Preparation of a Stable Sulfonato-Cobalt(III) Complex by Oxidation of a Sulfinato-*O* Complex

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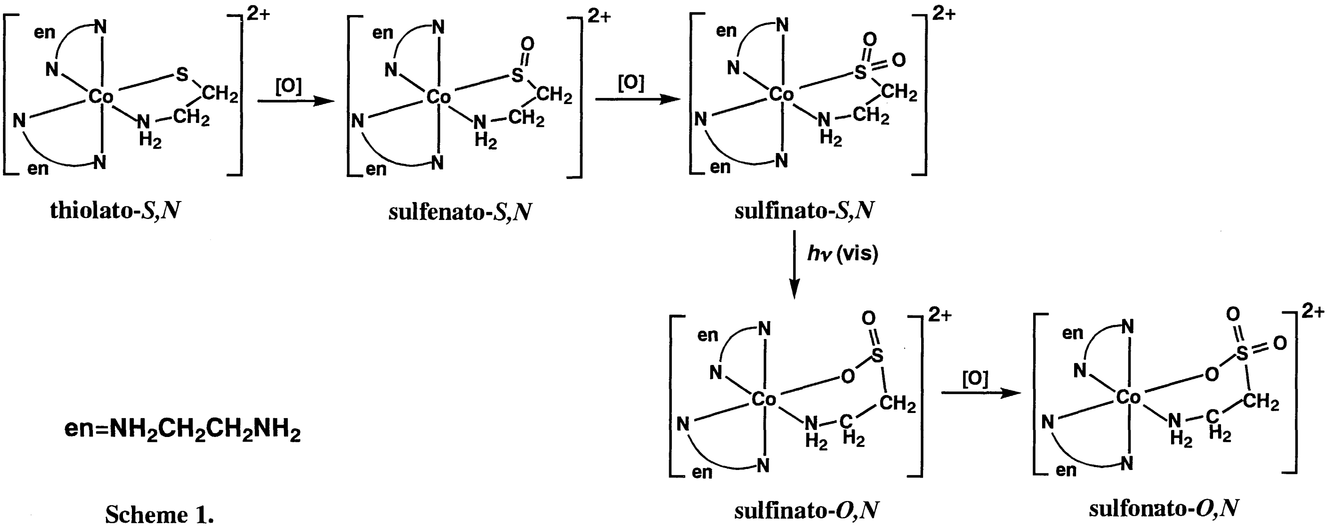
A stable sulfonato complex, $[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$, was prepared upon oxidation of $[Co\{OS(O)CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$ in acid media. This sulfonato complex was resolved by SP-Sephadex column chromatography (eluent: 0.1 mol dm^{-3} $Na_2[Sb_2\{(+)\text{-tartrate}\}_2]$). The absolute configuration of the slower eluted $(-)_{589}$-isomer was determined to be Δ by the X-ray method.

Oxidation of $[Co(SCH_2CH_2NH_2\text{-}S,N)(en)_2]^{2+}$ with H_2O_2 resulted in the formation of the corresponding sulfenato,[1] $[Co\{S(O)CH_2CH_2NH_2\text{-}S,N\}(en)_2]^{2+}$, and sulfinato,[2] $[Co\{S(O)_2CH_2CH_2NH_2\text{-}S,N\}(en)_2]^{2+}$, complexes. The sulfur atom remains coordinated during and after the oxidation reaction. Recently, Adamson and co-workers reported the linkage isomerization from Co-S to Co-O in the photolysis of $[Co\{S(O)_2CH_2CH_2NH_2\text{-}S,N\}(en)_2]^{2+}$.[3] The sulfur atom of the sulfinato-*O,N* complex, $[Co\{OS(O)CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$, seems to be susceptible to further oxidation to the sulfonato complex, $[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$. Generally the coordination ability of a monodentate sulfonate ligand is low. The formation of chelate ring might give sulfonate-cobalt bonding of the sulfonato complex stable enough to be isolated. According to this strategy, we actually prepared the first stable sulfonato cobalt(III) complex. Thus, a series of sulfur oxidation from $[Co(SCH_2CH_2NH_2\text{-}S,N)(en)_2]^{2+}$ to $[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$ is established (Scheme 1).

