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A Photochemically Prepared *O*-Bonded Sulfinato Complex of Cobalt(III). Optical Resolution and X-Ray Structure of (2-Aminoethanesulfinato-*O*,*N*) [tris(2-aminoethyl)amine]cobalt(III)

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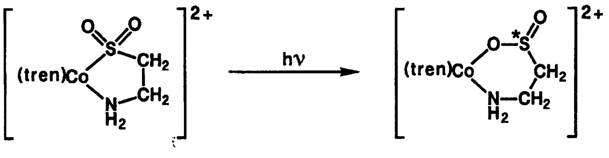
(Received September 13, 1993)

Synopsis. The *cis*(*t*-N, O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}{N(CH$_2$CH$_2$NH$_2$)$_3$}]$^{2+}$ (*t*-N=*tertiary* amine nitrogen) complex was prepared by photolysis of the corresponding *S*,*N*-chelate sulfinato complex. The structure of the linkage-isomerized product was determined by the X-ray method. Optical resolution of the *O*,*N*-chelate complex was achieved by SP-Sephadex column chromatography, and the racemization of the complex was studied.

Most cobalt(III) complexes containing a sulfinato ligand show Co–S bonding. Recently, Adamson and co-workers[1,2] reported linkage isomerization from Co–S to Co–O in the photolysis of [Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(en)$_2$]$^{2+}$ (en=ethylenediamine). A similar photoisomerization is expected for [Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(tren)]$^{2+}$ (tren = tris(2-aminoethyl)amine). The sulfur atom becomes chiral upon photoisomerization, and the product, [Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$, seems to be suited for a kinetic study of racemization around the sulfur atom (Scheme 1).

We report here on the photochemical preparation of *cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$, its X-ray structure, and the optical resolution and racemization of the complex.



Scheme 1.

Experimental

Measurements. Absorption (AB) and circular dichroism (CD) spectra were recorded on a JASCO Ubest-30 spectrophotometer and a JASCO J-500A spectropolarimeter, respectively. ^{13}C NMR spectra were measured with a Varian VXR-500 spectrometer.

Preparation of *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(tren)](ClO$_4$)$_2$. This complex was prepared by oxidation of the corresponding thiolato complex. To a suspension of *cis*(*t*-N,S)-[Co(SCH$_2$CH$_2$NH$_2$-*S*,*N*)(tren)](ClO$_4$)$_2$[3] (1.6 g, 3.3 mmol) in 0.1 M HClO$_4$ (30 cm^3, 1 M=1 mol dm^{-3}) was added 35% H$_2$O$_2$ (1.8 g, 18 mmol) in 0.1 M HClO$_4$ (20 cm^3) dropwise with stirring. The color of the solution changed from brown to yellow, and the starting material dissolved completely by a reaction with hydrogen peroxide. The mixture was left overnight at room temperature, and then evaporated under reduced pressure to ca. 10 cm^3. NaClO$_4$ was added to the concentrate to yield yellow crystals, which were collected by filtration and washed with methanol. Yield: 1.0 g, Found: C, 18.43; H, 4.67; N, 13.34%. Calcd for C$_8$H$_{24}$Cl$_2$CoN$_5$O$_{10}$S: C, 18.76; H, 4.72; N, 13.67%. A piece of the crystal was used for the X-ray diffraction study.

Photolysis of *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(tren)](ClO$_4$)$_2$. An aqueous solution (150 cm^3) of *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(tren)](ClO$_4$)$_2$ (0.40 g, 0.78 mmol) was irradiated at ca. 5 °C for 60 min by a 400-W high-pressure mercury lamp (internal irradiation type) fitted with a Pyrex glass filter. The color of the solution changed from yellow to red. Photolysis resulted in a nearly quantitative conversion to the *O*,*N*-chelate sulfinato complex. The solvent was evaporated to dryness under reduced pressure to yield a red solid. It was recrystallized from hot water. Found: C, 18.18; H, 4.92; N, 13.25%. Calcd for C$_8$H$_{26}$Cl$_2$CoN$_5$O$_{11}$S=[Co{OS(O)CH$_2$CH$_2$NH$_2$–*O*,*N*}(tren)](ClO$_4$)$_2$·H$_2$O: C, 18.12; H, 4.94, N, 13.21%.

