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Photochemistry of Cobalt(III) Complexes Containing a Sulfinate-*S* Ligand. Linkage and Geometrical Isomerization

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Photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$ (**1**, *t*-N = tertiary amine nitrogen; tren = tris(2-aminoethyl)amine) with visible light yielded two complexes, orange and red. The molecular structure of the orange complex perchlorate was determined by the X-ray method to be *cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]ClO$_4$·H$_2$O (**2**, O(S) = oxygen of sulfinate group); geometrical isomerization as well as linkage isomerization took place upon photolysis. A mechanism for the geometrical isomerization was proposed. The red complex, which was assigned as *trans*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]$^+$ (**3**), is thermally unstable and reverts to the starting complex. This observation is in accord with molecular mechanics calculations, which estimate the starting complex to be more stable. The kinetic studies were performed using the HPLC method in the temperature range 28—70 °C, giving $\Delta H^\ddagger = 100$ kJ mol^{-1} and $\Delta S^\ddagger = -23$ J K^{-1} mol^{-1}. Photolysis of a cobalt(III) complex containing the L-cysteinesulfinate-*S,N* ligand, *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(tren)]$^{2+}$ (**4**) with visible light provided two types of linkage isomers, *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2{}^-$)COO-*N,O*}(tren)]$^+$ (**4b**, O(C) = oxygen of carboxylate group) with an uncoordinated sulfinate group, and a pair of diastereomers of *cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O,N*}(tren)]$^{2+}$ (**4a**). The molecular structures of the perchlorate of **4b** and the bromide of **4a** with the (*S*)-sulfur atom have been determined by X-ray diffraction. Isomerization (epimerization) from **4a-*R*** to **4a-*S*** was studied in the temperature range 55—75 °C, giving $\Delta H^\ddagger = 105$ kJ mol^{-1} and $\Delta S^\ddagger = -20$ J K^{-1} mol^{-1}. Photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(tren)]$^{2+}$ (**5**) yielded six products. Three of them were the same as those obtained by the photolysis of **4**, indicating that geometrical isomerization took place.

Photochemistry has been used for the synthesis of thermodynamically unstable compounds. Adamson and coworkers[1—3] reported that irradiation of a cobalt(III) complex containing an *S*-bonded sulfinate ligand yielded a sulfinato-*O* complex, and that the linkage isomerized sulfinato-*O* complex thermally reverts to the starting complex. Recently, we reported the preliminary results of our investigation of the photochemistry of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$, where not only the sulfinato-*S*-to-sulfinato-*O* linkage isomerization but also the trans-to-cis geometrical isomerization took place to yield *trans*(*t*-N,O(S))- and *cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]$^+$.[4] This result led us to study the photochemistry of the related cobalt(III) complex with the L-cysteinesulfinate-*N,S* ligand, since the present ligand contains four kinds of potential donor atoms (nitrogen, sulfur, sulfinate oxygen, and carboxylate oxygen), and many kinds of photoisomerizations can be expected (Fig. 1).

This paper deals with the novel photoisomerization of cobalt(III)-sulfinato-*S* complexes and the mechanism of the reaction. A part of this study has already been briefly reported.[4,5]

Experimental

Preparation of *cis*(*t*-N,S)- and *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(tren)](ClO$_4$)$_2$·H$_2$O (4, 5). These complexes were prepared by oxidizing the corresponding isomers of the L-cysteinato-*S,N* complex with H$_2$O$_2$, using the same method as for [Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S,N*}(en)$_2$]$^{2+}$.[6] Yield: 30%. Found for the *cis*(*t*-N,S)isomer (**4**): C, 18.89; H, 4.56; N, 12.05; S, 5.88%. Found for the *trans*(*t*-N,S)isomer (**5**): C, 19.02; H, 4.74; N, 11.86; S, 5.98%. Calcd for C$_9$H$_{26}$Cl$_2$CoN$_5$O$_{13}$S: C, 18.82; H, 4.57; N, 12.19; S, 5.58%.

Photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]ClO$_4$ (1) and Isolation of the Products. An aqueous solution (200 cm^3) of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]ClO$_4$[7] (**1**, 0.10 g) was irradiated at ca. 5 °C for 25 min with a 400 W high-pressure mercury lamp (internal irradiation type) equipped with a Pyrex glass filter. The reaction mixture was passed through an SE-Toyopearl[8] column (ϕ3.0 cm×70 cm). A recycling chromatographic technique was employed at 4 °C with an eluent of 0.05 M sodium (+)-tartrate (1 M = 1 mol dm^{-3}). After ten recyclings, two bands, red and orange, were separately eluted in this order. The abundance of the red band relative to that of the orange band was ca. 1 : 1. The eluate containing the orange band

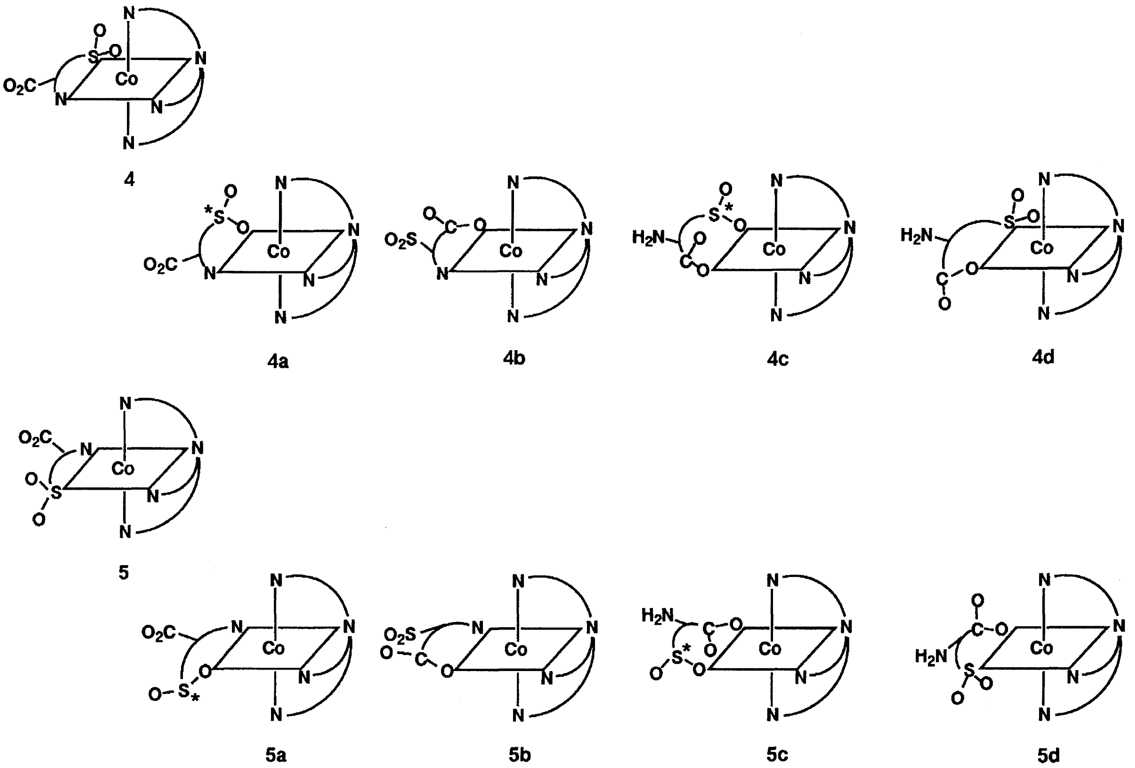


Fig. 1. Possible isomers of $[Co(L\text{-cysteinesulfinate})(tren)]^+$.

was collected and evaporated to a small volume. Methanol was added to the concentrate, and sodium (+)-tartrate, which precipitated, was filtered out. To the filtrate, sodium perchlorate was added to yield the orange crystals (**2**). They were collected by filtration and recrystallized from water. Found: C, 21.66; H, 5.03; N, 12.57%. Calcd for $C_8H_{22}ClCoN_4O_9S$=$[Co\{OS(O)CH_2COO\text{-}O,O\}(tren)]ClO_4 \cdot H_2O$: C, 21.61; H, 4.99; N, 12.60%.

