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Photolysis of Cobalt(III) Complexes Containing Sulfinate-*S* Ligands. Formation of Organic Peroxide Complexes through Desulfurization

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The photolysis of *trans*(*t*-N,S)-$[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(tren)]^+$ (*t*-N= tertiary amine nitrogen; tren = tris(2-aminoethyl)amine) with visible light yielded three complexes: pink, red-1, and red-2. The molecular structure of the pink complex tetraphenylborate was determined by the X-ray method to be *trans*(*t*-N,O(C))-$[Co\{OOCH(CH_3)COO\text{-}O,O\}(tren)][B(C_6H_5)_4]\cdot CH_3OH\cdot H_2O$ (O(C) = oxygen of carboxylate group); irradiation induced desulfurization and yielded an organic peroxide complex. Crystal data: $C_{34}H_{48}BCoN_4O_6$, FW 678.52, triclinic, $P\bar{1}$ (No. 2), $a=19.583(3)$, $b=19.838(4)$, $c=9.996(1)$ Å, $\alpha=103.60(1)$, $\beta=102.13(1)$, $\gamma=70.29(1)^\circ$, $V=3517(1)$ Å^3, $Z=4$, $D_x=1.29$ g cm^{-3}, $\mu=0.533$ mm^{-1} for Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). The red-2 complex is thermally stable, while the red-1 one thermally reverts to the starting complex. The red-1 and red-2 complexes were assigned as linkage isomerized sulfinato-*O* complexes, *trans*(*t*-N,O(S))- and *cis*(*t*-N,O(S))-$[Co\{OS(O)CH(CH_3)COO\text{-}O,O\}(tren)]^+$ (O(S) = oxygen of sulfinate group), respectively, on the basis of the UV-vis and IR spectra and thermal stability. The irradiation of *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)]^+$ and $[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(en)_2]^+$ also yielded both peroxide complexes and linkage isomerized sulfinato-*O* complexes.

Although photochemical reactions have been used for a long time in the preparation of organic compounds, only recently has greater attention been paid to the use of photochemical reactions for the synthesis of metal complexes. Photochemical reactions are useful in preparing thermodynamically less stable complexes.[1] Adamson and coworkers[2—4] reported that the irradiation of a cobalt(III) complex containing an *S*-bonded sulfinate ligand yielded a sulfinato-*O* complex, and that the complex thermally reverted to the starting complex. In a preceding paper,[5] we reported that during the photolysis of *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)]^+$ both linkage and geometrical isomerization took place to yield *cis*(*t*-N,O(S))- and *trans*(*t*-N,O(S))-$[Co\{OS(O)CH_2COO\text{-}O,O\}(tren)]^+$ (O(S) = oxygen of sulfinate group). Here, we report on the formation of a new type of organic peroxide–cobalt(III) complexes through desulfurization upon photolysis of the same complex and closely related complexes, $[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(en)_2]^+$ and *trans*(*t*-N,S)-$[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(tren)]^+$. The X-ray crystal structure of a peroxide complex, $[Co\{OOCH(CH_3)COO\}(tren)][B(C_6H_5)_4]\cdot CH_3OH\cdot H_2O$ is also given. A part of this study has already been briefly reported.[6]

Experimental

Caution! Perchlorate salts of metal complexes can be explosive and should be handled with care.

Preparation of $[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(en)_2]ClO_4$. This complex was prepared by the same procedure as for *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)]ClO_4$ by oxidizing $[Co\{SCH(CH_3)COO\text{-}S,O\}(en)_2]ClO_4$ with H_2O_2.[7] Found: C, 20.16; H, 4.89; N, 13.25; S, 8.01%. Calcd for $C_7H_{20}ClCoN_4O_8S$: C, 20.27; H, 4.86; N, 13.51; S, 7.73%. UV-vis (H_2O) 450 (ε 256), 297 (9800), and 223 nm (13960).

Photolysis of *trans*(*t*-N,S)-$[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(tren)]ClO_4$ (1) and Isolation of the Products. An aqueous solution (200 cm^3) of *trans*(*t*-N,S)-$[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(tren)]ClO_4$[7] (**1**, 0.10 g) was irradiated with visible light 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 irradiated solution was passed through a recycling column (ϕ 1.5 cm × 70 cm) of SE-Toyopearl,[8] and the adsorbed complexes were eluted with 0.05 M (1 M= 1 mol dm^{-3}) Na_2 (+)-tartrate. After three recyclings at 5 °C, three bands (pink, yellow, and red) were eluted in this order, and the eluates containing the two faster eluted bands were collected separately. The remaining red band was further recycled seven times and the band was separated into red-1 and red-2. The formation ratio, pink : yellow : red-1 : red-2, was about 3 : 6 : 5 : 5. The yellow complex was the unreacted starting complex.