Optical Resolution of *cis*(*t*-N, O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$ and Racemization of the Complex. *cis*(*t*-N, O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)](ClO$_4$)$_2$·H$_2$O (ca. 70 mg) was charged at the top of an SP-Sephadex C-25 column (ϕ 2.7 cm×120 cm). Upon elution with 0.1 M K$_2$[Sb$_2${(+)-tartrate}$_2$], the band showed an indication of resolution. The initial and final fractions with a constant dissymmetry factor ($\Delta\varepsilon/\varepsilon$) were collected. Each of the fractions was diluted with water, poured again onto a small column (ϕ1.5 cm×7.0 cm), and the adsorbed complex was eluted with 1.0 M NaClO$_4$. The eluates were used for spectral measurements and a racemization study. Optically active *cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$ was racemized in 1.0 M NaClO$_4$ at 70 °C, and the decrease in CD strength at 540 nm was recorded. A plot of ln ($\Delta\varepsilon_t$(540 nm)) vs. time gave a straight line for at least three half-lives, where $\Delta\varepsilon_t$(540 nm) denotes the CD strength at time *t* and at 540 nm. No detectable change in the absorption spectrum was observed during the racemization.

Crystal Structure Determination. A red prismatic crystal having dimensions of 0.2×0.2×0.5 mm^3 was used for the measurement. Crystal data: C$_8$H$_{24}$Cl$_2$CoN$_5$O$_{10}$S·H$_2$O, FW 530.2, monoclinic $P2_1/n$, a=17.272(2), b=7.666(2), c=16.304(2) Å, β=113.81(1)°, V=1975(8) Å^3, Z=4, D_x=1.78 g cm^{-3}, μ(Mo $K\alpha$)=13.01 cm^{-1}. Diffraction data were collected to 2θ=50° using graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) and the θ–2θ scan mode (scan range; 0.80+0.35 tan θ/°) on an Enraf Nonius CAD-4 diffractometer. Lattice constants were determined from 25

2θ reflections ($22<2\theta<29°$). Three standard reflections were monitored every 2 h and showed no detectable changes during the data collection. The intensities were corrected for both Lorentz and polarization effects, and an empirical absorption correction was applied. All of the calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS-III.[4] The location of cobalt was determined by direct methods with MULTAN 78;[5] the other non-hydrogen atoms were found by the usual Fourier methods. Among the 5786 $\pm h$, $+k$, $+l$ reflections measured, 4311 had $|F_o|>3\sigma(|F_o|)$. The structure was refined to R=0.054 and R_w=0.065. The atomic parameters of the non-hydrogen atoms are listed in Table 1.[6]

Results and Discussion

Figure 1 shows a perspective view of *cis*(*t*-N,O)-[Co{OS(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$. Selected bond lengths and angles are listed in Table 2. The coordination geometry around the cobalt atom is approximately octahedral. The 2-aminoethanesulfinato ligand coordinates to cobalt with the oxygen and nitrogen atoms instead of the sulfur and nitrogen atoms in the starting complex, *cis*(*t*-N,S)-[Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(tren)]$^{2+}$. The geometrical configuration of the starting complex is retained, and the product has a *cis*(*t*-N,O) structure. The sulfur–oxygen bond lengths, S–O1 (1.540(3) Å) and S–O2 (1.496(4) Å), are longer than those in [Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-*S*,*N*}(en)$_2$]ClO$_4$·NO$_3$ (1.456(4) and 1.476(4) Å).[7] The seleninato complex formed by the oxidation of [Co{SeCH$_2$CH$_2$NH$_2$-*Se*,*N*}(en)$_2$]$^{2+}$ has been shown, in contrast to the related sulfinato complex, to have Co–O bonding, [Co{OSe(O)CH$_2$CH$_2$NH$_2$-*O*,*N*}(en)$_2$]$^{2+}$.[8] The six-membered *O*,*N*-chelate ring in the present photoproduct adopts a distorted chair conformation, and the conformation is similar to that in the seleninato-*O*,*N* complex. The Co–O1 bond length (1.925(3) Å) is almost the same as that in the seleninato-*O*,*N* complex (1.922(4) Å).