The red complex (**3**) was also isolated as the perchlorate. Found: C, 21.69; H, 4.69; N, 13.00; S, 7.55%. Calcd for $C_8H_{22}ClCoN_4O_9S$=$[Co\{OS(O)CH_2COO\text{-}O,O\}(tren)]ClO_4 \cdot H_2O$ (**3**): C, 21.61; H, 4.99; N, 12.60; S, 7.21%. However, this isolated complex involved the starting complex (ca. 10%) as determined by the high-performance liquid chromatographic (HPLC) method, since the complex thermally reverts to the starting sulfinato-*S* complex (vide infra). Thus, the eluate containing the red band was used for the measurements.

Photolysis of *cis*(*t*-N,S)- and *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2CH(COOH)NH_2\text{-}S,N\}(tren)]^{2+}$ (4, 5) and Isolation of the Products. The photolysis of the cis complex was carried out in two ways, (i) and (ii): (i) *cis*(*t*-N,S)-$[Co\{S(O)_2CH_2CH(COOH)NH_2\text{-}S,N\}(tren)](ClO_4)_2 \cdot H_2O$ (**4**, 0.30 g) in 500 cm^3 of water was placed in a 500 cm^3 reaction vessel, the pH of the solution being ca. 4. The solution was irradiated with visible light for 90 min by the same method as for *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)](ClO_4)$ (**1**). Isosbestic points were observed only in the beginning (ca. 20 min). The irradiated solution was neutralized with an aqueous solution of Na_2CO_3 and then passed through an SP-Sephadex C-25 column (ϕ5 cm×80 cm). After three recyclings at 5 °C with an eluent of 0.1 M Na_2SO_4, two yellow bands (yellow-1 and yellow-2) and three red bands (red-1, red-2, and red-3′) were separately eluted in this order. The formation ratio, yellow-1 : yellow-2 : red-1 : red-2 : red-3′ was about 3 : 3 : 3 : 10 : 1. The yellow-2 complex was the unreacted starting complex, and the red-3′ complex, which was eluted very slowly, seemed to be a highly charged species.

(ii) The cis complex perchlorate (**4**, 0.12 g) in 200 cm^3 of water was also placed in a 500 cm^3 reaction vessel. The solution filled only one-fourth of the vessel from the bottom when the lamp was immersed in the solution, and thus the solution was remote from the light source. The rest of the procedure was the same as for (i). Isosbestic points were retained throughout the reaction. The column showed four bands, yellow-1, yellow-2, red-1, and red-2 in the ratio of 1 : 1 : 2 : 2.

Photolysis of *trans*(*t*- N, S)- $[Co\{S(O)_2CH_2CH(COOH)NH_2\text{-}S,N\}(tren)](ClO_4)_2 \cdot H_2O$ (**5**) was done by the same methods, (i) and (ii), as for the cis complex.

(i) Column chromatography of the irradiated solution developed six bands: yellow-1, yellow-2′, red-1, red-2, yellow-3, and red-3′. The formation ratio of yellow-1 : red-1 : red-2 : yellow-3 was 3 : 3 : 9 : 2. Here, the yellow-3 complex was the unreacted starting complex.

(ii) The column showed six bands: yellow-1, yellow-2′, red-1, red-2, yellow-3, and red-3 in the ratio of 5 : 1 : 5 : 5 : 7 : 5.

The eluate containing the yellow-1 band was evaporated to a small volume using a rotary evaporator. Methanol was added to precipitate Na_2SO_4, and after filtration the filtrate was again evaporated using a rotary evaporator. $NaClO_4$ was added to the concentrate and then acetone was added to give a yellow gummy precipitate. This was dissolved in water and passed through a small SP-Sephadex column. The adsorbed complex was eluted with 1 M $NaClO_4$. The eluate containing the yellow band was collected and evaporated in a desiccator over P_2O_5 to form orange crystals (**4b**). Found: C, 18.49; H, 4.05; N, 11.94; S, 5.58%. Calcd for $C_9H_{23}Cl_2CoN_5NaO_{12}S$=$[Co\{NH_2CH(CH_2SO_2^-)COO\}(tren)]ClO_4 \cdot NaClO_4$: C, 18.69; H, 4.02; N, 12.11; S, 5.54%.

The red-1 and red-2 complexes were isolated as bromides. The complexes were first precipitated as the tetraphenylborates, and then converted to the bromides using the anion exchanger Dowex 1 X 8 (Br^- form). Found for the red-1 complex (**4a-*R***): C, 20.93; H, 4.73; N, 13.55; S, 6.31%. Found for the red-2 complex (**4a-*S***): C, 20.70; H, 4.68; N, 13.51; S, 6.18%. Calcd for $C_9H_{24}Br_2CoN_5O_4S$=[Co{OS(O)CH_2CH(COOH)NH_2}(tren)]-Br_2: C, 20.90; H, 4.68; N, 13.54; S, 6.20%. The red-1 complex was contaminated with the red-2 complex as evidenced by the CD spectrum, since the red-1 isomer is thermally unstable and isomerizes to the red-2 complex. The eluate containing the red-1 band was used for the measurements.

The red-3 complex could not be isolated because of its thermal instability. We could not characterize the yellow-2′ and red-3′ complexes.

Spectroscopic Measurements. UV-vis and circular dichroism (CD) spectra were recorded on a JASCO Ubest-30 spectrophotometer and a JASCO J-720 spectropolarimeter, respectively. Infrared (IR) spectra were measured as KBr pellets using a JASCO IR-810 spectrophotometer.

Thermal Kinetics. Kinetics of linkage isomerization from *trans*(*t*-N, O(S))-[Co{OS(O)CH_2COO-*O*,*O*}(tren)]$^+$ (**3**, the red complex) to *trans*(*t*-N,S)-[Co{S(O)$_2$$CH_2$COO-*S*,*O*}(tren)]$^+$ (**1**, the starting complex) were studied in 0.05 M sodium (+)-tartrate using the HPLC method[9] in the temperature range 28—70 °C. Portions of the reaction mixture were withdrawn at timed intervals and chromatographed using a column (ϕ0.46 cm × 150 cm) of JASCO CrestPak C18S and 0.05 M sodium heptanesulfonate in acetonitrile–water (8 : 92 v/v) as the eluent. The complexes were detected at 325 nm.

The rate of isomerization (epimerization) from (*R*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH_2CH(COOH)NH_2-*O*,*N*}(tren)]$^{2+}$ (**4a-*R***, the red-1 complex) to (*S*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH_2CH(COOH)NH_2-*O*,*N*}(tren)]$^{2+}$ (**4a-*S***, the red-2 complex) was studied in 0.1 M Na_2SO_4 by following the CD strength change at 542 nm in the temperature range 55—75 °C. Isodichroic points were observed throughout the reaction.

Kinetic studies of linkage isomerization from *trans*(*t*-N,O(S))-[Co{OS(O)CH_2CH(COO^-)NH_2-*O*,*N*}(tren)]$^+$ (**5a**, the red-3 complex) to the starting complex, *trans*(*t*-N,S)-[Co{S(O)$_2$$CH_2$CH-($COO^-$)$NH_2$-*S*,*N*}(tren)]$^+$ (**5**) were performed in 0.1 M Na_2SO_4 by observing the absorbance change at 300 nm in the temperature range 25—58 °C.

X-Ray Structure Determination. Each crystal of *cis*(*t*-N,O(S))-[Co{OS(O)CH_2COO-*O*,*O*}(tren)]ClO_4·H_2O (**2**, the orange complex), *cis*(*t*-N, O(C))-[Co{NH_2CH($CH_2SO_2^-$)COO-*N*,*O*}(tren)]ClO_4·$NaClO_4$ (**4b**, the yellow-1 complex), or *cis*(*t*-N, O(S))-[Co{OS(O)CH_2CH(COOH)NH_2-*O*,*N*}(tren)]Br_2 (**4a-*S***, the red-2 complex) was mounted on a glass fiber. The unit cell dimensions were determined using 25 reflections in the 2θ range 22 and 23°. Diffraction measurements were made using a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ = 0.71073 Å) at the X-Ray Laboratory of Okayama University. The intensities of three standard reflections were monitored every 97 reflections; in all cases no significant variations were found. The structures were solved by a direct method and refined by a full-matrix least squares procedure. The calculations were performed using TEXSAN.[10] Crystal data and experimental details are listed in Table 1, and the atomic parameters of the non-hydrogen atoms are found in Table 2. The tables of the atomic coordinates for hydrogen atoms, equivalent isotropic temperature factors for hydrogen atoms, the anisotropic temperature factors for non-hydrogen atoms, intermolecular distances involving the non-hydrogen atoms, and the observed and calculated structure factors are deposited as Document No. 69010 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Molecular Mechanics Calculations. Strain-energy minimization calculations were carried out for some isomers with a modified MM2 computer program[11,12] in order to obtain their relative strain energy and to estimate the stable structure between the isomers. The parameters for the present force fields were mainly adopted from those of MM2 (1985), MM2 and MMP2 (1986), and the literature.[13] The electrostatic interactions were not considered for these calculations.

