter, respectively. The ^{13}C NMR spectra were recorded on a Hitachi R-90H spectrometer in a D_2O solution relative to the internal reference of dioxane (67.4 ppm).

Crystallography. X-Ray Data Collection. A single crystal (ca. 0.15×0.18×0.30 mm^3) of $(-)^{CD}_{537}$-$[Co(CH_2SCH_2COO)(dien)]ClO_4$ was used for data collection on an Enraf Nonius CAD4 diffractometer with graphite-monochromatized Mo *Kα* (0.71073 Å) radiation. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $16° < 2\theta < 20°$.

Crystal Data: $C_7H_{17}ClCoN_3O_6S$, F. W. = 365.68, Monoclinic, space group $P2_1$(No.4), $a=6.962(1)$, $b=13.411(1)$, $c=7.663(1)$ Å, $\beta=101.921(8)°$, $V=700.1(2)$ $Å^3$, $Z=2$, $D_c=1.73$ $g\,cm^{-3}$, $F(000)=376$, $\mu(Mo\,K\alpha)=15.8$ cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan technique up to $2\theta=60°$ with a scan width of $(0.5+0.35\tan\theta)°$; the scan rate varied from 1 to 5 ° min^{-1} (on ω). The intensities were corrected for Lorentz and polarization. Empirical absorption corrections based on a series of ψ scans were applied (max and min transmission factors 0.999 and 0.904). A total of 2057 independent reflections with $F_o > 3\sigma(F_o)$ of the measured 2256 reflections were considered as 'observed' and were used for a structure determination.

Determination of Crystal Structure. The position of cobalt was determined by the heavy-atom method. Successive difference Fourier maps based on the Co atom position revealed the other non-hydrogen atom positions. The hydrogen atoms on the C–H and N–H units were fixed by geometrical and thermal constrains (C–H=N–H=0.95 Å and $B=5$ $Å^2$). The structure was refined by a full-matrix least-squares on F using the anisotropic thermal parameters for non-hydrogen atoms and the isotropic thermal parameters for hydrogen atoms. All of the calculations were performed on a VAX computer using the crystallographic package MOLEN.[12)] When the refinements were carried out using a set of atomic parameters containing the $\Delta\Lambda\Delta$ configuration of the complex cation, the residual values converged to $R=0.032$ and $R_w=0.040$ ($w=4F_o^2/\sigma^2(F_o)^2$). On the contrary, a refinement of the enantiomeric atomic parameters (the $\Lambda\Delta\Lambda$ configuration) resulted in residual values of $R=0.037$ and $R_w=0.044$. These facts indicate that the former is probably the correct choice, namely, the $(-)^{CD}_{537}$ complex cation has the $\Delta\Lambda\Delta$ configuration. The largest parameter shift was 0.02-times esd, and $|\Delta\rho|_{max}$ in the final difference Fourier map was 0.44 $eÅ^{-3}$. The final atomic coordinates for non-hydrogen atoms are given in Table 1.[13)]

Results and Discussion

Structure of $(-)^{CD}_{537}$-*fac*-*trans*(NH, O)-[Co(CH$_2$SCH$_2$COO)(dien)]$^+$ ($(-)^{CD}_{537}$-1). The irradiation of UV-light to *u-fac*- (**2**) and *s-fac*-[Co(tda)(dien)]$^+$ (**3**) gave the same purple complex (**1**), of which perchlorate was spontaneously resolved. A crystal of **1** perchlorate, which was picked up from the bulk, was used for an X-ray structural analysis, and was confirmed to be the $(-)^{CD}_{537}$ isomer. A perspective drawing of the complex cation is shown in Fig. 1, together with its atomic numbering scheme. The bond distances and angles within the complex cation are summarized in Table 2.

The cobalt atom is octahedrally surrounded by three N atoms of the dien ligand and a C atom, an S atom, and an O atom of the tridentate $^-CH_2SCH_2COO^-$ ligand. The two tridentate ligands coordinate to the Co atom in fac form, and the secondary N of the dien and the O of the $^-CH_2SCH_2COO^-$ ligand are situated in trans positions to each other [*fac-trans*(NH,O)]. The $(-)^{CD}_{537}$-isomer of **1** takes the $\Delta\Lambda\Delta$ configuration and the ligating S atom takes the *R* configuration. The discovery of such a complex cation attests to the occurrence of the photodecarboxylation in **2** and **3**.