The eluate containing the pink complex was concentrated with a rotary evaporator, and Na_2 (+)-tartrate was precipitated by the addition of methanol and filtered. The filtrate was again concentrated and NH_4PF_6 was added to the concentrate. If there was any precipitate, the solution was again filtered and the filtrate was allowed to evaporate slowly. The resulting red crystals were recrystallized from water, filtered, washed with ethanol, and dried under vacuum. Found: C, 23.97; H, 4.89; N, 12.67%. Calcd for $[Co\{OOCH(CH_3)COO\text{-}O,O\}(tren)]PF_6$ = $C_9H_{22}CoF_6N_4O_4P$: C, 23.80; H, 4.88; N, 12.34%. UV-vis (H_2O) 513 (ε 140), 375 (sh, 240), 291 (4985), and 219 nm (16160). ^{1}H NMR (DMSO-d_6) δ = 1.19 (3H, d, CH_3), 4.29 (1H, q, CH), 2.22—3.07 (12H, m, CH_2), and 4.37—5.00 (6H, m, NH_2). ^{13}C NMR (DMSO-d_6) $\delta = 16.10$ (q), 42.03 (t), 43.58 (t), 44.44 (t), 59.96 (t), 60.22 (t), 61.20 (t), 80.28 (d), and 174.24 (s). This complex was dissolved in a minimum amount of water and an aqueous solution of sodium tetraphenylborate was added to give a precipitate of the tetraphenylborate of the complex. The precipitate was collected by filtration and dissolved in a mixture of water, methanol, and ethanol. The solution was then filtered and allowed to evaporate slowly at room temperature to give the red crystals. The crystals were found to lose their solvent of crystallization in the air. One of these crystals was used for X-ray crystallography.

The red-2 complex was isolated as the perchlorate by the same process as for the orange complex obtained from *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)]^+$.[5] Found C, 23.45; H, 5.24; N, 12.31; S, 7.19%. Calcd for $[Co\{OS(O)CH(CH_3)COO\text{-}O,O\}(tren)]ClO_4\cdot H_2O = C_9H_{23}ClCoN_4O_9S$: C, 23.56; H, 5.27; N, 12.21; S, 6.99%. UV-vis (H_2O) 510 (ε 163), 328 (3240), and 215 nm (13910). ^{1}H NMR (DMSO-d_6) $\delta = 1.19$ (3H, d, CH_3), 3.53 (1H, q, CH), 2.49—3.45 (12H, m, CH_2),and 4.40—5.37 (8H, m, NH_2).

The red-1 complex could not be isolated, since the complex is thermally unstable and reverts to the starting complex. UV-vis (0.05 M Na_2 (+)-tartrate) 515 (ε 179) and 332 nm (3200).[11]

Photolysis of *trans*(*t*- N, S)- $[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)]ClO_4$ (2). The irradiation of *trans*(*t*-N,S)-$[Co\{S(O)_2CH_2COO\text{-}S,O\}(tren)]ClO_4$ (**2**) under the same conditions as for *trans*(*t*-N,S)-$[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(tren)]ClO_4$ (**1**) yielded only linkage isomerized sulfinato-*O* complexes, *cis*(*t*-N,O(S))-$[Co\{OS(O)CH_2COO\text{-}O,O\}(tren)]^+$ and *trans*(*t*-N,O(S))-$[Co\{OS(O)CH_2COO\text{-}O,O\}(tren)]^+$,[5] and a peroxide complex was not formed. However, when the complex was irradiated for a longer time (40 min), column chromatography on SE-Toyopearl showed many bands. The fastest moving pink band was assigned to a peroxide complex, since the UV-vis spectrum was very similar to that for the peroxide complex, $[Co\{OOCH(CH_3)COO\}(tren)]^+$ from (**1**).

Photolysis of $[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(en)_2]ClO_4$ (3) and Isolation of the Products. $[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(en)_2]ClO_4$ (**3**) was also irradiated and chromatographed in the same way as for *trans*(*t*-N,S)-$[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(tren)]ClO_4$ (**1**). After two recyclings at room temperature, four bands (yellow-1, pink-1, yellow-2, and red) were eluted separately in this order. The formation ratio, yellow-1 : pink-1 : yellow-2 : red, was about 4 : 1 : 2 : 2. The yellow-2 complex was the unreacted starting complex (**3**). Complex **3** also gave a noncationic species (UV-vis: 485 and 294 nm), which was not adsorbed on an SE-Toyopearl cation exchanger.

The eluate containing the yellow-1 band was concentrated with a rotary evaporator, and Na_2 (+)-tartrate was precipitated by the addition of methanol and filtered. The filtrate was again concentrated and $NaClO_4$ was added. If there was any precipitate, the solution was again filtered. From the filtrate, the complex was precipitated by the addition of ethanol. The precipitate was dissolved in a minimum amount of water and the solution was passed through a small SP-Sephadex C-25 column and the adsorbed complex was eluted with 1 M $NaClO_4$. The yellow portion of the eluate was collected and slowly evaporated under vacuum. The resulting yellow-brown crystals were filtered, washed with ethanol, and dried under vacuum. Found: C, 12.31; H, 4.97; N, 14.23; S, 8.50%. Calcd for $[Co(SO_3)(H_2O)(en)_2]ClO_4\cdot H_2O$[9] $= C_4H_{20}ClCoN_4O_9S$: C, 12.17; H, 5.11; N, 14.20; S, 8.12%. UV-vis (H_2O) 465 (ε 205), 340 (sh, 375), and 273 nm (19460). This complex was also isolated as the hexafluorophosphate. Found: C, 11.12; H, 4.29; N, 12.82; S, 7.43%. Calcd for $C_4H_{20}CoF_6N_4O_5PS$: C, 10.91; H, 4.57; N, 12.72; S, 7.28%.

The pink-1 complex was isolated as the hexafluorophosphate by following the same procedure as for the pink complex. Found: C, 19.72; H, 5.48; N, 12.50%. Calcd for $[Co\{OOCH(CH_3)COO\text{-}O,O\}(en)_2]PF_6\cdot 0.5H_2O = C_7H_{21}CoF_6N_4O_{4.5}P$: C, 19.23; H, 4.84; N, 12.82%. UV-vis (H_2O) 507 (ε 167), 375 (sh, 275), 293 (5330), and 208 nm (22000).

