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Photochemical Reaction of (L-cysteinesulfinato-*N,S*){tris(2-aminoethyl)amine}cobalt(III). Formation of a Cobalt(III) Complex with an Uncoordinated Sulfinate Group

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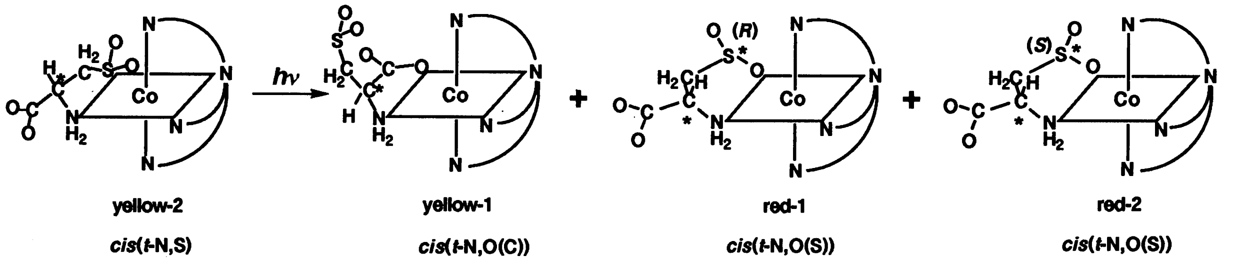
On photolysis of *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(tren)]$^{2+}$ (*t*-N= tertiary amine nitrogen; tren=tris(2-aminoethyl)amine) with visible light two types of linkage isomerization took place to yield *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$)COO-*N,O*}(tren)]$^+$ (O(C)=oxygen 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)]$^{2+}$ (O(S)=oxygen of sulfinate group).

S-bonded sulfinato cobalt(III) complexes isomerize to *O*-bonded sulfinato ones when irradiated with visible light.$^{1-5)}$ The L-cysteinesulfinate(2-) ligand, NH$_2$CH(CH$_2$SO$_2^-$)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. However, photolysis of [Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(en)$_2$]$^{2+}$ (en=ethylenediamine) has been reported to result in a nearly quantitative conversion to the thermodynamically less stable sulfinato-*O* complex (*O,N*-chelation).$^{2)}$ In this letter, we report that on photolysis of [Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(tren)]$^{2+}$ two types of linkage isomerization take place to yield *cis*(*t*-N,O(C))-[Co{NH$_2$CH(CH$_2$SO$_2$)COO-*N,O*}(tren)]$^+$ and *cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O,N*}(tren)]$^{2+}$.

The starting L-cysteinesulfinato-*S,N* complex, *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH(COOH)NH$_2$-*S,N*}(tren)]-(ClO$_4$)$_2$ was prepared by oxidizing the corresponding L-cysteine-*S,N* complex$^{6)}$ with H$_2$O$_2$. About 0.3 g of the complex was dissolved in 500 cm^3 of water, pH of the solution being *ca.* 4. This solution was irradiated at 5 °C for 90 min with a 400 W high-pressure mercury lamp (internal irradiation type) fitted with a Pyrex glass filter. The reaction mixture was neutralized with an aqueous solution of Na$_2$CO$_3$ and then passed through an SP-Sephadex C-25 column (ϕ5 cm x 80 cm). A recycling chromatographic technique was employed at 5 °C with an eluent of 0.1 M Na$_2$SO$_4$. After three times of recycling, 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 slowest moving red-3 complex seemed to be a highly charged species. From the eluate containing the yellow-1 band, crystals of the complex perchlorate were obtained. Found: C, 18.49; H, 4.05; N, 11.94; S, 5.58%. Calcd for C$_9$H$_{23}$Cl$_2$CoN$_5$NaO$_{12}$S=[Co{NH$_2$CH(CH$_2$SO$_2$)COO}{N(CH$_2$CH$_2$NH$_2$)$_3$}]ClO$_4$·NaClO$_4$: C, 18.69; H, 4.02; N, 12.11; S, 5.54%. The IR spectrum of the yellow-1 complex shows a strong absorption at 1650 cm^{-1} attributable to the coordinated COO stretching band.[7)] The yellow-1 complex shows the first d-d absorption band at the same position (470 nm) as *cis*(*t*-N,O(C))-[Co{$NH_2CH(CH_2SCH_3)COO$-*N,O*}(tren)]$^{2+}$ and *cis*(*t*-N,O(C))-[Co(NH_2CH_2COO-*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).[6,7)] From these data, the yellow-1 complex can be assigned to *cis*(*t*-N,O(C))-[Co{NH_2CH-$(CH_2SO_2)COO$-*O,N*}(tren)]$^+$; linkage isomerization from sulfinato-*S* to carboxylato-*O* is suggested (Scheme 1). This assignment was confirmed by the X-ray structure determination.