Complex **1** has a novel three-membered Co–C–S ring. The Co–C(7) bond length (1.961(5) Å) is similar to those found in the photolysis products of the (amino carboxylato)cobalt(III) complexes,[6,14,15] and the bond length of Co–S (2.216(1) Å) is within the range normally observed for the sulfidecobalt(III) complexes.[16—18] The C(7)–S bond length (1.761(5) Å) is somewhat shorter than those (1.8—1.9 Å) in the sulfidecobalt(III) complexes described above. However, such short C–S bond lengths are found in the (2-aminoethyl 3-aminopropyl sulfide)cobalt(III) complexes in which the ligand coordinates to the cobalt through the carbon atom adjacent to the sulfur atom.[7,9]

Table 1. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($B_{\mathrm{eq}}/\text{Å}^2$) [a)]

Atom	x	y	z	B_{eq}
Co	0.74067(7)	0.633	0.34925(6)	1.652(7)
S	0.7557(2)	0.5837(1)	0.6279(1)	2.50(2)
O(1)	1.0188(4)	0.6147(3)	0.3849(4)	2.35(6)
O(2)	1.2992(5)	0.5706(4)	0.5633(5)	3.65(8)
N(1)	0.7109(6)	0.5979(3)	0.0971(5)	2.60(7)
N(2)	0.4599(5)	0.6639(3)	0.2917(5)	2.30(7)
N(3)	0.7793(6)	0.7829(3)	0.3355(5)	2.70(8)
C(1)	0.5049(9)	0.5651(5)	0.0311(7)	3.6(1)
C(2)	0.3760(7)	0.6420(6)	0.1000(6)	3.33(9)
C(3)	0.4337(7)	0.7683(4)	0.3383(7)	3.3(1)
C(4)	0.5856(9)	0.8315(4)	0.2721(8)	3.8(1)
C(5)	1.1204(6)	0.5864(4)	0.5353(6)	2.49(8)
C(6)	1.0195(7)	0.5731(5)	0.6916(6)	3.1(1)
C(7)	0.7045(7)	0.5005(4)	0.4465(6)	2.53(8)
Cl	1.0669(2)	0.3520(1)	0.1327(2)	3.89(3)
O(1c)	1.0733(9)	0.2659(4)	0.0264(8)	7.4(1)
O(2c)	0.959(1)	0.3264(7)	0.2602(9)	12.4(2)
O(3c)	1.005(2)	0.4340(5)	0.0333(9)	13.6(3)
O(4c)	1.242(2)	0.379(1)	0.237(2)	20.9(5)

a) $B_{\mathrm{eq}}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

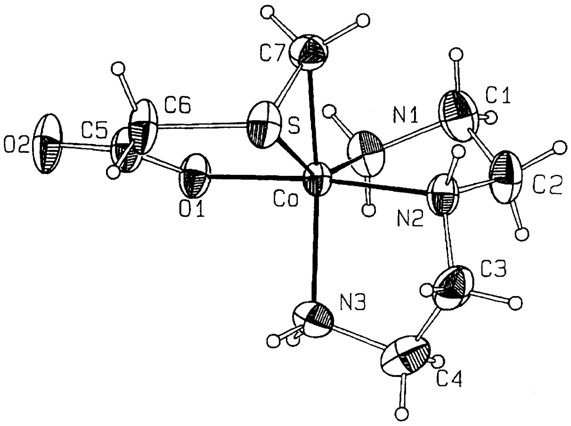

Fig. 1. A perspective drawing of the $(-)^{\mathrm{CD}}_{537}$-*fac-trans*(NH, O)- $[\mathrm{Co(CH_2SCH_2COO)(dien)}]^+$ complex with the atom-numbering scheme.