The red complex was isolated as the hexafluorophosphate by following the same procedure as for the pink complex. Found: C, 17.93; H, 4.41; N, 11.87; S, 6.60%. Calcd for $[Co\{OS(O)CH(CH_3)COO\text{-}O,O\}(en)_2]PF_6 = C_7H_{20}CoF_6N_4O_4PS$: C, 18.27; H, 4.38; N, 12.17; S, 6.97%. UV-vis spectrum (H_2O), 510, 328, and 218 nm.

Preparation of *trans*(*t*-N, O(C))-$[Co\{OCH(CH_3)COO\text{-}O,O\}(tren)]ClO_4\cdot H_2O$. $[CoCl_2(tren)]Cl$ (1.0 g, 0.3 mmol) was dissolved in 15 cm^3 of water, and a solution of lactic acid (0.30 g, 0.3 mmol) in water (15 cm^3) was added to this solution. The mixture was then made alkaline by adding 0.12 g (0.3 mmol) of NaOH and stirred. The color of the solution changed from violet to pink. After stirring for 1 h at 55 °C, the reaction mixture was cooled and 6 g of $NaClO_4$ was added. The mixture was then allowed to stand for a few hours, and then mixed with 10 cm^3 of ethanol. Pink crystals were formed, which were recrystallized from water. They were collected by filtration, washed with ethanol and dried under vacuum. Yield 40%. Found: C, 26.27; H, 5.80; N, 13.77%. Calcd for $[Co\{OCH(CH_3)COO\text{-}O,O\}(tren)]ClO_4\cdot H_2O = C_9H_{24}ClCoN_4O_8$: C, 26.32; H, 5.89; N, 13.64%. This complex was also isolated as the hexafluorophosphate. Found: C,23.77; H, 5.21; N, 12.37%. Calcd for $[Co\{OCH(CH_3)COO\text{-}O,O\}(tren)]PF_6\cdot H_2O = C_9H_{24}CoF_6N_4O_4P$: C, 23.69; H, 5.30; N, 12.28%. UV-vis (H_2O) 522 (ε 119), 418 (sh, 91), 362 (139), and 218 nm (20600). ^{1}H NMR (DMSO-d_6) δ=1.14 (3H, d, CH_3), 3.76 (1H, q, CH), 2.59—3.29 (12H, m, CH_2), and 4.19—4.86 (6H, m, NH_2). ^{13}C NMR (DMSO-d_6) δ=23.56 (q), 43.42 (t), 44.10 (t), 44.15 (t), 58.23 (t), 60.98 (t), 61.06 (t), 73.50 (d), and 188.23 (s).

Measurements. UV-vis spectra were recorded on a JASCO Ubest-30 spectrophotometer. Infrared (IR) spectra were measured as KBr pellets using a JASCO IR-810 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-500 spectrometer. Thermal analysis was carried out with a ULVAC TA-1500 thermal analyzer.

X-Ray Crystallography. A crystal of the tetraphenylborate of *trans*(*t*-N,O(C))-$[Co\{OOCH(CH_3)COO\text{-}O,O\}(tren)][B(C_6H_5)_4]\cdot CH_3OH\cdot H_2O$ (pink) was sealed in a glass capillary with the mother liquor and the data collection was carried out on a Rigaku AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at Institute for Molecular Science. The unit cell dimensions were determined using 25 reflections in the 2θ range 20 and 24°. The intensities of three standard reflections were monitored every 150 reflections; no significant variations were found. The structure was solved by a direct method (SHELXS 86)[12] and a subsequent Fourier synthesis. Refinement was carried out by a block-diagonal least-squares procedure using the Xtal 3.2 software.[13] The crystal data and experimental details are listed in Table 1, and the atomic parameters of the non-hydrogen atoms can be found in Table 2. The tables of the atomic coordinates for hydrogen atoms, equivalent isotropic temperature factors for hydrogen atoms and the anisotropic temperature factors for non-hydrogen atoms, and the observed and calculated structure factors are deposited as Document No. 69057 at the Office of the Editor of Bull. Chem. Soc. Jpn.

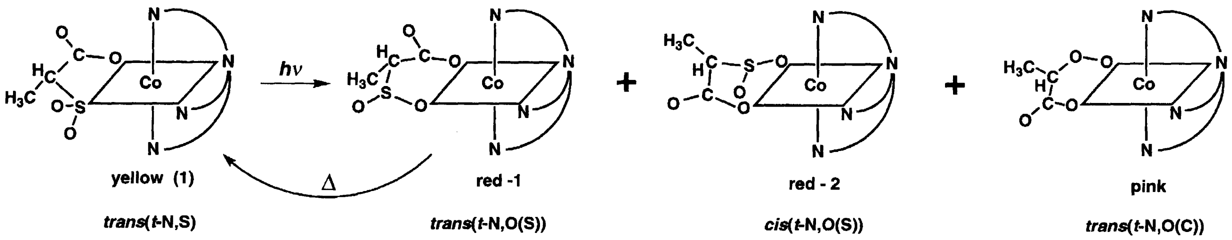
Table 1. Crystal Data and Experimental Details