A yellow orange prismatic crystal of approximate dimensions of 0.23 x 0.23 x 0.43 mm^3 was used for X-ray structure analysis. The crystal data are as follows: $C_9H_{23}ClCoN_5O_8S{\cdot}NaClO_4$, FW 578.20, triclinic, *P*1, a=8.801(3), b=8.894(7), c=6.781(2) Å, α=92.26(4), β=91.30(3), γ=70.50(4)°, V=499.9(8) $Å^3$, Z=1, Dx=1.920 g cm^{-3}, μ=1.315 mm^{-1} for Mo $K\alpha$ (λ=0.7107 Å). Intensity measurements were carried out for



Scheme 1.

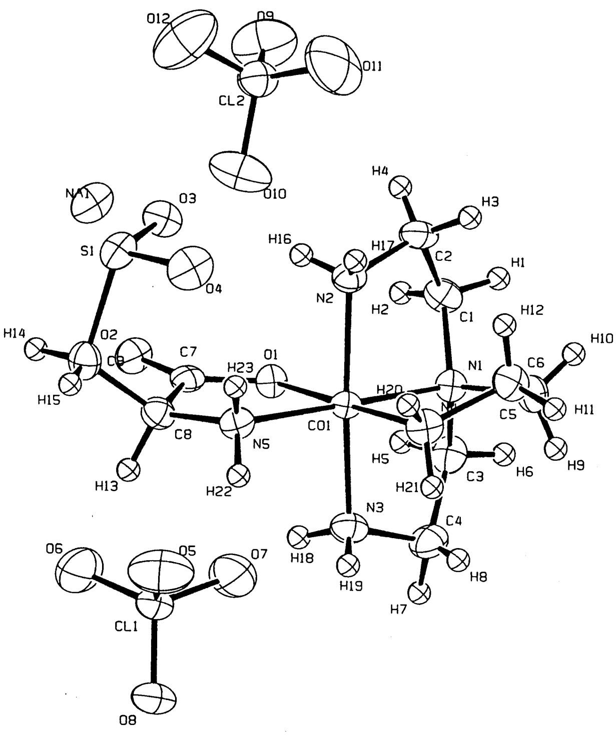


Fig. 1. ORTEP drawing of the yellow-1 complex, *cis*(*t*-N,O(C))-[Co{$NH_2CH(CH_2SO_2)COO$-*N,O*}(tren)]-$ClO_4{\cdot}NaClO_4$ (*t*-N= tertiary amine nitrogen; O(C)= oxygen of carboxylate group).