The photolysis of $[\mathrm{Co(glycinato)(bpy)_2}]^{2+}$ provided a novel complex, $[\mathrm{Co(CH_2NH)(bpy)_2}]^{2+}$, the structure of which was revealed by the X-ray diffraction method.[19] The C–N bond length (1.35 Å) of the $\mathrm{CH_2NH}$ fragment is far shorter than the value which is characteristic of a C–N single bond (1.49 Å), and is close to the value which is typical of a C–N double bond (1.27—1.30 Å). Thus, the complex $[\mathrm{Co(CH_2NH)(bpy)_2}]^{2+}$ is thought to be a η^2-complex of Co(II) with iminomethylene. However, in the case of **1**, the idea of "η^2-bond formation" between Co(II) and $\mathrm{H_2C{=}S}$– may not be anticipated, judging from the bond-length data described above.

The formation of the three-membered Co–C–S ring introduces significant distortions into the octahedral coordination around the Co atom. Since the ∠S–Co–C(7) angle (49.4(1)°) is fairly reduced from the octahedral angle, the ∠S–Co–N(1) (148.7(1)°) and ∠C(7)–Co–N(3) (160.6(2)°) angles differ significantly from 180°. The elongation of the Co–N(3) bond length (2.036(4) Å) can be attributed to a trans influence of the ligating C(7) atom. A similar trans influence has been noted for a number of Co(III) complexes containing Co–C bonds.[6,14,15]

^{13}C NMR Spectrum. Complex **1** exhibited a slight broad peak at 26.45 ppm, which was assigned to the carbon (C(7)) bonded to cobalt by a comparison of the ^{13}C NMR spectra in Fig. 2 and by refer-

Table 2. Selected Bond Distances (Å) and Angles (°) for *fac-trans*(NH,O)-$[\mathrm{Co(CH_2SCH_2COO)(dien)}]^+$

Co–S	2.216(1)	O(2)–C(5)	1.237(5)
Co–O(1)	1.914(3)	N(1)–C(1)	1.485(7)
Co–N(1)	1.957(4)	N(2)–C(2)	1.493(6)
Co–N(2)	1.958(3)	N(2)–C(3)	1.465(7)
Co–N(3)	2.036(4)	N(3)–C(4)	1.486(7)
Co–C(7)	1.961(5)	C(1)–C(2)	1.530(9)
S–C(6)	1.806(5)	C(3)–C(4)	1.521(9)
S–C(7)	1.761(5)	C(5)–C(6)	1.519(7)
O(1)–C(5)	1.280(5)		
S–Co–O(1)	88.9(1)	C(6)–S–C(7)	101.1(2)
S–Co–N(1)	148.7(1)	Co–O(1)–C(5)	121.4(3)
S–Co–N(2)	97.3(1)	Co–N(1)–C(1)	107.8(3)
S–Co–N(3)	111.3(1)	Co–N(2)–C(2)	110.4(3)
S–Co–C(7)	49.4(1)	Co–N(2)–C(3)	108.5(3)
O(1)–Co–N(1)	90.5(1)	C(2)–N(2)–C(3)	112.7(4)
O(1)–Co–N(2)	173.0(2)	Co–N(3)–C(4)	109.2(3)
O(1)–Co–N(3)	89.6(2)	N(1)–C(1)–C(2)	106.1(5)
O(1)–Co–C(7)	92.1(2)	N(2)–C(2)–C(1)	109.5(4)
N(1)–Co–N(2)	86.1(2)	N(2)–C(3)–C(4)	108.7(5)
N(1)–Co–N(3)	100.0(2)	N(3)–C(4)–C(3)	107.0(5)
N(1)–Co–C(7)	99.4(2)	O(1)–C(5)–O(2)	123.8(4)
N(2)–Co–N(3)	85.1(2)	O(1)–C(5)–C(6)	119.0(4)
N(2)–Co–C(7)	94.5(2)	O(2)–C(5)–C(6)	117.1(4)
N(3)–Co–C(7)	160.6(2)	S–C(6)–C(5)	112.8(3)
Co–S–C(6)	97.3(2)	Co–C(7)–S	72.9(2)
Co–S–C(7)	57.7(2)		

ence to the assigned resonances of the complexes with the Co–C bond.[4,6—9,20] The C(7) resonance is found at a relatively low field compared with that of the corresponding carbon in complexes with a Co–C bond formed by photodecarboxylation of amino carboxylato complexes, e.g., −7—−2 ppm for [Co(eedmp, Me$_2$eedmp, or etnmp)(en)]$^+$ [6,21] and −1—8 ppm for [Co(eedmp)(phen)]$^+$.[4,21] This difference in the chemical shift suggests that the Co–C bond in **1** has a more covalent character than that in [Co(eedmp)(en or phen)]$^+$ and its analogs.[20,21] The resonances due to the carbons of the dien ligand in **1** were observed as two overlapping peaks at 42.39 and 53.58 ppm, even though **1** has C_1 symmetry.