trans(*t*-N,O(C))-[Co{OOCH(CH$_3$)COO-*O*,*O*}(tren)][B(C$_6$H$_5$)$_4$]·CH$_3$OH·H$_2$O	
Chemical formula	C$_{34}$H$_{48}$BCoN$_4$O$_6$
Formula weight	678.52
Crystal color	Red
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Crystal size/mm	$0.2\times0.4\times0.5$
No. of reflections used for unit cell determination (2θrange/°)	(20—24)25
a/Å	19.583(3)
b/Å	19.838(4)
c/Å	9.996(1)
α/°	103.60(1)
β/°	102.13(1)
γ/°	70.29(1)
V/Å^3	3517(1)
Z	4
D_x/Mg m^{-3}	1.29
F(000)	1440
μ(Mo$K\alpha$)/cm^{-1}	5.33
T/K	298
Scan type	ω–2θ
Scan width in ω/°	0.997+0.50tan θ
Scan speed in ω/° min^{-1}	8
2$\theta_{\max}$/°	55
Range of h, k, l	$0\leq h\leq23$ $-24\leq k\leq24$ $-12\leq l\leq12$
No. of reflections measured	13989
No. of reflections obsd [$\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$]	6555
No. of parameters refined	830
$R^{a)}$/$R_w^{b)}$	0.077/0.091
$S^{c)}$	2.67
$\Delta\rho_{\max}$/eÅ^{-3}	0.77
$\Delta\rho_{\min}$/eÅ^{-3}	−0.50

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

Results and Discussion

The photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S*,*O*}(tren)]$^+$ (**1**) with visible light yielded three products: red-1, red-2, and pink (Scheme 1). The pH of the solution decreased upon irradiation. The formation of the pink complex gradually increased, while those of the red-1 and red-2 complexes decreased as the irradiation was prolonged. The red-1 and red-2 complexes were also observed to give the pink complex and to interconvert to each other upon irradiation. The red-1 and red-2 complexes were assigned as linkage isomerized sulfinato-*O* complexes on the basis of the UV-vis spectra (Fig. 1).[11] The red-1 and red-2 complexes have a CT band attributable to the transition from the oxygen of the sulfinate moiety to cobalt(III) at 332 nm and 328 nm, respectively, instead of the strong S→Co CT band at 303 nm of the starting complex. The d–d absorption bands of the red-1 complex (515 nm) and the red-2 complex (510 nm) are at a longer wavelength than that of the starting complex (435 nm). Generally, an *O*,*O*-chelate complex has a much weaker



Scheme 1.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2)