Results and Discussion

Photochemistry of *trans*(*t*-N,S)-[Co{S(O)$_2$$CH_2$COO-*S*,*O*}(tren)]$^+$ (1). From the photolysis of *trans*(*t*-N, S)-[Co{S(O)$_2$$CH_2$COO-*S*,*O*}(tren)]$^+$ (**1**) with visible light, two products, the orange and the red complexes, were obtained (Scheme 1). The orange complex was assigned to be a linkage isomerized sulfinato-*O* complex on the basis of the UV-vis and IR spectra, and the characterization details have been reported.[4] This assignment was confirmed by the X-ray structure determination. Figure 2 shows a perspective view of the orange complex perchlorate, *cis*(*t*-N,O-(S))-[Co{OS(O)CH_2COO-*O*,*O*}(tren)]ClO_4·H_2O (**2**). Bond lengths and angles are listed in Table 3. The coordination geometry around the cobalt atom is approximately octahedral. The 2-sulfinatoacetate ligand coordinates to cobalt with the two oxygen atoms instead of the sulfur and oxygen atoms in the starting complex, *trans*(*t*-N,S)-[Co{S(O)$_2$$CH_2$COO-*S*,*O*}(tren)]$ClO_4$ (**1**). The number of chelate-ring members increases from five to six upon linkage isomerization from sulfinato-*S* to sulfinato-*O*. The orange complex has the *cis*(*t*-N,O(S)) structure; geometrical

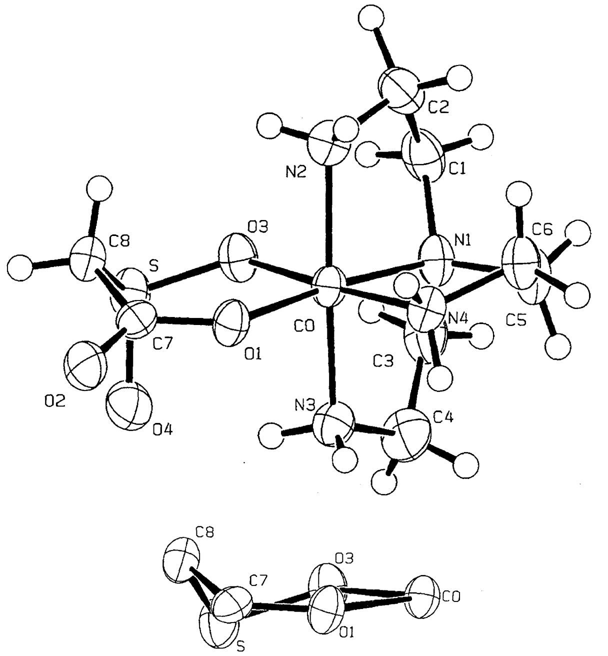
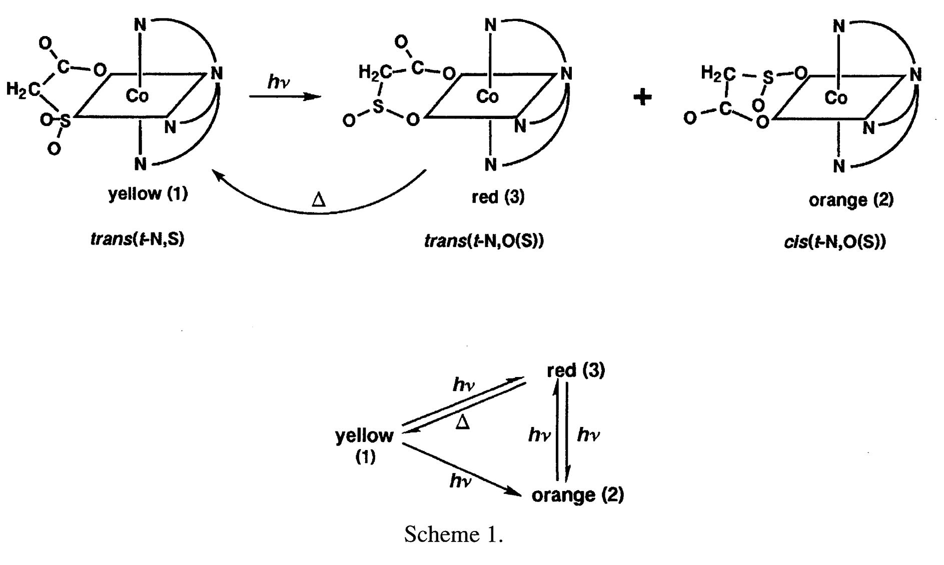


Fig. 2. ORTEP drawing of the orange complex cation, *cis*(*t*-N,O(S))-[Co{OS(O)CH_2COO-*O*,*O*}(tren)]$^+$ (**2**) and edge-on view of the six-membered *O*,*O*-chelate ring.

Table 1. Crystal Data and Experimental Details

	Orange (**2**)	Yellow-1 (**4b**)	Red-2 (**4a**-*S*)
Chemical formula	$C_8H_{22}ClCoN_4O_9S$	$C_9H_{23}Cl_2CoN_5NaO_{12}S$	$C_9H_{24}Br_2CoN_5O_4S$
Formula weight	444.73	578.20	517.12
Crystal color	Orange red	Yellow orange	Red
Crystal habits	Prismatic	Prismatic	Prismatic
Crystal size/mm	0.25 × 0.23 × 0.35	0.23 × 0.23 × 0.43	0.50 × 0.45 × 0.50
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$C2/c$	$P1$	$P2_12_12_1$
a/Å	23.316(4)	8.801(3)	11.386(8)
b/Å	8.005(1)	8.894(7)	16.81(1)
c/Å	18.631(4)	6.781(2)	9.189(7)
$\alpha/°$		92.26(4)	
$\beta/°$	108.03(1)	91.30(3)	
$\gamma/°$		70.50(4)	
$V/Å^3$	3307(2)	500.0(8)	1759(2)
Z	8	1	4
$D_x/\mathrm{Mg\,m^{-3}}$	1.786	1.920	1.953
$F(000)$	1840	296	1032
$\mu(\mathrm{Mo}K\alpha)/\mathrm{mm^{-1}}$	1.369	1.315	5.61
T/K	298	295	295
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan width in $\omega/°$	$1.05+0.30\tan\theta$	$1.57+0.30\tan\theta$	$1.15+0.30\tan\theta$
Scan speed in $\omega/°\mathrm{min^{-1}}$	6	6	6
$2\theta_{\max}/°$	55.0	55.1	55.0
Range of h, k, l	$-29 \le h \le 28$	$-11 \le h \le 11$	$0 \le h \le 14$
	$0 \le k \le 10$	$-11 \le k \le 11$	$0 \le k \le 21$
	$0 \le l \le 24$	$0 \le l \le 8$	$-1 \le l \le 11$
R_{int}	0.015	0.023	0.016
No. of reflections used	2503	2199	2200
	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$
No. of parameters	306	369	296
$R^{a)}/R_w^{b)}$	0.035/0.026	0.020/0.021	0.027/0.022
$S^{c)}$	1.77	2.09	2.10
$(\Delta/\delta)_{\max}$	0.13	0.02	0.35
$\Delta\varrho_{\max}/\mathrm{e\,Å^{-3}}$	0.31	0.35	0.73
$\Delta\varrho_{\min}/\mathrm{e\,Å^{-3}}$	−0.27	−0.20	−0.40

a) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}$. c) $S=[(\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$.



Scheme 1.