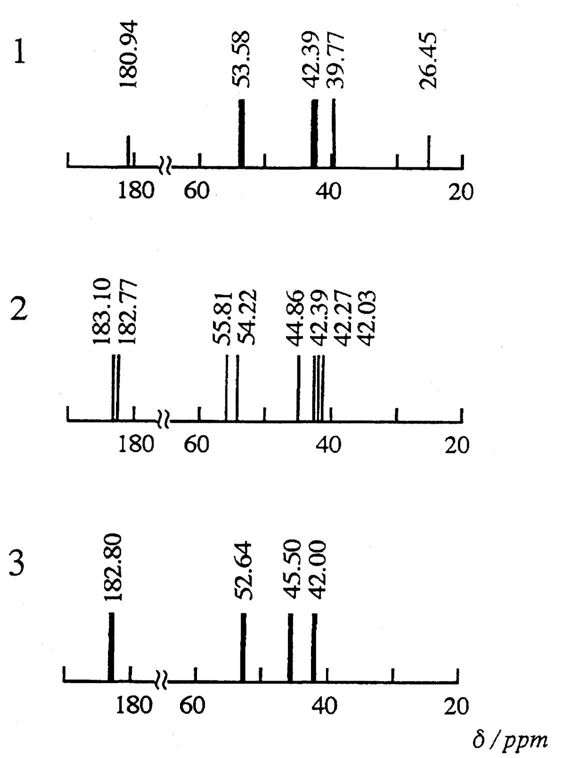

Fig. 2. ^{13}C chemical shift patterns of the complexes: 1, *fac-trans*(NH,O)-[Co(CH$_2$SCH$_2$COO)(dien)]$^+$; 2, *u-fac*-[Co(2,2′-thiodiacetato)(dien)]$^+$; 3, *s-fac*-[Co(2,2′-thiodiacetato)(dien)]$^+$.

Absorption and CD Spectra. The absorption spectrum of **1**, measured in an aqueous solution, is shown in Fig. 3, together with those of **2** and **3**. The numerical data are summarized in Table 3. The position of the first d–d band of **1** is red-shifted by 1100—1600 cm^{-1} relative to those of **2** and **3**. This fact is a lit-

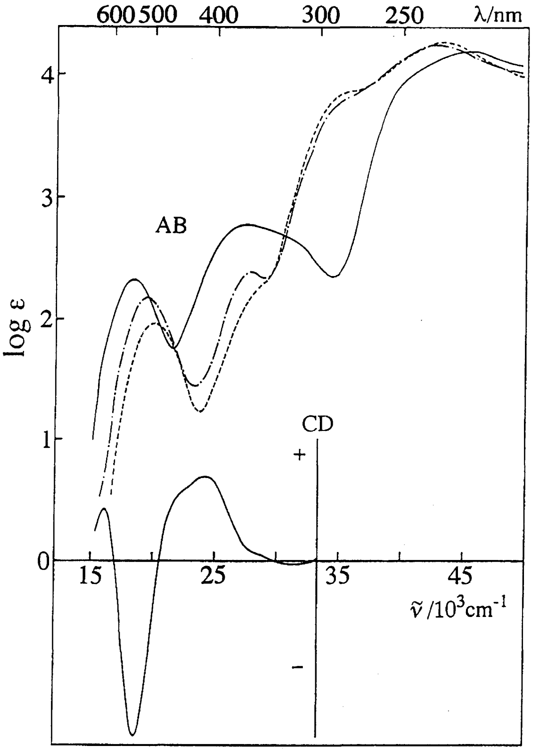

Fig. 3. Absorption (AB) and CD spectra of the complexes: *fac-trans*(NH,O)-[Co(CH$_2$SCH$_2$COO)(dien)]$^+$ (**1**) (——); *u-fac*-[Co(2,2′-thiodiacetato)(dien)]$^+$ (**2**) (–•–); *s-fac*-[Co(2,2′-thiodiacetato)(dien)]$^+$ (**3**) (---). (The CD spectrum was measured in a solid state.)