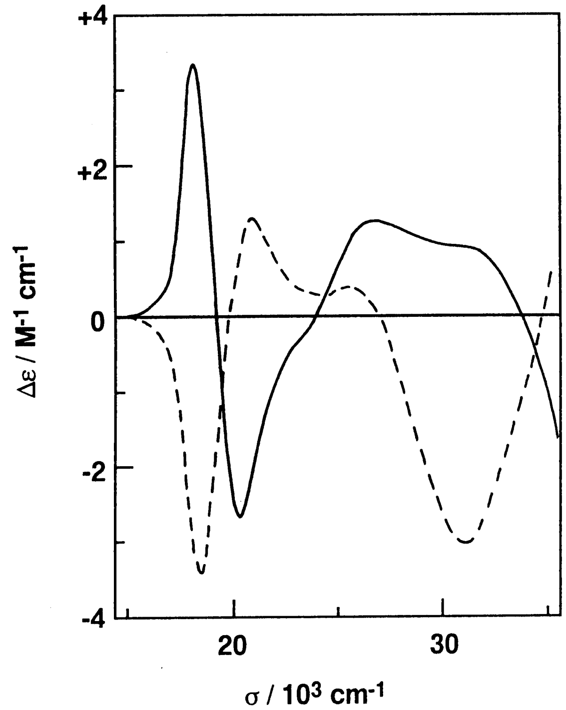


Fig. 2. CD spectra of the red-1 complex, (*R*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (——),11) and the red-2 complex, (*S*)-*cis*(*t*-N,O(S))-[Co{OS(O)CH$_2$CH(COOH)NH$_2$-*O*,*N*}(tren)]$^{2+}$ (– – –).

$2\theta \leq 55$ ° on a Rigaku AFC-5R diffractometer at the X-Ray Laboratory of Okayama University. Among 2496 reflections (2300 were unique) measured in the range $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $0 \leq l \leq 8$, those of 2200 had $I \geq 3\sigma(I)$. The structure was solved by a direct method and refined by a full-matrix least squares procedure to R=0.020 and R_w=0.021.8)

Figure 1 shows a perspective view of the yellow-1 complex. In this complex, the L-cysteinesulfinate ligand coordinates to cobalt with the carboxylate oxygen atom and the nitrogen atom instead of the sulfur and nitrogen atoms in the starting complex. As far as we know, this is the first cobalt(III) complex which has a free sulfinate group.

The red-2 complex was isolated as the bromide. Found: 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$_2$CH(COOH)NH$_2$}{N(CH$_2$CH$_2$NH$_2$)$_3$}]Br$_2$: C, 20.90; H, 4.68; N, 13.54; S, 6.20%. The IR and absorption spectra of the red-2 complex are in agreement with the change of coordination from sulfur to sulfinate oxygen.1,9) For example, the red-2 complex shows the first d-d absorption band at 503 nm, while that of the starting complex appears at 446 nm. We tried to isolate the red-1 complex. However, the CD spectrum showed that the complex isolated was contaminated with the red-2 complex, suggesting that the red-1 complex was thermally unstable and isomerized to the red-2 complex (*vide infra*). Thus, the eluate containing the red-1 band was used for spectral measurements. The absorption spectrum of the red-1 complex is very similar to that of the red-2 complex. This suggests that the red-1 complex is also an *O*-bonded sulfinato complex. Since the sulfur atom becomes chiral (*R* and *S*) upon linkage isomerization (Scheme 1)3,5,10) and there is an asymmetric carbon atom (*R*), a pair of diastereomers are possible for the L-cysteinesulfinato-*O* complex. The presence of two isomers is also in agreement with linkage isomerization from sulfinato-*S* to sulfinato-*O*. Figure 2 compares the CD spectra of the red-1 and red-2 complexes.11) Although the optical activity of the complexes originates from two chiral centers, the fact that the CD spectra are almost enantiomeric to each other (Fig. 2) suggests that the CD contribution from the chiral sulfur atom dominates over that from the carbon atom. The CD spectrum of the red-2 complex is similar to that of (*S*)-*cis*(*t*-N,O)-$[Co\{OS(O)CH_2CH_2NH_2\text{-}O,N\}(tren)]^{2+}$,5) and the absolute configuration about the sulfur atom for the red-2 complex is assigned to (*S*). The red-1 complex can be assigned to have the (*R*)-sulfur atom in a similar manner. Generally, *O*-bonded sulfinato complexes are thermally unstable and revert back to the *S*-bonded species.1,2) However, the red-1 and red-2 complexes are stable toward a thermal back-reaction. The red-1 complex changes to the red-2 complex, while the red-2 complex remains unchanged. At 56 °C, the CD spectrum of the red-1 complex became almost identical to that of the red-2 complex in 36 h. A slow CD change was observed for the red-1 complex even at 5 °C. Similar thermal stability to the red-1 complex has been observed for *cis*(*t*-N,O)-$[Co\{OS(O)CH_2CH_2NH_2\text{-}O,N\}(tren)]^{2+}$; 5) the latter complex is also stable toward a thermal back-reaction and undergoes racemization at the chiral sulfur center.

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