Table 2. Fractional Atomic Coordinates and Equivalent Thermal Parameters B_{eq} with Their esd's in Parentheses

Atom	*x*	*y*	*z*	$B_{eq}{}^{a)}/\text{Å}^2$
2 (orange)				
Co	0.60554(2)	0.08878(5)	0.10154(2)	2.21(2)
Cl	0.83187(4)	0.1163(1)	0.12677(5)	3.78(4)
S	0.68009(4)	−0.2063(1)	0.07069(5)	3.16(4)
O1	0.57584(8)	0.0431(2)	−0.0049(1)	2.61(8)
O2	0.56632(9)	−0.0896(3)	−0.1111(1)	3.6(1)
O3	0.67339(8)	−0.0614(3)	0.1223(1)	2.79(9)
O4	0.6281(1)	−0.3239(3)	0.0598(1)	3.9(1)
O5	0.8201(1)	0.1027(4)	0.1976(1)	5.9(1)
O6	0.8916(1)	0.1715(4)	0.1401(2)	7.9(2)
O7	0.7923(2)	0.2365(5)	0.0840(2)	9.1(2)
O8	0.8237(2)	−0.0371(4)	0.0898(2)	9.6(2)
O9	0.9467(1)	0.0530(4)	0.0346(2)	4.4(1)
N1	0.6264(1)	0.1380(3)	0.2082(1)	2.8(1)
N2	0.6625(1)	0.2664(4)	0.0968(2)	2.9(1)
N3	0.5570(1)	−0.0946(4)	0.1201(1)	2.9(1)
N4	0.5406(1)	0.2477(4)	0.0875(2)	2.6(1)
C1	0.6893(2)	0.2069(5)	0.2305(2)	3.5(2)
C2	0.6938(2)	0.3339(5)	0.1733(2)	3.4(2)
C3	0.6226(2)	−0.0245(5)	0.2457(2)	3.6(2)
C4	0.5649(2)	−0.1102(6)	0.2020(2)	4.0(2)
C5	0.5822(2)	0.2600(5)	0.2224(2)	3.5(2)
C6	0.5527(2)	0.3623(5)	0.1526(2)	3.3(2)
C7	0.5976(1)	−0.0453(4)	−0.0479(2)	2.6(1)
C8	0.6630(1)	−0.0989(5)	−0.0191(2)	2.9(1)
4b (yellow-1)				
Co	0.5892	0.5152	1.0027	1.46(2)
Cl1	0.9247(1)	0.6766(1)	0.4504(1)	2.29(4)
Cl2	0.3384(1)	0.1362(1)	0.4132(1)	2.82(5)
S	0.8534(1)	0.0038(1)	0.9257(1)	2.30(4)
Na	0.7333(2)	0.0510(2)	0.4458(2)	2.79(7)
O1	0.6284(3)	0.4609(3)	0.7306(3)	1.8(1)
O2	0.7941(3)	0.2938(3)	0.5179(3)	2.4(1)
O3	0.7141(3)	0.0679(3)	0.7838(3)	2.4(1)
O4	0.7966(3)	0.0660(3)	1.1299(3)	3.1(1)
O5	0.9358(4)	0.5891(4)	0.6225(5)	4.9(2)
O6	0.9850(4)	0.5758(4)	0.2807(5)	5.3(2)
O7	0.7559(3)	0.7630(4)	0.4126(5)	4.9(2)
O8	1.0052(3)	0.7909(3)	0.4793(4)	3.0(1)
O9	0.2505(4)	0.1546(4)	0.2314(5)	5.5(2)
O10	0.4401(4)	0.2332(4)	0.4170(5)	4.9(2)
O11	0.2400(5)	0.1747(6)	0.5799(6)	7.4(3)
O12	0.4394(5)	−0.0251(4)	0.4245(5)	6.5(2)
N1	0.3733(3)	0.6593(3)	0.9450(4)	1.8(1)
N2	0.4893(4)	0.3469(4)	1.0061(5)	2.0(2)
N3	0.6648(4)	0.6964(4)	0.9624(5)	2.2(2)
N4	0.5419(4)	0.5723(4)	1.2797(4)	2.1(2)
N5	0.8067(3)	0.3685(4)	1.0482(4)	2.0(1)
C1	0.2894(4)	0.5610(4)	0.8327(5)	2.4(2)
C2	0.3170(4)	0.4097(4)	0.9434(5)	2.4(2)
C3	0.3949(4)	0.7871(4)	0.8256(5)	2.3(2)
C4	0.5235(5)	0.8421(4)	0.9211(6)	2.7(2)
C5	0.2870(4)	0.7290(5)	1.1337(5)	2.3(2)
C6	0.3640(4)	0.6285(4)	1.3065(5)	2.4(2)
C7	0.7630(4)	0.3492(3)	0.6864(4)	1.8(1)
C8	0.8857(4)	0.3013(4)	0.8560(5)	2.1(2)
C9	0.9771(4)	0.1227(4)	0.8627(5)	2.4(2)
4a-*S* (red-2)				
Br1	−0.24647(5)	0.15405(3)	0.32801(6)	3.04(2)
Br2	−0.09643(4)	0.50979(3)	−0.29859(6)	2.52(2)
Co	−0.05121(5)	0.38099(4)	0.09004(7)	1.39(2)
S	0.0523(1)	0.20728(7)	0.0611(1)	1.91(5)
O1	−0.1086(4)	0.1993(3)	−0.3820(4)	3.7(2)
O2	−0.2477(3)	0.2855(2)	−0.3184(4)	2.8(2)
O3	−0.0146(3)	0.2802(2)	0.1474(4)	2.1(1)
O4	0.1560(3)	0.2289(2)	−0.0309(4)	2.7(2)
N1	0.0283(3)	0.4291(2)	0.2570(4)	1.8(2)
N2	0.0908(4)	0.4079(3)	−0.0224(5)	2.2(2)
N3	−0.1755(4)	0.3497(3)	0.2254(5)	2.0(2)
N4	−0.1218(4)	0.4848(3)	0.0590(5)	2.0(2)
N5	−0.1313(3)	0.3384(2)	−0.0834(5)	1.8(2)
C1	0.1555(5)	0.4196(4)	0.2280(7)	2.9(3)
C2	0.1789(5)	0.4451(4)	0.0745(7)	2.7(3)
C3	−0.0138(5)	0.3836(4)	0.3871(6)	2.8(2)
C4	−0.1464(5)	0.3757(4)	0.3748(6)	2.7(2)
C5	−0.0043(5)	0.5159(3)	0.2713(6)	2.5(2)
C6	−0.0510(5)	0.5483(3)	0.1310(6)	2.6(2)
C7	−0.1567(4)	0.2533(3)	−0.2969(6)	2.1(2)
C8	−0.0777(4)	0.2715(3)	−0.1670(5)	1.7(2)
C9	−0.0642(5)	0.1987(3)	−0.0718(6)	2.1(2)