Table 3. Absorption Spectral Data of the Complexes

Complex ion	Absorption maxima $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})
fac-trans(NH,O)-[Co(CH$_2$SCH$_2$COO)(dien)]$^+$ (**1**)	18.28 (2.33)
	27.47 (2.79)
	ca.31.0 (2.7)sh
	44.84 (4.19)
u-fac-[Co(2,2′-thiodiacetato)(dien)]$^+$ (**2**)	19.34 (2.19)
	27.62 (2.40)
	ca.35.0 (3.8)sh
	42.37 (4.26)
s-fac-[Co(2,2′-thiodiacetato)(dien)]$^+$ (**3**)	19.90 (1.97)
	ca.28.0 (2.2)sh
	ca.35.0 (3.9)sh
	42.91 (4.27)

a) sh denotes a shoulder.

tle abnormal, because the ligand field of the ligating C atom is thought to be stronger than that of the ligating O atom. In complexes with a ligating C atom formed by the photolysis of (amino carboxylato)cobalt(III), such a red-shift was not observed.[4,6] The shoulder bands at ca. 35×10^3 cm^{-1} found in the absorption spectra of **2** and **3** have been assigned to the S(sulfide)-to-cobalt charge-transfer bands.[11] However, **1**, which has nevertheless a Co–S bond, does not exhibit an intense absorption band in this 35×10^3 cm^{-1} region; a weak shoulder band is only observed at ca. 31×10^3 cm^{-1}. The abnormal absorption behaviors in the first d–d band and S(sulfide)-to-cobalt charge-transfer band regions may be correlated for the peculiar structure of the Co–C–S three membered ring, which must be further investigated.

The perchlorate of **1** is spontaneously resolved. The CD spectra of the crystals, which were picked up from the bulk, were measured by the paste method using liquid paraffin. The $\Delta\Lambda\Delta$-isomer of **1** showed a (−)-CD sign at 537 nm (Fig. 3). The absorption spectrum of **1**, measured by the paste method, showed the d–d band maxima at 552 and 363 nm, which agreed closely with those obtained in an aqueous solution (548 and 364 nm). However, neither of the crystals showed any CD in water and DMSO, indicating that racemization took place very rapidly. It was quite natural that optically active **1** could not be obtained in the photolysis reaction of optically active **2**. This racemization is of interest in connection with the coordination-site exchange reaction mechanism proposed for the (amino carboxylato)cobalt(III) complexes.[10,22,23)]

Photolysis of *mer*-[Co(3,3′-thiodipropionato)(dien)]$^+$ (4). The photodecarboxylation of the (amino carboxylato)cobalt(III) complexes with glycinate (five-membered) and β-alaninate (six-membered) rings leads to products having corresponding three- and four-membered chelate rings. These products have the same structure, except for the chelate ring size, and the complex with three-membered chelate ring is thermally unstable in solution due to its high strain.

Irradiation with a mercury lamp on **4**, which has the S–CH_2–CH_2–COO^- six-membered ring, gave an orange-yellow product and some unknown by-products. The orange-yellow complex was thermally unstable, but gradually decomposed during the chromatographic separation. The qualitative absorption spectrum of this complex is quite different from that of **1**; the absorption maxima were observed at 387 (1) and 296 (1.57) nm, where the values in the parentheses designate the relative absorption strength. This observation makes it very unlikely that the orange-yellow complex and **1** have the same structure, only except for the chelate ring size. It is necessary to investigate the photolysis of the complex containing the S–$(CH_2)_n$–COO^- chelate ring in more detail.

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21) Abbreviations used: eedmp, $^-CH_2CH_2NHCH_2CH_2NHCH_2CH_2COO^-$; Me$_2$eedmp, $^-CH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2COO^-$; etnmp, $^-CH_2CH_2NHCH_2$-

$CH_2CH_2NHCH_2CH_2COO^-$; eddp, $(-CH_2NHCH_2CH_2COO^-)_2$.

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