Atom	x/a	y/b	z/c	U_{eq} [a]	Atom	x/a	y/b	z/c	U_{eq} [a]
Co(1)	0.27818(6)	0.57294(6)	0.3646(1)	0.0521(5)	C(27)	0.1181(4)	0.3218(4)	0.4930(7)	0.044(3)
Co(2)	0.32114(7)	0.05389(6)	0.8721(1)	0.0634(6)	C(28)	0.0887(4)	0.2705(4)	0.3993(8)	0.053(4)
O(1)	0.2940(3)	0.5526(3)	0.1807(5)	0.074(3)	C(29)	0.0460(4)	0.2358(4)	0.4355(8)	0.061(4)
O(2)	0.3566(3)	0.4904(3)	0.4100(5)	0.066(3)	C(30)	0.0301(4)	0.2527(4)	0.5714(9)	0.062(4)
O(3)	0.3098(4)	0.4755(3)	0.1317(6)	0.087(3)	C(31)	0.0573(5)	0.3038(4)	0.6649(8)	0.065(4)
O(4)	0.4618(3)	0.4046(4)	0.3773(7)	0.103(4)	C(32)	0.0988(4)	0.3382(4)	0.6279(7)	0.054(4)
O(11)	0.3319(3)	0.0116(3)	0.6890(5)	0.073(3)	C(33)	0.1409(4)	0.3753(4)	0.2867(7)	0.052(4)
O(12)	0.3969(4)	−0.0261(3)	0.9393(6)	0.087(3)	C(34)	0.1863(5)	0.3643(4)	0.1896(8)	0.071(4)
O(13)	0.3393(3)	−0.0649(3)	0.6694(6)	0.078(3)	C(35)	0.1570(6)	0.3826(5)	0.0563(9)	0.097(6)
O(14)	0.4959(4)	−0.1230(3)	0.9184(7)	0.104(4)	C(36)	0.0838(7)	0.4107(5)	0.0226(9)	0.111(6)
O(20)	0.4954(4)	0.5758(6)	0.3359(9)	0.183(7)	C(37)	0.0364(6)	0.4228(5)	0.115(1)	0.095(6)
O(21)	0.4512(5)	0.9928(5)	0.231(1)	0.178(6)	C(38)	0.0652(5)	0.4041(5)	0.2439(8)	0.069(4)
O(22)	0.4031(4)	0.6461(4)	0.6866(7)	0.117(4)	C(39)	0.2548(4)	0.3006(4)	0.4481(7)	0.054(4)
O(23)	0.6152(9)	0.7839(8)	0.849(2)	0.32(1)	C(40)	0.3168(5)	0.3235(5)	0.456(1)	0.096(6)
N(1)	0.1988(3)	0.6598(3)	0.3362(6)	0.056(3)	C(41)	0.3873(6)	0.2763(6)	0.453(1)	0.133(8)
N(2)	0.3420(4)	0.6341(4)	0.3950(7)	0.070(4)	C(42)	0.3983(6)	0.2031(6)	0.442(1)	0.130(7)
N(3)	0.2064(4)	0.5219(3)	0.3108(6)	0.062(3)	C(43)	0.3396(5)	0.1768(5)	0.432(1)	0.094(5)
N(4)	0.2649(3)	0.5992(4)	0.5625(6)	0.058(3)	C(44)	0.2687(4)	0.2251(4)	0.4372(8)	0.061(4)
N(11)	0.2450(4)	0.1377(3)	0.8146(6)	0.067(3)	C(51)	0.1075(4)	0.8296(4)	0.9998(7)	0.044(3)
N(12)	0.2421(4)	0.0126(4)	0.8587(8)	0.079(4)	C(52)	0.0824(4)	0.7740(4)	0.9093(8)	0.056(4)
N(13)	0.3910(4)	0.1004(4)	0.8518(8)	0.095(4)	C(53)	0.0302(5)	0.7476(4)	0.9349(9)	0.065(4)
N(14)	0.3103(5)	0.1035(4)	1.0661(8)	0.120(5)	C(54)	−0.0000(4)	0.7751(5)	1.0545(9)	0.071(5)
C(1)	0.4011(5)	0.4456(5)	0.3295(9)	0.072(5)	C(55)	0.0220(5)	0.8317(5)	1.1492(9)	0.073(5)
C(2)	0.3847(5)	0.4395(5)	0.1744(9)	0.076(5)	C(56)	0.0746(4)	0.8573(4)	1.1212(8)	0.056(4)
C(3)	0.3981(7)	0.3614(6)	0.103(1)	0.125(7)	C(57)	0.1730(4)	0.9331(4)	1.0786(8)	0.051(4)
C(4)	0.2287(5)	0.7055(5)	0.284(1)	0.087(5)	C(58)	0.2163(5)	0.9299(4)	1.2089(9)	0.074(4)
C(5)	0.2992(5)	0.7078(5)	0.365(1)	0.089(6)	C(59)	0.2148(5)	0.9901(5)	1.309(1)	0.096(5)
C(6)	0.1431(5)	0.6344(5)	0.2280(9)	0.078(5)	C(60)	0.1681(6)	1.0574(5)	1.286(1)	0.091(5)
C(7)	0.1322(5)	0.5702(5)	0.2660(9)	0.077(5)	C(61)	0.1232(5)	1.0629(4)	1.1630(9)	0.073(4)
C(8)	0.1681(4)	0.6961(4)	0.4693(8)	0.066(4)	C(62)	0.1262(4)	1.0014(4)	1.0616(8)	0.060(4)
C(9)	0.2234(5)	0.6767(5)	0.5935(8)	0.068(4)	C(63)	0.1473(4)	0.8762(4)	0.8057(8)	0.049(4)
C(11)	0.4374(5)	−0.0835(5)	0.8663(9)	0.077(5)	C(64)	0.0729(5)	0.9059(5)	0.7514(8)	0.066(4)
C(12)	0.4137(4)	−0.1027(5)	0.7106(9)	0.072(4)	C(65)	0.0520(5)	0.9241(5)	0.6182(9)	0.083(5)
C(13)	0.4201(5)	−0.1837(5)	0.667(1)	0.100(6)	C(66)	0.1069(6)	0.9123(5)	0.5373(9)	0.082(5)
C(14)	0.1841(5)	0.1101(5)	0.7290(9)	0.075(4)	C(67)	0.1781(5)	0.8841(5)	0.5874(9)	0.073(5)
C(15)	0.1711(5)	0.0601(5)	0.805(1)	0.096(6)	C(68)	0.1981(4)	0.8651(4)	0.7178(8)	0.054(4)
C(16)	0.2789(6)	0.1685(5)	0.733(1)	0.089(5)	C(69)	0.2507(4)	0.7958(4)	0.9772(7)	0.046(3)
C(17)	0.3520(6)	0.1715(6)	0.801(1)	0.109(7)	C(70)	0.3157(5)	0.8136(5)	0.9929(9)	0.071(4)
C(18)	0.2195(6)	0.1926(5)	0.942(1)	0.094(5)	C(71)	0.3857(5)	0.7612(6)	1.008(1)	0.091(5)
C(19)	0.2442(9)	0.1645(6)	1.072(1)	0.20(1)	C(72)	0.3905(6)	0.6908(5)	1.006(1)	0.101(6)
C(21)	0.1719(4)	0.4344(4)	0.5595(7)	0.044(3)	C(73)	0.3288(5)	0.6717(5)	0.987(1)	0.080(5)
C(22)	0.1188(4)	0.5000(4)	0.5480(8)	0.055(4)	C(74)	0.2617(4)	0.7225(4)	0.9729(8)	0.056(4)
C(23)	0.1138(5)	0.5626(4)	0.648(1)	0.073(4)	C(80)	0.5572(9)	0.553(1)	0.231(2)	0.22(1)
C(24)	0.1620(5)	0.5610(5)	0.7681(9)	0.082(5)	C(81)	0.424(1)	0.939(1)	0.315(2)	0.25(2)
C(25)	0.2155(5)	0.4976(5)	0.7882(9)	0.082(5)	B(1)	0.1726(5)	0.3579(5)	0.4479(9)	0.045(4)
C(26)	0.2201(5)	0.4357(5)	0.6830(9)	0.068(4)	B(2)	0.1703(5)	0.8579(5)	0.9651(9)	0.045(4)

[a] $U_{eq}=1/3\{\sum_i\sum_j \mathrm{U}_{ij}a_i^{*}a_j^{*}\boldsymbol{a}_i\cdot\boldsymbol{a}_j\}$.