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

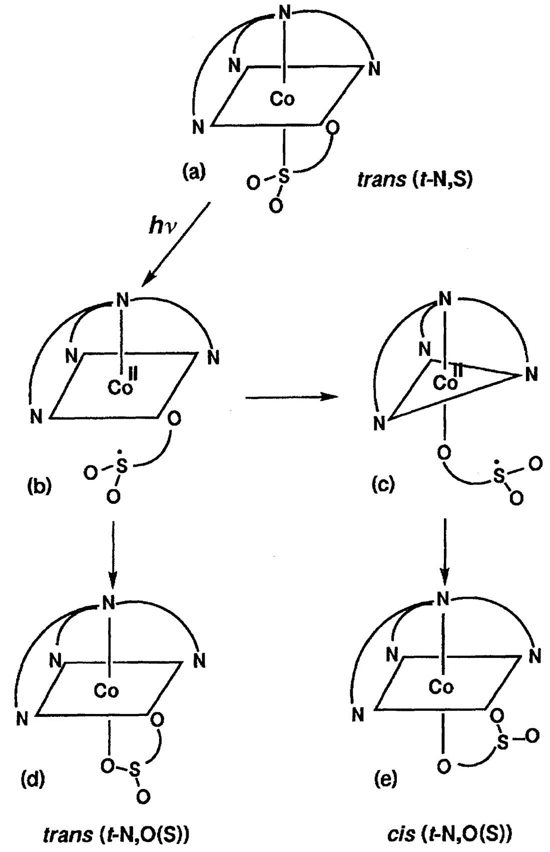
isomerization as well as linkage isomerization took place upon photolysis. The overall structure of the tren moiety is very similar to those of the related cobalt(III)-tren complexes.[14,15] The sulfur–oxygen bonds, S–O3 (1.545(2) Å) and S–O4 (1.499(2) Å), are longer than those in the *S*-bonded $[\mathrm{Co\{S(O)_2CH_2CH_2NH_2}$-*S*,*N*$\}(\mathrm{en})_2](\mathrm{ClO_4})\mathrm{NO_3}$ complex[6] (1.456(4) and 1.476(4) Å), and are comparable to those in the *O*-bonded *cis*(*t*-N,O)-$[\mathrm{Co\{OS(O)CH_2CH_2NH_2}$-*O*,*N*$\}(\mathrm{tren})](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ complex[15] (1.540(3) and 1.496(4) Å). The cobalt–sulfinate oxygen bond length, Co–O3 (1.928(2) Å), is also very close to that (1.925(3) Å) in *cis*(*t*-N,O)-$[\mathrm{Co\{OS(O)CH_2CH_2NH_2}$-*O*,*N*$\}(\mathrm{tren})]^{2+}$.[15] The geometry about the carboxylate group of the present orange complex is similar to that of *cis*(*t*-N,O)-$[\mathrm{Co(NH_2CH_2COO}$-*N*,*O*$)(\mathrm{tren})]^{2+}$;[14] the Co–O1 (1.923(2) Å), O1–C7 (1.284(3) Å), and O2–C7 (1.231(3) Å) bond lengths are comparable with those (1.915(2), 1.288(4), and 1.239(4) Å, respectively) in the latter complex. The conformation of the six-membered chelate ring can be described as a half-chair (Fig. 2). The bond angle of O1–Co–O3 (95.71 (8)°) is slightly larger than the N–Co–O angle (94.2(1)°) for the six-membered chelate ring in *cis*(*t*-N,O)-$[\mathrm{Co\{OS(O)CH_2CH_2NH_2}$-*O*,*N*$\}(\mathrm{tren})]^{2+}$.[15] The bond angles around the sulfur atom are 100.5(1)–108.8(1)°. These values are reasonable for the sulfur atom whose tetrahedral positions are occupied by three bonding pairs and a lone pair. The *O*-bonded sulfinate ligand does not exert a trans influence. This is in marked contrast to the large trans influence (0.049(5) Å) associated with the *S*-bonded sulfinate ligand in $[\mathrm{Co\{S(O)_2CH_2CH_2NH_2}$-*S*,*N*$\}(\mathrm{en})_2]^{2+}$.[6]

The mechanism for geometrical isomerization is worth dis-

Table 3. Bond Lengths (l/Å) and Bond Angles (ϕ/°) of *cis*(*t*- N, O(S))- [Co{OS(O)CH$_2$COO- *O*,*O*}(tren)]-ClO$_4$·H$_2$O (**2**, the Orange Complex)

Atom	Atom	Bond length	Atom	Atom	Bond length
Co	O1	1.923(2)	O1	C7	1.284(3)
Co	O3	1.928(2)	O2	C7	1.231(3)
Co	N1	1.936(2)	N1	C1	1.501(4)
Co	N2	1.966(3)	N1	C3	1.492(4)
Co	N3	1.949(3)	N1	C5	1.499(4)
Co	N4	1.932(3)	N2	C2	1.488(4)
Cl	O5	1.433(2)	N3	C4	1.484(4)
Cl	O6	1.409(3)	N4	C6	1.478(4)
Cl	O7	1.400(3)	C1	C2	1.499(5)
Cl	O8	1.391(3)	C3	C4	1.505(5)
S	O3	1.545(2)	C5	C6	1.510(5)
S	O4	1.499(2)	C7	C8	1.513(4)
S	C8	1.813(3)			

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	Co	O3	95.71(8)	O4	S	C8	103.6(1)
O1	Co	N1	173.75(9)	Co	O1	C7	131.4(2)
O1	Co	N2	97.1(1)	Co	O3	S	125.3(1)
O1	Co	N3	89.8(1)	Co	N1	C1	105.7(2)
O1	Co	N4	88.2(1)	Co	N1	C3	105.7(2)
O3	Co	N1	89.52(9)	Co	N1	C5	110.2(2)
O3	Co	N2	86.4(1)	C1	N1	C3	112.6(3)
O3	Co	N3	88.9(1)	C1	N1	C5	112.2(3)
O3	Co	N4	175.8(1)	C3	N1	C5	110.0(3)
N1	Co	N2	86.6(1)	Co	N2	C2	110.9(2)
N1	Co	N3	86.9(1)	Co	N3	C4	110.5(2)
N1	Co	N4	86.7(1)	Co	N4	C6	110.8(2)
N2	Co	N3	172.0(1)	N1	C1	C2	109.3(3)
N2	Co	N4	91.7(1)	N2	C2	C1	108.2(3)
N3	Co	N4	92.7(1)	N1	C3	C4	108.4(3)
O5	Cl	O6	108.8(2)	N3	C4	C3	109.0(3)
O5	Cl	O7	107.2(2)	N1	C5	C6	110.9(3)
O5	Cl	O8	110.6(2)	N4	C6	C5	106.9(3)
O6	Cl	O7	109.1(2)	O1	C7	O2	121.5(3)
O6	Cl	O8	109.9(2)	O1	C7	C8	119.1(3)
O7	Cl	O8	111.1(2)	O2	C7	C8	119.4(3)
O3	S	O4	108.8(1)	S	C8	C7	111.7(2)
O3	S	C8	100.5(1)				



Scheme 2.

cussing. Adamson et al.[2] noted that the photolinkage isomerization of [Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(en)$_2$]$^{2+}$ is analogous to the nitro-to-nitrito (nitrito-*N*-to-nitrito-*O*) linkage isomerization observed for [Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$.[16] They proposed that the photolinkage isomerization of sulfinato complexes takes place from a low-lying CT state through a cage recombination of redox products.[1—3] A possible mechanism for the photochemical reaction of *trans*(*t*-N,S)-[Co{S-(O)$_2$CH$_2$COO-*S*,*O*}(tren)]$^+$ (**1**) is given in Scheme 2. The excitation of the LMCT state of the complex will lead to the homolytic Co–S bond fission yielding a radical pair,[1—3] in which the cobalt(II) ion is bonded to the ligand radical via the oxygen atom of the carboxylate group ((b) in Scheme 2). The oxygen atom of the sulfinate group can combine with the cobalt(II) ion and reoxidize it to produce the sulfinato-*O*–cobalt(III) complex. Since a five-coordinate complex containing the tripod-like tren ligand favors three-fold axial symmetry, as indicated in such complexes as [Zn(NCS)(tren)]-SCN[17] and [Cu(NCS)(tren)]SCN,[18] transformation from the square pyramidal configuration (b) to the trigonal bipyramidal one (c) may take place. If recombination of the redox products occurs after configurational change into the bipyramidal structure, not only linkage isomerization but also geometrical isomerization will take place ((e) in Scheme 2).

The UV-vis and IR spectra of the red complex (**3**) are very similar to those of the orange complex (**2**), and the spectra are characteristic of a sulfinato-*O* complex.[1] Thus, the red complex (**3**) was also assigned to a linkage isomerized sulfinato-*O* complex. Since the orange complex (**2**) has been determined to have the *cis*(*t*-N,O(S)) structure, the red complex (**3**) should be *trans*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O*,*O*}(tren)]$^+$. The red complex (**3**) thermally reverts to the starting complex (**1**), and the kinetics were studied using the HPLC method in the temperature range 28—70 °C. The rate was first order and the rate constants were 2.18×10^{-6}, 1.00×10^{-5}, 3.38×10^{-5}, 1.10×10^{-4}, and $3.30\times10^{-4}\,\mathrm{s}^{-1}$ at 28, 40, 50, 60, and 70 °C, respectively. The activation parameters were $\Delta H^{\ddagger}=100\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger}=-23\,\mathrm{J\,K\,mol^{-1}}$. A thermal back-reaction has also been reported for [Co{OS-(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(en)$_2$]$^{2+}$;[1,3] the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values being 91 kJ mol^{-1} and −66 J K^{-1} mol^{-1}, respectively. The orange complex (**2**) is thermally stable, and no detectable change was observed in the absorption spectrum and in the chromatogram for at least 360 h at 25 °C. The difference in stability for a thermal linkage isomerization between the orange (**2**) and red (**3**) complexes can be explained by considering the difference in the intramolecular strain between the respective *S*-bonded isomers into which the *O*-bonded ones should change. While the strain energies of *O*-bonded isomers (**2** and **3**) are very similar, the *S*-bonded *cis*(*t*-N,S) isomer is much less stable than the *S*-bonded *trans*(*t*-N,S) isomer (**1**, Table 4). It can be expected that the *O*-bonded red complex (**3**) will easily change to the more stable *S*-bonded one (**1**). On the other hand, the *O*-bonded orange complex (**2**) will not change to the corresponding less stable *S*-bonded one. The thermal stability of the photoisomerized *O*-bonded orange complex is in accord with the molecular mechanics calculations.

