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Photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$ (*t*-N=tertiary amine nitrogen; tren=tris(2-aminoethyl)amine). Linkage and Geometrical Isomerization

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On photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$ with visible light, both linkage isomerization (sulfinato-*S* to sulfinato-*O*) and geometrical isomerization (*trans* to *cis*) took place to yield *cis*(*t*-N,O(S))- and *trans*(*t*-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]$^+$ (O(S)=oxygen of sulfinate group).

Cobalt(III) complexes containing sulfinato ligands generally show Co-S bonding. Adamson and co-workers reported the preparation of a cobalt(III) complex containing an *O*-bonded sulfinato ligand by photolysis ($\lambda > 300$ nm) of a sulfinato-*S* complex.1) Recently, decarboxylation of aminocarboxylato-cobalt(III) complexes by irradiation with UV light has been reported to yield organo-cobalt(III) complexes.2) Thus, it must be interesting to study the photolysis of a 2-sulfinatoacetato-*S,O*-cobalt(III) complex, since the ligand contains both sulfinate and carboxylate groups. In this letter, we report the photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$ with visible light, characterization of the products, and X-ray structure analysis of one of the isomers.

An aqueous solution (200 cm^3) of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]ClO$_4$ 3) (0.10 g) was irradiated at *ca.* 5 °C for 25 min with a 400 W high-pressure mercury lamp equipped with a Pyrex glass filter. The reaction mixture was passed through an SE-Toyopearl4) column (ϕ 3.0 cm x 70 cm). A recycling chromatographic technique was employed at 4 °C with an eluent of 0.05 M sodium (+)-tartrate. After ten times of recycling, 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. From the eluate containing the orange band, crystals of the perchlorate of the complex were obtained as the monohydrate by slow evaporation. Found; C, 21.66; H, 5.03; N, 12.57%.

Calcd for $C_8H_{22}ClCoN_4O_9S$=[Co{OS(O)CH_2COO-*O,O*}(tren)]ClO_4·H_2O: C, 21.61; H, 4.99; N, 12.60%. The red complex was also isolated as the perchlorate, however, the complex isolated involved the starting complex (*ca.* 10%) as determined by a high-performance liquid chromatographic (HPLC) method, since the complex thermally reverts to the starting sulfinato-*S* complex (*vide infra*).

The orange complex monohydrate was subjected to X-ray structure analysis. The crystal data are as follows: $C_8H_{20}ClCoN_4O_8S·H_2O$, FW 444.73, monoclinic, *C2/c*, a=23.316(4), b=8.005(1), c=18.631(4) Å, β=108.03(1)°, V=3307(1) $Å^3$, Z=8, Dx=1.786 g cm^{-3}, μ(Mo Kα)=1.37 mm^{-1}. Intensity measurements were carried out for $2\theta \leq 55°$ on a Rigaku AFC5R diffractometer at the X-Ray Laboratory of Okayama University. Among 4194 reflections measured in the range $-30 \leq h \leq 28$, $0 \leq k \leq 10$, $0 \leq l \leq 24$, those of 2503 had $|Io| \geq 3\sigma(|I|)$. The structure was solved by a direct method and refined by a full-matrix least squares procedure to R=0.037 and Rw=0.029 for 2503 unique reflections.[5)]

Figure 1 shows a perspective view of the orange complex cation. In the orange complex cation, the 2-sulfinatoacetato ligand coordinates to cobalt with the two oxygen atoms instead of the sulfur and oxygen atoms in the starting complex, and the number of chelate-ring members increases from five to six. The orange complex has the *cis*(*t*-N,O(S)) structure; geometrical isomerization as well as linkage isomerization took place upon photolysis (Scheme 1).

