Photochemical Desulfurization of a Sulfinato-*S*-Cobalt(III) Complex. Formation of an Organic Peroxide Complex

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The photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S,O*}(tren)]$^+$ (*t*-N=tertiary amine nitrogen; tren=tris(2-aminoethyl)amine) with visible light induced desulfurization to yield an organic peroxide complex, *trans*(*t*-N, O(C))-[Co{OOCH-(CH$_3$)COO-*O,O*}(tren)]$^+$, (O(C)=oxygen of carboxylate group) the structure of which was determined by X-ray analysis.

In the preceding paper,[1] we reported that during the photolysis of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*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$_2$COO-*O,O*}(tren)]$^+$ (O(S)= oxygen of sulfinate group). Here we report the formation of a new type of organic peroxide-cobalt(III) complex through desulfurization upon photolysis of a closely related sulfinate-*S*-cobalt(III) complex, *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S,O*}(tren)]$^+$. Although there are several reports[2] of the photochemical insertion of molecular oxygen into the Co-C bond of an organocobaloxime yielding a peroxide complex, Co^{III}-O-O-R, the formation mechanism of the present complex might be different from the reported ones.

The photolysis was carried out in the same way as for *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]ClO$_4$.[1] An aqueous solution (200 cm^3) of *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S,O*}(tren)]ClO$_4$[3] (0.10 g) was irradiated at *ca.* 5 °C for 25 min using a 400 W high-pressure mercury lamp (internal irradiation type) equipped with a Pyrex glass filter. Isosbestic points were retained throughout the reaction. The irradiated solution was passed through a recycling chromatographic column (ø1.5 cm x 70 cm) of SE-Toyopearl.[5] After three recyclings at 5 °C (eluent: 0.05 M sodium (+)-tartrate), three bands, pink, yellow, and red, were separately eluted in this order, and the eluates containing the two faster eluted bands were separately collected. 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 red-1 and red-2 complexes can be assigned as linkage isomerized sulfinato-*O* complexes on the basis of the UV-Vis spectra.[1,6] The red-2 complex is thermally stable, while the red-1 complex thermally reverts to the starting complex. All these properties have been also observed in the two photoproducts of *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]$^+$.[1] 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.

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 sulfur was confirmed by the elemental analysis, and the IR spectrum was consistent with the absence of a sulfinate 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$_{22}$CoN$_4$F$_6$O$_4$P: C, 23.80; H, 4.88; N, 12.34%) or an alcoholate complex, [Co{OCH(CH$_3$)COO-*O,O*}(tren)]PF$_6$·H$_2$O (=C$_9$H$_{24}$CoN$_4$F$_6$O$_4$P: C, 23.69; H, 5.30; N, 12.28%). 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$_4$. 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, and the changes have been attributed to an acid-base equilibrium of the alcoholic proton.[7] 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 one. Although we tried to determine the structure using X-ray analysis, it was difficult to reduce the *R* value because of poor crystallinity. By converting the hexafluorophosphate into the tetraphenylborate, we could obtain crystals suitable for X-ray structure analysis.[8]

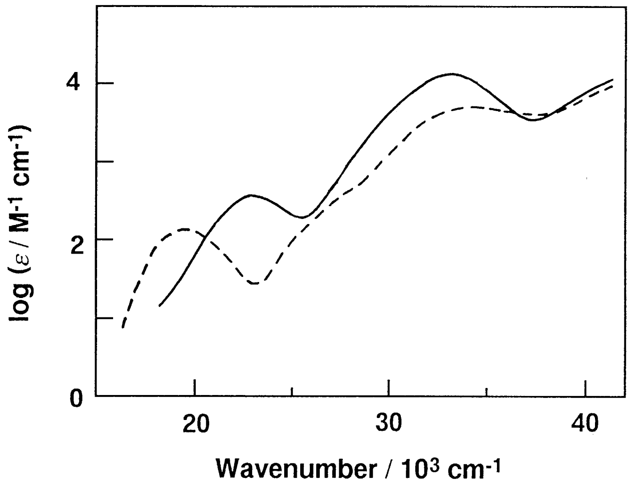
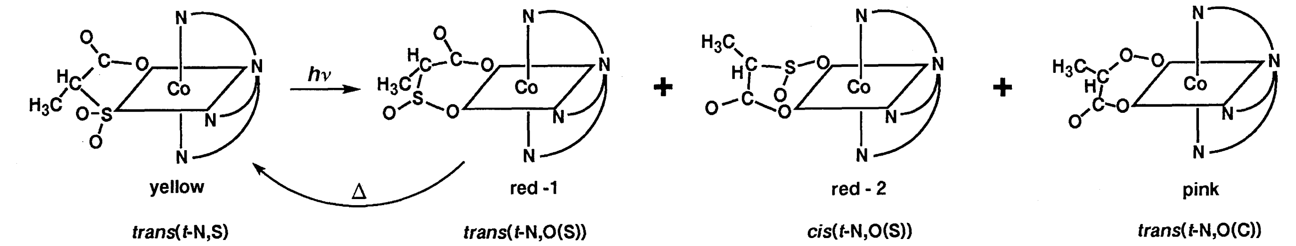


Figure 1. UV-Vis spectra of the starting complex, *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH$_3$)COO-*S,O*}(tren)]$^+$ (—, *t*-N=tertiary amine nitrogen) and *trans*(*t*-N,O(C))-[Co{OOCH(CH$_3$)COO-*O,O*}-(tren)]$^+$ (- - -, O(C)=oxygen of carboxylate group).