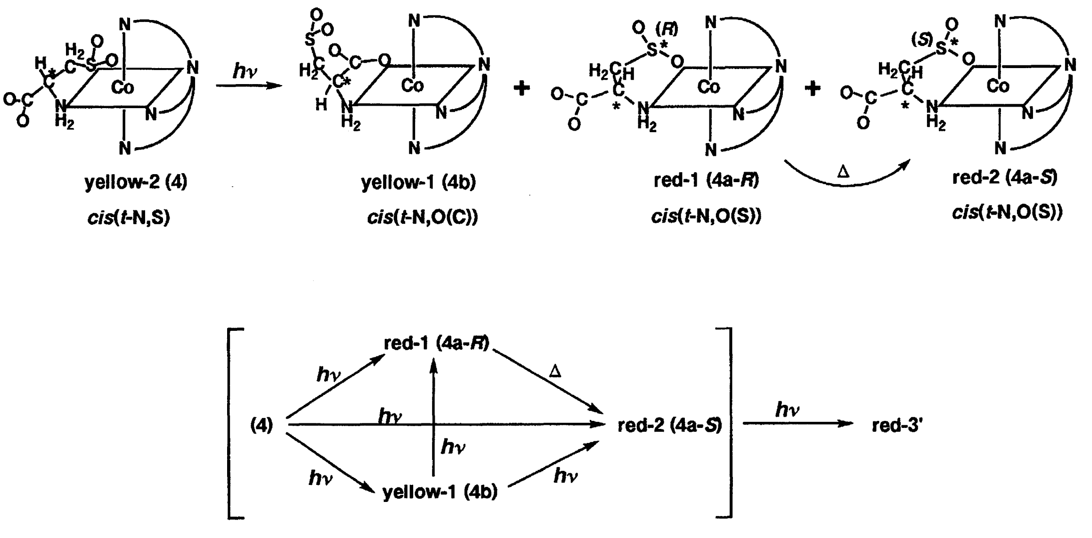
Photochemistry of *cis*(*t*-N,S)- and *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S*,*N*}(tren)]$^{2+}$ (4 and 5). The L-cysteinsulfinate(2-) ligand, $NH_2CH(CH_2SO_2^-)COO^-$, has four kinds of potential donor atoms: nitrogen, sulfur, sulfinate oxygen, and carboxylate oxygen. When the ligand functions as a didentate chelate, many kinds of linkage isomers are possible (Fig. 1). Photolysis of *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S*,*N*}(tren)]$^{2+}$ (**4**) with visible light yielded three products: the yellow-1, red-1, and red-2 complexes (Scheme 3).

The IR spectrum of the yellow-1 complex shows a strong absorption at 1650 cm^{-1} attributable to the coordinated COO stretching.[19] In the UV-vis spectrum, the yellow-1 complex does not show a strong absorption in the near UV region characteristic of a sulfinato-*S* (ca. 300 nm) or a sulfinato-*O* (ca. 325 nm) complex[1] (Fig. 3). The first d–d absorption band is at the same position (470 nm) as *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SCH$_3$)COO-*N*,*O*}(tren)]$^{2+}$ and *cis*(*t*-N,O(C))-[Co(NH$_2$CH$_2$COO-*N*,*O*)(tren)]$^{2+}$, and the corresponding *trans*(*t*-N,O(C)) isomers of the latter two complexes show the first band at longer wavelengths (ca. 498 nm).[19,20] From these data, the yellow-1 complex can be assigned to *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$$^-$)COO-*N*,*O*}(tren)]$^+$ (**4b**). This assignment was confirmed by the X-ray analysis.

Figure 4 shows a perspective view of the yellow-1 complex, *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$$^-$)COO-*N*,*O*}(tren)]$^+$ (**4b**), the bond lengths and angles being listed in Table 5. In this complex, the L-cysteinesulfinate ligand is chelated in the octahedral complex through the carboxylate oxygen atom and the nitrogen atom instead of the sulfur and nitrogen atoms in the starting complex (**4**), and the position of the nitrogen atom with respect to the tren ligand remains the same, i.e. trans to the tertiary amine nitrogen. As far as we know, this is the first cobalt(III) complex which has a free sulfinate group. The sulfinate group is at the axial position and the two sulfinate oxygen atoms are hydrogen bonded: O3···H–N2 (O3···H 2.18(4) Å) and O4···H–N5 (O4···H 2.07(4) Å). The L-cysteinesulfinate chelate is slightly puckered, the conformation being δ (Fig. 4). The formation of this complex is quite remarkable, since photolysis of the corresponding ethylenediamine (en) complex, [Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S*,*N*}(en)$_2$]$^{2+}$ has been reported to result in a nearly quantitative conversion

Table 4. Final Energy Terms (kJ mol^{-1}) from the Minimization for Cobalt(III) Complexes Containing a Sulfinate Ligand

Complex	Total	Bond	Angle	Nonbonded	Tortion
cis(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O*,*O*}(tren)]$^+$ (**2**)	85.3	5.7	38.7	8.6	32.3
trans(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O*,*O*}(tren)]$^+$ (**3**)	84.8	5.4	38.8	8.4	32.2
cis(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S*,*O*}(tren)]$^+$	96.9	7.2	32.9	22.2	34.6
trans(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S*,*O*}(tren)]$^+$ (**1**)	65.8	5.6	23.7	10.8	25.6
(*R*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (**4a-*R***)	70.4	7.7	29.7	18.8	14.3
(*S*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (**4a-*S***)	71.1	7.4	32.3	16.8	14.7



Scheme 3.

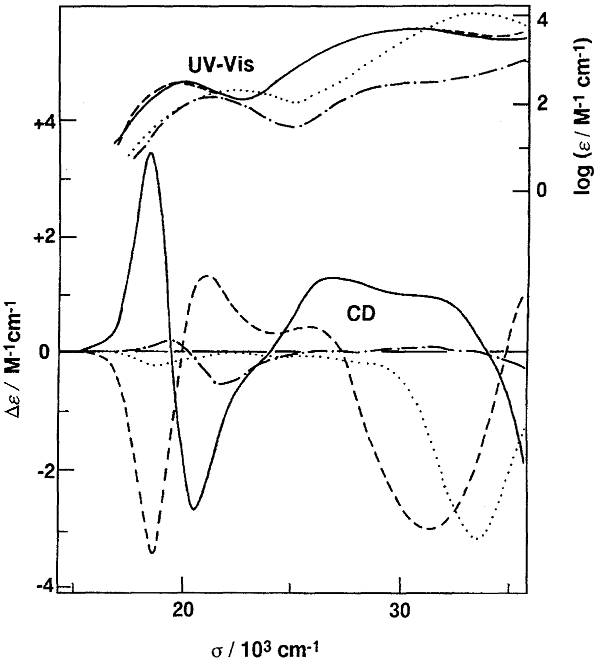


Fig. 3. UV-vis and CD spectra of *cis*(*t*-N, S)-[Co{S-(O)$_2$CH$_2$CH(COOH)NH$_2$-*S*,*N*}(tren)]$^{2+}$ (**4**, ······), (*R*)-*cis*-(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (**4a**-***R***, the red-1 complex, ——), (*S*)-*cis*(*t*-N,O(S))-[Co{OS-(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (**4a**-***S***, the red-2 complex, - - -), and *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$$^-$)-COO-*N*,*O*}(tren)]$^+$ (**4b**, the yellow-1 complex, –·–).

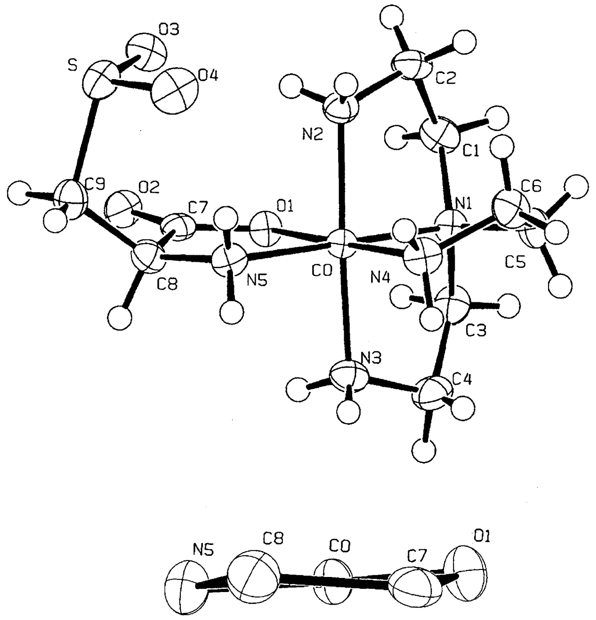


Fig. 4. ORTEP drawing of the yellow-1 complex cation, *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$$^-$)COO-*N*,*O*}(tren)]$^+$ (**4b**) and edge-on view of the *N*,*O*-chelate ring.