ligand field than an *S*,*N*-chelate complex,[2—4] and thus the red-1 and red-2 complexes are assigned to the *O*-sulfinato complexes. Two *O*-sulfinato complexes from **1** are possible when both linkage and geometrical isomerization occur. We have proposed a mechanism for such isomerization.[5] The red-1 complex is thermally unstable and reverts back to the starting complex **1**, while the red-2 complex is thermally stable. All of these properties have been observed in the two photoproducts of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S*,*O*}(tren)]$^+$ (**2**).[5] Thus, the red-1 and red-2 complexes can be assigned to *trans*(*t*-N,O(S))- and *cis*(*t*-N,O(S))-[Co{OS(O)CH(CH$_3$)COO-*O*,*O*}(tren)]$^+$, respectively. The IR spectrum of the red-2 complex is consistent with a change in the coordination from sulfur to sulfinate oxygen. The strong absorption at 1170 cm^{-1}, due to the sulfur-oxygen asymmetric stretching of the starting complex, is absent in the red-2 complex; instead, a new absorption appears at 950 cm^{-1} attributable to the asymmetric Co–O–S stretching mode. The red-1 complex was not isolated because of its instability.

From the eluate containing the pink band, the complex was isolated as the hexafluorophosphate. (Found: C, 23.97; H, 4.89; N, 12.67%). The absence of sul-

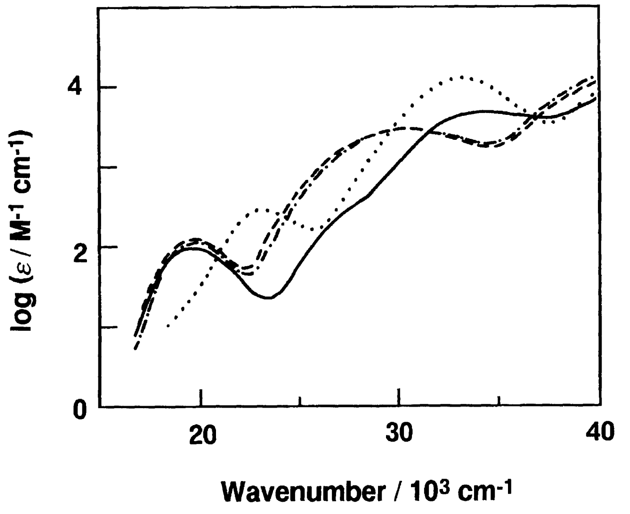


Fig. 1. UV-vis spectra of the starting complex, *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S*,*O*}(tren)]$^+$ (**1**, ····, *t*-N=tertiary amine nitrogen), the peroxide complex, *trans*(*t*-N,O(C))-[Co{OOCH(CH$_3$)COO-*O*,*O*}(tren)]$^+$ (pink, —, O(C) = oxygen of carboxylate group), and the sulfinato-*O* complexes, *trans*(*t*-N,O(S))-[Co{OS(O)CH(CH$_3$)COO-*O*,*O*}(tren)]$^+$ (red-1, - - -, O(S) = oxygen of sulfinate group) and *cis*(*t*-N,O(S))-[Co{OS(O)CH(CH$_3$)COO-*O*,*O*}(tren)]$^+$ (red-2, – • –) in water.

fur was confirmed by the elemental analysis, and the IR spectrum was consistent with the absence of a sulfinate group. The IR spectrum indicated the presence of a coordinated carboxyl group. The ^{1}H and ^{13}C NMR spectra indicated the presence of a methine, a methyl, and a carbonyl group as well as the tren ligand. From these results, we concluded that the pink complex should be either a peroxide complex, [Co{OOCH(CH$_3$)COO-*O*,*O*}(tren)]PF$_6$ (= C$_9$H$_{22}$CoF$_6$N$_4$O$_4$P: C, 23.80; H, 4.88; N, 12.34%) or an alcoholate complex monohydrate, [Co{OCH(CH$_3$)COO-*O*,*O*}(tren)]PF$_6$·H$_2$O (= C$_9$H$_{24}$CoF$_6$N$_4$O$_4$P: C, 23.69; H, 5.30; N, 12.28%). A thermal analysis revealed that there was no weight loss up to 150 °C, indicating the absence of water of crystallization. Figure 1 compares the absorption spectrum of the pink complex with that of the starting complex, *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S*,*O*}(tren)]ClO$_4$ (**1**). The pink complex shows the first d–d absorption band at 513 nm, which is consistent with the CoN$_4$O$_2$ chromophore. Alcoholate complexes are known to show an instantaneous and reversible spectral change with a change in the pH of the solution; this change has been attributed to an acid-base equilibrium of the alcoholic proton.[14] We actually prepared the alcoholate complex, [Co{OCH(CH$_3$)COO-*O*,*O*}(tren)]$^+$, although the geometrical configuration is unknown. This complex consists of a single isomer and shows a reversible spectral change with a change in the pH as expected. The present pink complex does not show such a spectral change in the pH range of 2—9, suggesting that the complex does not involve an alcoholic ligand. Thus, we can assign the pink complex as the peroxide complex.