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($B_{\mathrm{eq}}=4/3\{\sum_i\sum_j Bij\boldsymbol{a}_i\cdot\boldsymbol{a}_j\}$)

Atom	x	y	z	B_{eq}/Å^2
Co	7592.2(3)	1633.6(5)	5270.7(3)	2.2
S1	6866 (1)	5181 (1)	5649 (1)	3.6
O1	7353 (2)	3451 (3)	5949 (2)	2.9
O2	7326 (2)	6328 (3)	5252 (2)	4.4
N1	8656 (2)	1207 (4)	6303 (2)	3.1
N2	7072 (2)	115 (4)	5873 (2)	3.5
N3	8229 (2)	3266 (4)	4862 (2)	3.1
N4	7894 (2)	−359 (4)	4706 (2)	3.7
N5	6531 (2)	1984 (4)	4197 (2)	3.3
C1	8430 (3)	849 (5)	7074 (2)	3.7
C2	7706 (3)	−417 (6)	6782 (3)	4.4
C3	9157 (2)	2849 (6)	6432 (3)	4.2
C4	9114 (2)	3457 (6)	5544 (3)	4.3
C5	9100 (3)	−346 (7)	6129 (3)	5.1
C6	8790 (3)	−723 (6)	5152 (3)	4.9
C7	5937 (3)	4490 (6)	4691 (3)	4.2
C8	6149 (2)	3738 (5)	3959 (3)	3.8
Cl1	6700 (1)	1555 (1)	1940 (1)	4.0
Cl2	4763 (1)	−1061 (1)	3471 (1)	4.0
O3	7347 (3)	1512 (6)	1621 (3)	7.3
O4	6015 (3)	645 (8)	1272 (4)	11.2
O5	6371 (3)	3223 (5)	1965 (4)	9.8
O6	6963 (4)	693 (10)	2741 (3)	13.8
O7	4544 (3)	728 (5)	3502 (3)	7.0
O8	5569 (3)	−1290 (6)	4126 (5)	14.1
O9	4818 (5)	−1417 (7)	2679 (4)	13.6
O10	4221 (3)	−2225 (6)	3614 (4)	9.9
O11	6027 (2)	−3131 (5)	1447 (2)	6.5

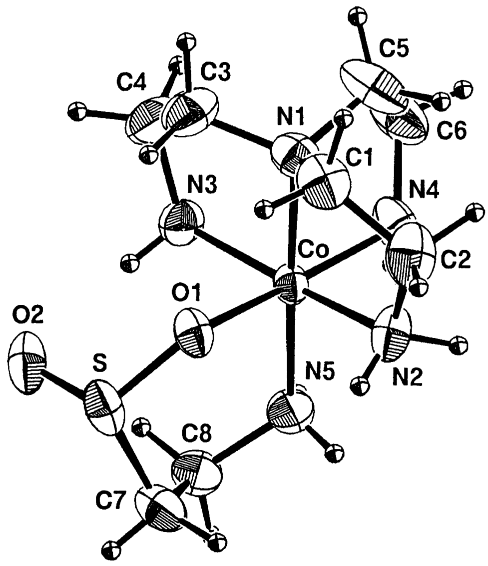


Fig. 1. Perspective view of *cis*(*t*-N,O)-[Co{OS(O)-CH$_2$CH$_2$NH$_2$-*O*,*N*}(tren)]$^{2+}$.