Table 5. Bond Lengths (l/Å) and Bond Angles (ϕ/°) of *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$$^-$)COO-*N*,*O*}(tren)]ClO$_4$·NaClO$_4$ (**4b**, the Yellow-1 Complex)

Atom	Atom	Bond length	Atom	Atom	Bond length
Co	O1	1.899(2)	C1	C2	1.512(5)
Co	N1	1.946(3)	C3	C4	1.501(5)
Co	N2	1.974(3)	C5	C6	1.508(5)
Co	N3	1.969(3)	C7	C8	1.532(4)
Co	N4	1.944(3)	C8	C9	1.525(5)
Co	N5	1.949(3)	Cl1	O5	1.411(3)
S	O3	1.509(2)	Cl1	O6	1.428(3)
S	O4	1.503(3)	Cl1	O7	1.449(3)
S	C9	1.820(4)	Cl1	O8	1.426(3)
O1	C7	1.299(4)	Cl2	O9	1.426(3)
O2	C7	1.226(4)	Cl2	O10	1.435(3)
N1	C1	1.497(4)	Cl2	O11	1.400(3)
N1	C3	1.486(4)	Cl2	O12	1.417(3)
N1	C5	1.506(4)	Na	O2	2.422(3)
N2	C2	1.488(5)	Na	O3	2.298(2)
N3	C4	1.497(5)	Na	O4	2.246(3)
N4	C6	1.490(5)	Na	O7	2.503(4)
N5	C8	1.497(4)	Na	O10	2.556(4)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	Co	N1	91.4(1)	N1	C1	C2	107.7(2)
O1	Co	N2	86.9(1)	N2	C2	C1	108.8(3)
O1	Co	N3	87.3(1)	N1	C3	C4	108.6(3)
O1	Co	N4	178.2(1)	N3	C4	C3	107.4(3)
O1	Co	N5	86.1(1)	N1	C5	C6	111.0(3)
N1	Co	N2	85.7(1)	N4	C6	C5	107.9(3)
N1	Co	N3	87.0(1)	O1	C7	O2	122.4(3)
N1	Co	N4	87.0(1)	O1	C7	C8	115.2(3)
N1	Co	N5	177.5(1)	O2	C7	C8	122.2(2)
N2	Co	N3	170.6(1)	N5	C8	C7	110.1(3)
N2	Co	N4	92.2(1)	N5	C8	C9	112.2(3)
N2	Co	N5	94.1(1)	C7	C8	C9	114.3(3)
N3	Co	N4	93.4(1)	S	C9	C8	114.2(2)
N3	Co	N5	93.0(1)	O5	Cl1	O6	112.4(2)
N4	Co	N5	95.5(1)	O5	Cl1	O7	108.1(2)
O3	S	O4	108.2(1)	O5	Cl1	O8	110.5(2)
O3	S	C9	100.2(1)	O6	Cl1	O7	107.2(2)
O4	S	C9	102.9(2)	O6	Cl1	O8	110.8(2)
Co	O1	C7	116.7(2)	O7	Cl1	O8	107.7(2)
Co	N1	C1	106.0(2)	O9	Cl2	O10	109.7(2)
Co	N1	C3	106.0(2)	O9	Cl2	O11	113.6(3)
Co	N1	C5	110.2(2)	O9	Cl2	O12	108.5(2)
C1	N1	C3	112.7(2)	O10	Cl2	O11	109.2(2)
C1	N1	C5	111.2(3)	O10	Cl2	O12	107.6(2)
C3	N1	C5	110.5(3)	O11	Cl2	O12	108.1(3)
Co	N2	C2	110.9(2)				
Co	N3	C4	109.5(2)				
Co	N4	C6	109.0(2)				
Co	N5	C8	110.4(2)				

to the thermodynamically less stable sulfinato-*O* complex, [Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(en)$_2$]$^{2+}$.[2)]

The IR spectra of both the red-1 and red-2 complexes are consistent with the isomerization from *S*-sulfinato to *O*-sulfinato. The strong absorption at 1190 cm^{-1} in the *S*-bonded starting complex (**4**) due to the asymmetric sulfur–oxygen stretching is not present in the products, and both the red-1 and red-2 complexes exhibit a new strong absorption at 960 cm^{-1} attributable to the Co–O–S stretching mode of an *O*-sulfinato complex.[1,21)] The spectra also show the stretching frequency at ca. 1720 cm^{-1}, indicating that the carboxyl group is not coordinated.[22—24)]

Figure 3 compares the UV-vis spectra of the red-1 and red-2 complexes with that of the starting complex, *cis*(*t*-N, S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S*,*N*}(tren)]$^{2+}$ (**4**). The intense S→Co charge transfer (CT) band at 300 nm disappears upon photolysis, and the new band at ca. 325 nm can be assigned to the CT transition from the oxygen of the sulfinate moiety to cobalt. The red-1 and red-2 complexes have a much weaker ligand field strength than does the *S*,*N*-chelate one; the latter shows the first d–d absorption band at 446 nm, while those of the former complexes appear at 503 nm. This position (503 nm) is very close to the first absorption band maximum of *cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$ (502 nm).[15] From these data, the red-1 and red-2 complexes can be assigned to *cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (**4a**). Upon linkage isomerization from sulfinato-*S* to sulfinato-*O*, the sulfur atom becomes chiral (*R* and *S*), and since there is also an asymmetric carbon atom (*R*), a pair of diastereomers are possible. The absolute configuration about the sulfur atom was assigned on the basis of the CD spectra. Although the optical activity of the complexes originates from the two chiral centers, the fact that the CD spectra for the two complexes are almost enantiomeric to each other (Fig. 3) suggests that the CD contribution from the chiral sulfur atom dominates over that from the carbon atom. This may be explained by the ligand polarization model: the more polarizable sulfur atom will contribute more to the optical activity than the oxygen atom.[25] The CD spectral pattern for the red-1 complex is quite similar to that for (*R*)-*cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$,[15] and thus the red-1 and red-2 complexes can be assigned to have the (*R*)- and the (*S*)-sulfur atom, respectively. The X-ray analysis of the red-2 complex supports these assignments.

An ORTEP drawing of the red-2 complex (**4a-*S***) is shown in Fig. 5. Selected bond lengths and angles are listed in Table 6. The L-cysteinesulfinate ligand coordinates to cobalt with the sulfinate oxygen and nitrogen atoms instead of the sulfur and nitrogen atoms of the starting complex. In this reaction, the geometrical configuration is retained, and the red-2 complex has a *cis*(*t*-N,O(S)) structure. The absolute configuration about the sulfur atom is (*S*). The six-membered *O*,*N*-chelate ring adopts a distorted chair conformation (Fig. 5). The overall structure is similar to *cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)](ClO$_4$)$_2$·H$_2$O.[15]

Both the red-1 and red-2 complexes are stable toward a thermal back-reaction. However, the red-1 complex changes to the red-2 complex; inversion at the chiral sulfur center occurs. The reaction follows first-order kinetics; it was studied in the temperature range 55—75 °C. The rate constants were 1.15×10^{-5}, 3.96×10^{-5}, and $1.10\times10^{-4}\,\mathrm{s}^{-1}$ at 55, 65, and 75 °C, respectively, and the activation parameters were $\Delta H^{\ddagger}=105$ kJ mol^{-1} and $\Delta S^{\ddagger}=-20$ J K^{-1} mol^{-1}. Racemization (inversion at sulfur) was also observed in *cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$ ($1.9\times10^{-5}\,\mathrm{s}^{-1}$ at 70 °C)[15] and [Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(en)$_2$]$^{2+}$ ($2.46\times10^{-6}\,\mathrm{s}^{-1}$ at 19 °C);[26,27] the former is stable toward a thermal back-reaction while the latter reverts thermally to the starting *S*,*N*-chelate complex (3.23×10^{-7} and $2.31\times10^{-5}\,\mathrm{s}^{-1}$ at 28 and 67 °C, respectively).[1,3] The red-2 complex is thermally stable. Molecular mechanics calculations on the two diastereomers, the red-1 and red-2 isomers, were carried out in the hope of supporting the observation that the red-2 isomer is more stable than the red-1 isomer. However, the result was not in accord with our observation; the red-1 isomer was calculated to be slightly more stable than the red-2 isomer (by ca. 0.2 kcal mol^{-1}). This inconsistency may be accounted for as follows. In the energy-minimized structure of the red-2 isomer, there is an intramolecular short contact of 2.50 Å between the uncoordinated oxygen atom (O4) bonded to the sulfur and one of the hydrogens attached to the nearest nitrogen atom (N2) of tren. There is no such short contact in the energy-minimized structure of the red-1 isomer. Thus, the red-2 isomer will be much more stabilized due to intramolecular hydrogen bonding and/or electrostatic interaction than the red-1 isomer.