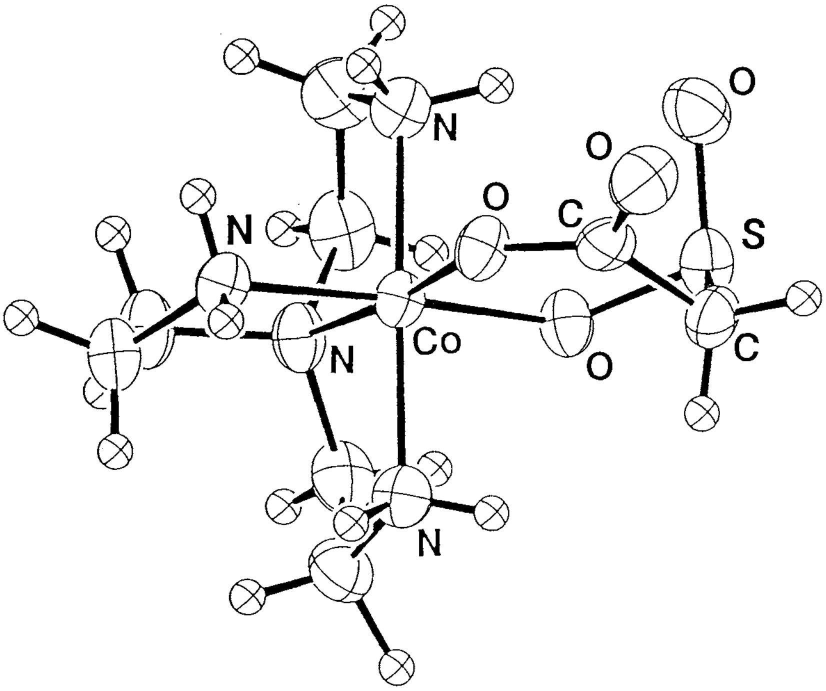
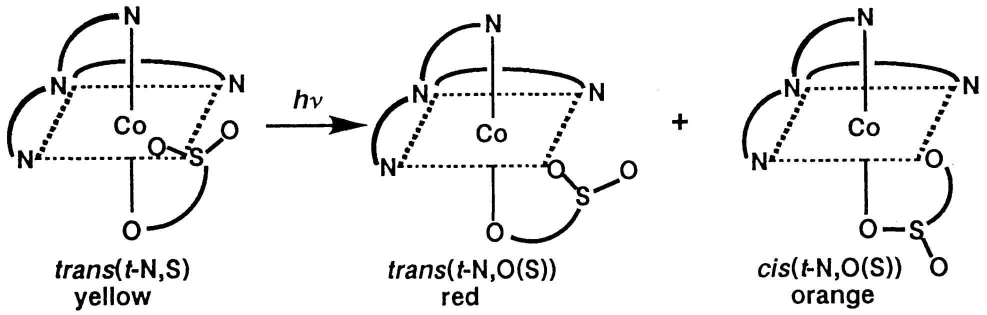


Fig. 1. ORTEP drawing of the orange complex cation, *cis*(*t*-N,O(S))-[Co{OS(O)CH_2COO-*O,O*}(tren)]$^+$ (*t*-N=tertiary amine nitrogen; O(S)=oxygen of sulfinate group).



Scheme 1.