Table 2. Selected Bond Lengths (l/Å) and Bond Angles (ϕ/°)

Co–O(1)	1.925(3)	Co–N(1)	1.955(3)
Co–N(2)	1.959(3)	Co–N(3)	1.952(3)
Co–N(4)	1.960(4)	Co–N(5)	1.976(3)
S–O(1)	1.540(3)	S–O(2)	1.496(4)
S–C(7)	1.809(5)	N(1)–C(1)	1.485(5)
N(1)–C(3)	1.493(6)	N(1)–C(5)	1.504(6)
N(2)–C(2)	1.500(6)	N(3)–C(4)	1.490(6)
N(4)–C(6)	1.447(6)	N(5)–C(8)	1.479(5)
C(1)–C(2)	1.500(7)	C(3)–C(4)	1.494(7)
C(5)–C(6)	1.490(7)	C(7)–C(8)	1.497(6)
O(1)–Co–N(1)	88.4(1)	O(1)–Co–N(2)	83.9(1)
O(1)–Co–N(3)	90.8(1)	O(1)–Co–N(4)	173.6(1)
O(1)–Co–N(5)	94.2(1)	N(1)–Co–N(2)	86.0(1)
N(1)–Co–N(3)	86.4(1)	N(1)–Co–N(4)	86.5(1)
N(1)–Co–N(5)	177.4(1)	N(2)–Co–N(3)	170.9(1)
N(2)–Co–N(4)	92.0(2)	N(2)–Co–N(5)	94.4(1)
N(3)–Co–N(4)	92.6(1)	N(3)–Co–N(5)	93.4(1)
N(4)–Co–N(5)	100.1(1)		

Figure 2 compares the absorption spectrum of *cis*(*t*-N,O)-[Co{OS(O)$CH_2CH_2NH_2$-*O*,*N*}(tren)]$^{2+}$ with that of *cis*(*t*-N,S)-[Co{S(O)$_2CH_2CH_2NH_2$-*S*,*N*}(tren)]$^{2+}$. The *S*,*N*-chelate complex has a much stronger ligand field strength than does the *O*,*N*-chelate complex; the former shows the first d–d absorption band at 446 nm, while that of the latter appears at 502 nm. The intense S→Co charge-transfer (CT) band at 298 nm disappears upon photolysis, and a new band at 320 nm can be assigned to the CT transition from O to Co. Similar differences in the absorption spectra have been reported between [Co{S(O)$_2CH_2CH_2NH_2$-*S*,*N*}(en)$_2$]$^{2+}$ and its photoproduct.1)