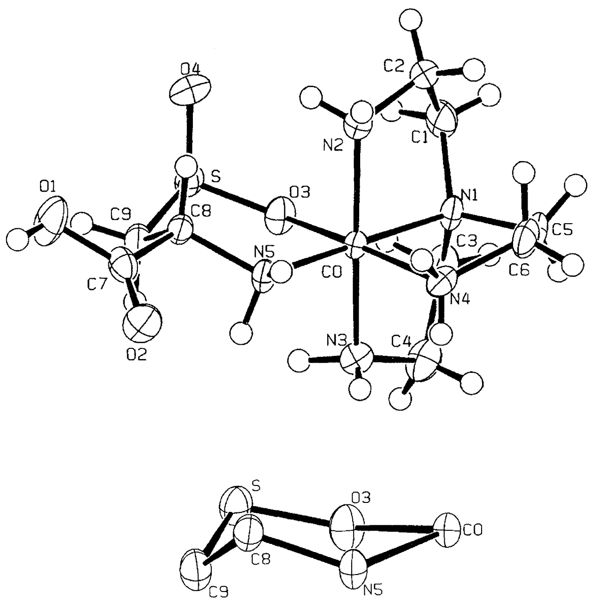
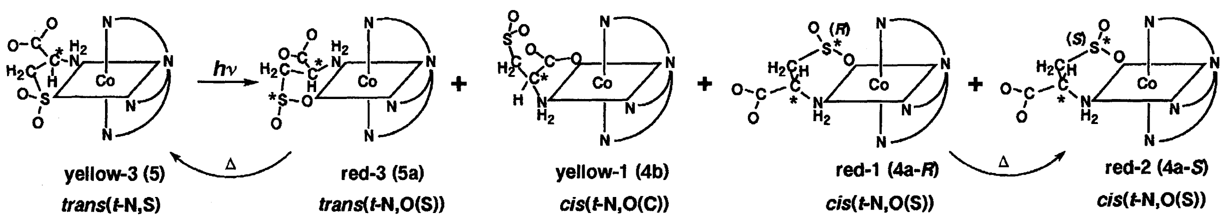
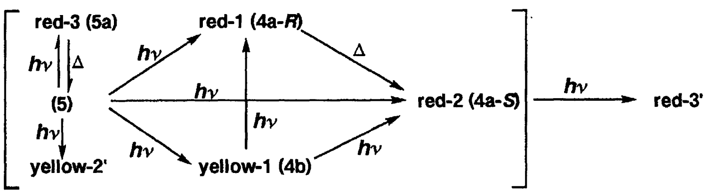


Fig. 5. ORTEP drawing of the red-2 complex cation, (*S*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (**4a-*S***) and edge-on view of the six-membered *O*,*N*-chelate ring.

Photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)-NH$_2$-*S*,*N*}(tren)]$^{2+}$ (**5**) with visible light by method (ii) yielded six products (see Experimental and Scheme 4). Three of them (the yellow-1, red-1, and red-2 complexes) were the same as those obtained by photolysis of the corresponding *cis*(*t*-N,S) isomer (**4**). The complex contained in the slowest-moving red-3 band in SP-Sephadex column chromatography (eluent: 0.1 M Na$_2$SO$_4$) could not be isolated, since it was thermally unstable and reverted to the starting complex. We could not study the back-reaction in detail; the reaction was accompanied by a decomposition reaction and the first-order plot deviated from a straight line after one half-life (11 h at 25 °C). The rate was about five times faster than *trans*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O*,*O*}(tren)]$^{+}$ (the red complex). The red-3 complex seems to have a CoN$_5$O chromophore,





Scheme 4.

Table 6. Bond Lengths (l/Å) and Bond Angles (ϕ/°) of *cis*(t-N, O(S))-[Co{OS(O)CH$_2$CH(COOH)-NH$_2$-*O*,*N*}(tren)]Br$_2$ (**4a**-*S*, the Red-2 Complex)

Atom	Atom	Bond length	Atom	Atom	Bond length
Co	O3	1.926(3)	N1	C3	1.498(7)
Co	N1	1.956(4)	N1	C5	1.511(6)
Co	N2	1.972(5)	N2	C2	1.479(7)
Co	N3	1.957(4)	N3	C4	1.478(7)
Co	N4	1.942(4)	N4	C6	1.493(7)
Co	N5	1.971(4)	N5	C8	1.492(6)
S	O3	1.522(3)	C1	C2	1.498(9)
S	O4	1.497(4)	C3	C4	1.520(8)
S	C9	1.808(5)	C5	C6	1.497(8)
O1	C7	1.318(6)	C7	C8	1.525(6)
O2	C7	1.185(6)	C8	C9	1.513(6)
N1	C1	1.481(7)			

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O3	Co	N1	88.2(1)	Co	N1	C5	110.7(3)
O3	Co	N2	91.5(2)	C1	N1	C3	113.6(4)
O3	Co	N3	82.6(2)	C1	N1	C5	111.1(4)
O3	Co	N4	172.5(2)	C3	N1	C5	110.2(4)
O3	Co	N5	94.7(2)	Co	N2	C2	109.7(3)
N1	Co	N2	86.4(2)	Co	N3	C4	110.4(3)
N1	Co	N3	87.0(2)	Co	N4	C6	110.7(3)
N1	Co	N4	86.3(2)	Co	N5	C8	120.1(3)
N1	Co	N5	176.8(2)	N1	C1	C2	108.2(5)
N2	Co	N3	171.2(2)	N2	C2	C1	109.0(4)
N2	Co	N4	93.2(2)	N1	C3	C4	107.6(4)
N2	Co	N5	92.2(2)	N3	C4	C3	108.5(5)
N3	Co	N4	92.0(2)	N1	C5	C6	111.3(4)
N3	Co	N5	94.7(2)	N4	C6	C5	108.2(4)
N4	Co	N5	90.9(2)	O1	C7	O2	125.4(5)
O3	S	O4	108.7(2)	O1	C7	C8	110.9(4)
O3	S	C9	102.1(2)	O2	C7	C8	123.6(5)
O4	S	C9	102.5(2)	N5	C8	C7	108.3(4)
Co	O3	S	132.5(2)	N5	C8	C9	110.7(4)
Co	N1	C1	105.5(3)	C7	C8	C9	110.5(4)
Co	N1	C3	105.5(3)	S	C9	C8	113.6(3)

since it gives the first d–d absorption band at the same position (512 nm) as [Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*, *N*}(en)$_2$]$^{2+}$.1) We assigned the red-3 complex as either of the two diastereomers of *trans*(t-N,O(S))-[Co{OS(O)CH$_2$CH(COO$^-$)NH$_2$-*O*, *N*}(tren)]$^+$ (**5a**). There is another possibility that the red-3 complex is a mixture of the two diastereomers. However, it was difficult to separate the isomers by column chromatography, since the red-3 complex reverted to the starting complex even at 5 °C. We could not characterize the yellow-2′ complex, since the yield was very small.

It should be noted that three out of six photoproducts of *trans*(t-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S*, *N*}(tren)]$^{2+}$ (**5**) were the same as those of *cis*(t-N,S)-[Co{S(O)$_2$CH$_2$CH-(COOH)NH$_2$-*S*, *N*}(tren)]$^{2+}$ (**4**); geometrical isomerization takes place and it can be explained by the same mechanism as shown in Scheme 2.

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