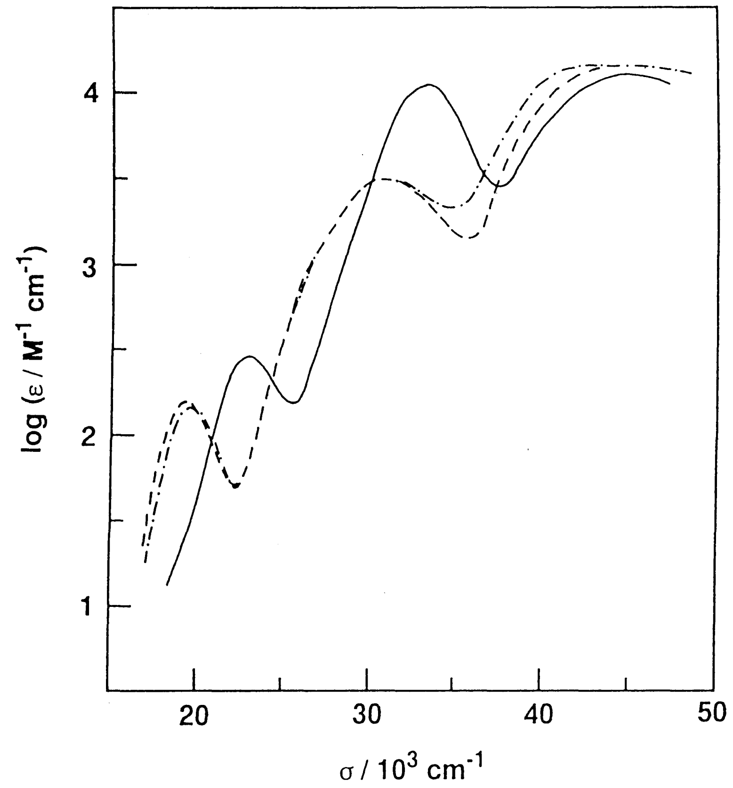


Fig. 2. Absorption spectra of the starting complex, *trans*(t-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$ (——), the orange complex, *cis*(t-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]$^+$ (— • —), and the red complex, *trans*(t-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]$^+$ (– – –).

Figure 2 compares the absorption spectrum of the orange complex, *cis*(t-N,O(S))-[Co{OS(O)CH$_2$COO-*O,O*}(tren)]$^+$ with that of the starting complex, *trans*(t-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$. The *O,O*-chelate orange complex has a much weaker ligand field strength than does the *S,O*-chelate one; the former shows the first d-d absorption band at 512 nm, while that of the latter appears at 435 nm. The intense S→Co charge-transfer (CT) band at 302 nm disappears upon photolysis, and the new band at 325 nm can be assigned to the CT transition from oxygen of the sulfinate moiety to cobalt. Similar differences in the absorption spectra have been reported between $[Co\{S(O)_2CH_2CH_2NH_2\text{-}S,N\}(en)_2]^{2+}$ (en= ethylenediamine) and its photoproduct.[1] The absorption spectrum of the red complex is very similar to that of the orange complex (Fig. 2).[6] This suggests that the red complex is also a linkage isomerized sulfinato-*O* complex. The infrared spectra also support this assignment. The strong absorption at 1190 cm^{-1} in the *S*-bonded starting complex due to the asymmetric sulfur-oxygen stretching is not present in the products, and both orange and red complexes exhibit a new strong absorption at *ca.* 930 cm^{-1} attributable to the Co-O-S stretching mode of an *O*-sulfinato ligand.[1] Since the orange complex has been determined to have the *cis*(*t*-N,O(S)) structure, the red complex can be assigned to the *trans*(*t*-N,O(S))-$[Co\{OS(O)CH_2COO\text{-}O,O\}(tren)]^{+}$ isomer (Scheme 1).

The red complex thermally reverts to the starting complex. The reaction is first order and isosbestic points were observed. The absorption spectrum at infinite time is identical with that of the *S,O*-chelate starting complex. A detailed kinetic study was performed in 0.05 M sodium (+)-tartrate using an HPLC method[7] in the temperature range of 28-70 °C, giving $\Delta H^{\ddagger}=100$ kJ mol^{-1} and $\Delta S^{\ddagger}=-23$ J K^{-1} mol^{-1}. The *O*- to *S*-bonded thermal isomerization has also been reported for $[Co\{OS(O)CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$ [1] and $[Co(CH_3SO_2\text{-}O)(NH_3)_5]^{2+}$.[8] It should be noted that the orange complex is thermally stable, and shows no detectable change in the absorption spectrum and in the chromatogram for at least 360 h at 25 °C.

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5) Full details of X-ray structure determination will be published separately.

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