The above assignment was confirmed by an X-

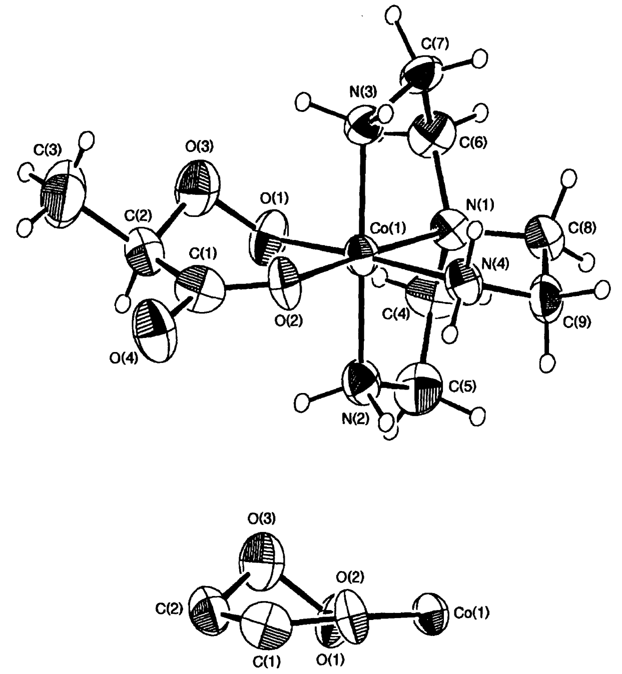


Fig. 2. ORTEP drawing of the pink complex cation, *trans* (*t*-N,O(C))-[Co{OOCH(CH$_3$)COO-*O*,*O*}(tren)]$^+$ (pink, O (C)= oxygen of carboxylate group) and edge-on view of the six membered *O*,*O*-chelate ring.

Table 3. Selected Bond Lengths (*l*/Å) of *trans*(*t*-N,O(C))-[Co{OOCH(CH$_3$)COO-*O*,*O*}(tren)][B(C$_6$H$_5$)$_4$]·CH$_3$OH·H$_2$O (Two Independent Molecules (**a** and **b**) Present in the Unit Cell)

Atom–Atom	**a** (distance)	**b** (distance)	Atom–Atom	**a** (distance)	**b** (distance)
Co(1)–O(1)	1.856(6)	1.849(5)	N(1)–C(6)	1.49(1)	1.49(1)
Co(1)–O(2)	1.899(5)	1.914(5)	N(1)–C(8)	1.50(1)	1.51(1)
Co(1)–N(1)	1.926(6)	1.933(6)	N(2)–C(5)	1.48(1)	1.47(1)
Co(1)–N(2)	1.953(8)	1.950(9)	N(3)–C(7)	1.49(1)	1.51(1)
Co(1)–N(3)	1.919(8)	1.95(1)	N(4)–C(9)	1.47(1)	1.44(2)
Co(1)–N(4)	1.973(6)	1.977(7)	C(1)–C(2)	1.50(1)	1.52(1)
O(1)–O(3)	1.437(8)	1.445(8)	C(2)–C(3)	1.51(1)	1.53(1)
O(2)–C(1)	1.28(1)	1.305(9)	C(4)–C(5)	1.46(1)	1.49(2)
O(3)–C(2)	1.42(1)	1.417(9)	C(6)–C(7)	1.50(2)	1.47(2)
O(4)–C(1)	1.26(1)	1.24(1)	C(8)–C(9)	1.50(1)	1.46(2)
N(1)–C(4)	1.47(1)	1.50(1)			

Table 4. Selected Bond Angles (ϕ/°) of *trans*(*t*-N,O(C))-[Co{OOCH(CH_3)COO-*O*,*O*}(tren)][B(C_6H_5)$_4$]·CH_3OH·H_2O (Two Independent Molecules (**a** and **b**) Present in the Unit Cell)

Atom–Atom–Atom	**a** (angle)	**b** (angle)	Atom–Atom–Atom	**a** (angle)	**b** (angle)
O(1)–Co(1)–O(2)	92.9(2)	92.1(2)	Co(1)–N(1)–C(8)	109.8(5)	109.7(5)
O(1)–Co(1)–N(1)	92.0(3)	91.0(2)	C(4)–N(1)–C(6)	110.8(7)	112.7(7)
O(1)–Co(1)–N(2)	85.1(3)	89.7(3)	C(4)–N(1)–C(8)	113.2(6)	111.2(7)
O(1)–Co(1)–N(3)	89.2(3)	82.7(3)	C(6)–N(1)–C(8)	110.9(7)	110.7(7)
O(1)–Co(1)–N(4)	176.3(3)	177.1(4)	Co(1)–N(2)–C(5)	110.6(6)	111.6(7)
O(2)–Co(1)–N(1)	174.9(2)	176.9(2)	Co(1)–N(3)–C(7)	112.0(6)	111.2(7)
O(2)–Co(1)–N(2)	93.4(3)	95.0(3)	Co(1)–N(4)–C(9)	109.1(5)	111.0(6)
O(2)–Co(1)–N(3)	94.5(3)	93.0(3)	O(2)–C(1)–O(4)	121.3(8)	122.4(8)
O(2)–Co(1)–N(4)	87.7(2)	89.6(3)	O(2)–C(1)–C(2)	122.1(7)	119.6(7)
N(1)–Co(1)–N(2)	85.7(3)	85.7(3)	O(4)–C(1)–C(2)	116.6(7)	118.0(7)
N(1)–Co(1)–N(3)	86.9(3)	86.7(3)	O(3)–C(2)–C(1)	111.1(7)	112.4(6)
N(1)–Co(1)–N(4)	87.3(3)	87.3(3)	O(3)–C(2)–C(3)	105.9(8)	105.8(7)
N(2)–Co(1)–N(3)	170.5(3)	169.2(3)	C(1)–C(2)–C(3)	111.2(8)	111.0(8)
N(2)–Co(1)–N(4)	91.2(3)	92.5(4)	N(1)–C(4)–C(5)	110.2(8)	107.9(7)
N(3)–Co(1)–N(4)	94.4(3)	94.8(4)	N(2)–C(5)–C(4)	109.3(8)	108.9(9)
Co(1)–O(1)–O(3)	108.7(5)	109.4(4)	N(1)–C(6)–C(7)	109.0(7)	111.5(8)
Co(1)–O(2)–C(1)	126.7(6)	127.6(5)	N(3)–C(7)–C(6)	106.9(8)	107(1)
O(1)–O(3)–C(2)	110.0(6)	108.4(6)	N(1)–C(8)–C(9)	111.7(6)	114.4(7)
Co(1)–N(1)–C(4)	106.5(5)	106.3(5)	N(4)–C(9)–C(8)	108.6(6)	112(1)
Co(1)–N(1)–C(6)	105.1(5)	105.9(5)			