Figure 2 also shows the CD spectrum of $(+)^{\mathrm{CD}}_{545}$-*cis*(*t*-N,O)-[Co{OS(O)$CH_2CH_2NH_2$-*O*,*N*}(tren)]$^{2+}$, obtained from the final fraction in SP-Sephadex column chromatography (eluent: 0.1 M $K_2[Sb_2\{(+)\text{-tartrate}\}_2]$. The optical activity of the complex originates from only the chiral sulfur atom of the 2-aminoethanesulfinato ligand, and the spectrum represents the vicinal effect of a chiral sulfur atom in a [$CoON_5$]-type complex. The CD spectrum in Fig. 2 is similar to the calculated vicinal CD curve for the (*R*)-sulfur atom derived from the CD spectra of Λ(*R*)- and Λ(*S*)-[Co{OS(O)$CH_2CH_2NH_2$-*O*,*N*}(en)$_2$]$^{2+}$.9) Thus, $(+)^{\mathrm{CD}}_{545}$-*cis*(*t*-N,O)-[Co{OS(O)-$CH_2CH_2NH_2$-*O*,*N*}(tren)]$^{2+}$ can be assigned to the (*R*)-isomer. The complex slowly loses its optical activity; a kinetic study of the racemization was performed by observing the change in the CD strength at 540 nm (Experimental). The rate constant was calculated to be 1.9×10^{-5} s^{-1} at 70 °C in 1.0 M $NaClO_4$. Although *cis*(*t*-N,O)-[Co{OS(O)$CH_2CH_2NH_2$-*O*,*N*}(tren)]$^{2+}$ undergoes racemization, the complex is stable toward a thermal back-reaction; no detectable change in the absorption spectrum was observed during the racemization (35 h at 70 °C). It should be noted that [Co{OS-(O)$CH_2CH_2NH_2$-*O*,*N*}(en)$_2$]$^{2+}$ reverts thermally to the starting *S*,*N*-chelate complex (3.23×10^{-7} and 2.31×10^{-5} s^{-1} at 28 and 67 °C, respectively),1,10) and also undergoes racemization at the chiral sulfur atom (2.46×10^{-6} s^{-1} at 19 °C),9,11) the latter process being faster than the former. The difference in stability to a thermal back-reaction between *cis*(*t*-N,O)-[Co{OS(O)$CH_2CH_2NH_2$-*O*,*N*}(tren)]$^{2+}$ and [Co{OS-(O)$CH_2CH_2NH_2$-*O*,*N*}(en)$_2$]$^{2+}$ may be explained by considering the difference in the intramolecular steric repulsion between the *O*-bonded and *S*-bonded isomers.12) Very recently, Jackson and co-workers11) reported on the preparation and reactivity of the *S*-bonded and *O*-bonded isomers of [Co(CH_3SO_2)-(NH_3)$_5$]$^{2+}$, and the optical resolution of the *O*-bonded isomer. They studied both the kinetics of the *O*- to *S*-bonded isomerization and the racemization. Although the racemization rate is not overwhelmingly greater than the isomerization rate (6×10^{-7} s^{-1} at 25 °C, H_2O), attempts to quantify it were thwarted by Co(II) catalysis.

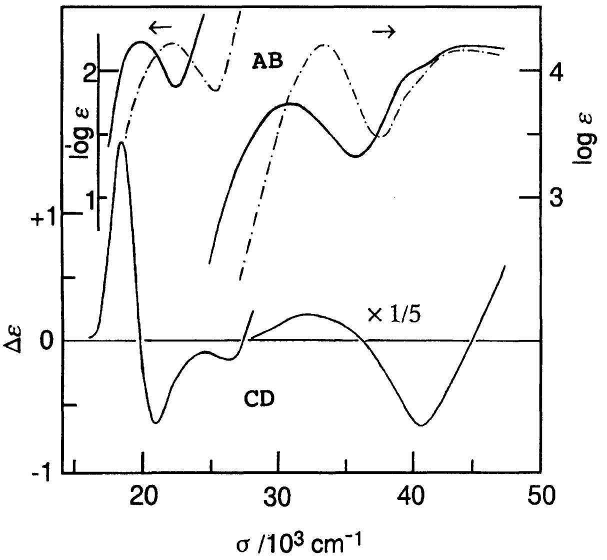


Fig. 2. Absorption (AB) spectra of *cis*(*t*-N,O)-[Co{OS(O)$CH_2CH_2NH_2$-*O*,*N*}(tren)]$^{2+}$ (—) and *cis*-(*t*-N,S)-[Co{S(O)$_2CH_2CH_2NH_2$-*S*,*N*}(tren)]$^{2+}$ (-·-) in water, and CD spectrum of *O*,*N*-chelate sulfinato complex (in 1.0 M $NaClO_4$) obtained from the final fraction in SP-Sephadex column chromatography (eluent: 0.1 M $K_2[Sb_2\{(+)\text{-tartrate}\}_2]$).

More kinetic data will be necessary to elucidate the mechanism of racemization and thermal back-isomerization for the present and related *O*-sulfinato complexes.

The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 03453051, 04740344, and 05403009 from the Ministry of Education, Science and Culture. The authors wish to thank the Institute for Molecular Science, Okazaki National Research Institutes for the use of X-ray and computation facilities.

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