Figure 2 shows a perspective view of the pink complex cation.[9] 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 tren ligand occupies



Scheme 1.

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 mechanistic study is now under way.

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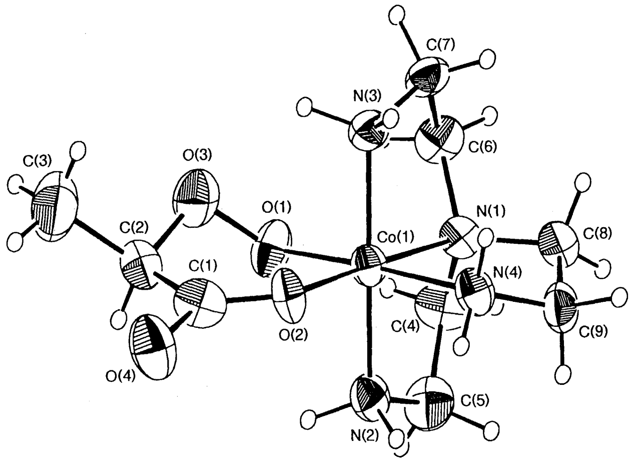

Figure 2. An ORTEP drawing for the complex cation, *trans*(*t*-N,O(C))-[Co{OOCH(CH_3)COO-*O,O*}(tren)]$^+$. Selected bond distances (Å) and bond angles (°): Co-O1 1.844(8), Co-O2 1.892(6), Co-N1 1.939(7), Co-N2 1.95(1), Co-N3 1.92(1), Co-N4 1.973(9), O1-O3 1.44(1), O3-C2 1.44(1), C1-C2 1.51(2), O2-C1 1.25(1), C2-C3 1.54(2), O4-C1 1.28(1), O1-Co-O2 94.5(3), Co-O1-O3 108.4(6), O1-O3-C2 109.3(8), O3-C2-C1 110.7(9), O2-C1-C2 122.9(9), Co-O2-C1 126.0(8).

References and Notes

1 F. MD. Akhter, M. Kojima, T. Yoshii, S. Kashino, and Y. Yoshikawa, *Chem. Lett.*, **1994**, 171.

2 B. D. Gupta and S. Roy, *Inorg. Chim. Acta*, **108**, 261 (1985) and references therein.

3 *trans*(*t*-N,S)-[Co{S(O)$_2$CH(CH_3)COO-*S,O*}(tren)]ClO$_4$ was prepared by the same method as that for *trans*(*t*-N,S)-[Co{S(O)$_2$CH$_2$COO-*S,O*}(tren)]ClO$_4$.[4]

4 M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 2958 (1983).

5 M. Fujita, Y. Yoshikawa, and H. Yamatera, *Chem. Lett.*, **1982**, 437.

6 H. Mäcke, V. Houlding, and A. W. Adamson, *J. Am. Chem. Soc.*, **102**, 6889 (1980).

7 T. Nishide, K. Ogino, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **47**, 3057 (1974).

8 Crystal data for [Co{OOCH(CH_3)COO}(tren)]B(C_6H_5)$_4$·CH_3OH·H_2O: $C_{34}H_{48}BCoN_4O_6$, FW 678.52, triclinic, $P\bar{1}$ (No. 2), a=19.558(6), b=19.816(6), c=9.991(4) Å, α= 103.71(3), β=102.17(3), γ=70.26(2) °, V=3504(2) Å^3, Z= 4, D_x=1.29 g cm^{-3}, μ=0.533 mm^{-1} for Mo $K\alpha$ radiation (λ=0.71073 Å). Intensity measurements were carried out on a Rigaku AFC-5R diffractometer. Among 5821 reflections measured in the range $0 \leq h \leq 18$, $-19 \leq k \leq 19$, $-9 \leq l \leq 9$, those of 3953 had $|F_o| > 3\sigma(|F_o|)$. The structure was solved by a direct method (SHELXS 86) and the subsequent Fourier synthesis. The refinement by a full-matrix least squares procedure using the Xtal 3.2 software converged to R=0.071 and R_w=0.089. Full details of X-ray structure determination will be published separately.

9 The unit cell contains two independent complex cations with nearly identical structure, and Figure 2 shows the structure of one of the cations.