ray structure determination of the tetraphenylborate of the pink complex, [Co{OOCH(CH_3)COO}(tren)][B(C_6H_5)$_4$]·CH_3OH·H_2O. The unit cell contains two independent cations with a nearly identical structure. Figure 2 shows a perspective view of one of the cations. Selected bond lengths and angles of the two independent molecules are listed in Tables 3 and 4, respectively. The coordination geometry around the cobalt atom is approximately octahedral. In this complex, the sulfur atom of 2-sulfinatopropionate is lost and 2-peroxidopropionate coordinates to cobalt with the carboxylate and peroxide oxygen atoms. The number of chelate ring members increases from five to six. The tren ligand occupies the remaining four coordination sites. Thus, the X-ray analysis confirms the above assignment. As far as we know, this is the first peroxide complex formed by photodesulfurization. It is noted that not only desulfurization but also geometrical isomerization took place upon photolysis. The relative position of the tertiary amine nitrogen atom of tren to the coordinating carboxylate oxygen atom changed from cis to trans (Scheme 1). The geometrical isomerization will proceed in the same way as that proposed for the geometrical isomerization in the linkage isomerization of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S*,*O*}(tren)]$^+$.[5]

As we showed in a preceding paper,[5] the photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S*,*O*}(tren)]$^+$ (**2**) under the same conditions as those for *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH_3)COO-*S*,*O*}(tren)]$^+$ (**1**) yielded only linkage isomerized sulfinato-*O* complexes, *cis*(*t*-N,O(S))- and *trans*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O*,*O*}(tren)]$^+$. However, on prolonged irradiation a pink peroxide complex was yielded as evidenced by the UV-vis spectrum. The presence of a methyl group in **1** seems to facilitate the formation of a peroxide complex.

The photolysis of [Co{S(O)$_2$CH(CH_3)COO-*S*,*O*}(en)$_2$]ClO_4 (**3**) under the same conditions as for *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH_3)COO-*S*,*O*}(tren)]$^+$ (**1**) yielded three products, the linkage isomerized sulfinato-*O* complex ([Co{OS(O)CH(CH_3)COO-*O*,*O*}(en)$_2$]$^+$), the desulfurized peroxide complex ([Co{OOCH(CH_3)COO-*O*,*O*}(en)$_2$]$^+$), and the sulfite complex ([Co(SO_3)(H_2O)(en)$_2$]$^+$).

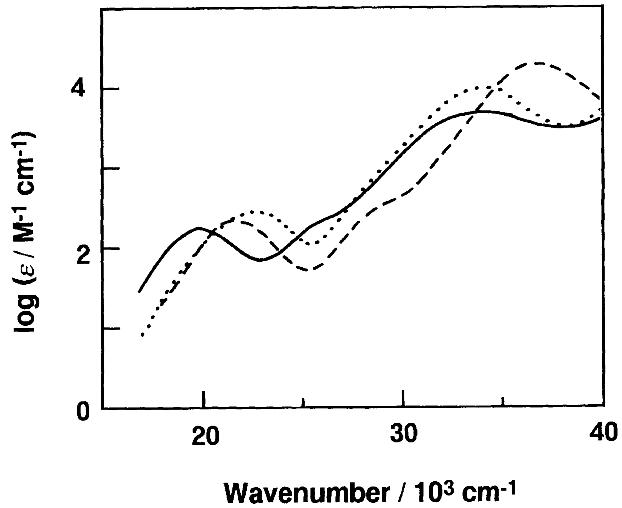


Fig. 3. UV-vis spectra of the starting complex, [Co{S(O)$_2$CH(CH_3)COO-*S*,*O*}(en)$_2$]$^+$ (**3**, ····), the peroxide complex, [Co{OOCH(CH_3)COO-*O*,*O*}(en)$_2$]$^+$ (pink-1, ——), and the sulfito complex, [Co(SO_3)(H_2O)(en)$_2$]$^+$ (yellow-1, - - -) in water.

Figure 3 shows the UV-vis spectra of [Co{S(O)$_2$CH(CH_3)COO-*S*,*O*}(en)$_2$]ClO_4 (the starting complex, **3**), [Co(SO_3)(H_2O)(en)$_2$]$^+$, and [Co{OOCH(CH_3)COO-*O*,*O*}(en)$_2$]$^+$ (pink-1).

Although we have not carried out a mechanistic study, the desulfurization reaction seems to proceed via removal of the sulfinate group; sulfur dioxide elimination is evidenced by the formation of $[Co(SO_3)(H_2O)(en)_2]^+$ in the photolysis of $[Co\{S(O)_2CH(CH_3)COO\text{-}S,O\}(en)_2]^+$ (**3**). The next step may involve a reaction with a dioxygen molecule, leading to the formation of a peroxide complex. Detailed study is required to elucidate the mechanism.

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