A mixture of 30% H_2O_2 (10 g, 88 mmol) and 60% $HClO_4$ (10 g) was added dropwise to a DMSO solution (15 cm^3) of $[Co\{OS(O)CH_2CH_2NH_2\text{-}O,N\}(en)_2](ClO_4)_2$[3] (1 g, 2 mmol) with stirring below 5 °C. The color of the solution changed from red to orange-red during the addition. The mixture was stirred for 30 min and left overnight in a refrigerator. The solution was diluted with water (1000 cm^3), poured onto a column (ϕ 3 cm × 5 cm) of SP-Sephadex C-25, and the adsorbed complex was eluted with 0.3 M (1 M = 1 mol dm^{-3}) $NaClO_4$. The column showed only a single orange-red band. The eluate containing the band was collected and then evaporated to *ca.* 5 cm^3 under reduced pressure to yield an orange-red precipitate. It was recrystallized from water. Anal. Found: C, 14.03; H, 4.86; N, 13.59; S, 6.14%. Calcd for $C_6H_{24}CoCl_2N_5O_{12}S$ = $[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2](ClO_4)_2\cdot H_2O$: C, 13.85; H, 4.65; N, 13.46; S, 6.16%. This complex (0.1 g, 0.2 mmol) was charged on top of an SP-Sephadex C-25 column (ϕ 3 cm × 90 cm). Two bands were developed upon elution with 0.1 M $Na_2[Sb_2\{(+)\text{-tartrate}\}_2]$. Each of the bands was diluted with water, poured again onto a small column (ϕ 3 cm × 7 cm) of SP-Sephadex C-25, and the adsorbed complex was eluted with 0.3 M $NaClO_4$. The eluate was concentrated to dryness in a desiccator over P_4O_{10}. It was recrystallized from water by adding ethanol. Anal. Found for the faster eluted isomer: C, 14.61; H, 4.55; N, 13.43; S, 5.78%. Found for the slower eluted isomer: C, 14.31; H, 4.62; N, 13.19; S, 6.99%. Calcd for $C_6H_{22}CoCl_2N_5O_{11}S$ = $[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2](ClO_4)_2$: C, 14.35; H, 4.42; N, 13.94; S, 6.39%.

Figure 1 shows the absorption and CD spectra of $[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2](ClO_4)_2$. The sulfonato complex has a slightly stronger ligand field strength than does the starting sulfinato-*O,N* one; the latter shows the first d-d absorption band at 512 nm, while that of the former appears at 501 nm. The shoulder around 300 nm can be assigned to the CT transition from O to Co. The slower eluted complex, $(-)_{589}$-$[Co\{OS(O)_2CH_2CH_2NH_2\text{-}O,N\}(en)_2]^{2+}$, was assigned to the Δ-configuration on the basis of the CD sign at *ca.* 535 nm in the first spin-allowed d-d band region.

Figure 2 shows a perspective view of the complex cation obtained from the eluate containing the slower eluted isomer,



Scheme 1.

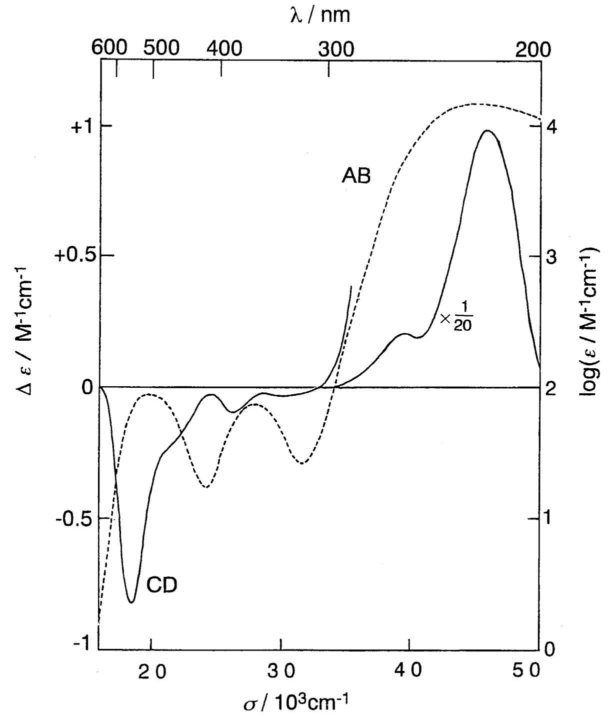


Figure 1. Absorption (AB, ---) and CD (—) spectra of $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*O,N*}(en)$_2$](ClO$_4$)$_2$.

$(-)_{589}$-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*O,N*}(en)$_2$]$^{2+}$.[4] The coordination geometry around the cobalt atom is approximately octahedral. The sulfonate ligand coordinates to cobalt with *O,N*-chelation. The absolute configuration was determined to be Δ.[5] Thus, the X-ray analysis confirmed the assignment from the pattern of the CD spectrum. The sulfur oxygen bond, S-O(1) 1.482(2) Å, is longer than those of S-O(2) 1.446(2) and S-O(3) 1.439(2) Å. The sulfonate oxygen atom in the complex does not induce a significant trans influence.

The hydrolysis of *cis*-[Co(NH$_2$CH$_2$CH$_2$SO$_3^-$-*N*)Cl(en)$_2$]Cl (the complex contains the same ligand but the oxygen atom is not bound), in an alkaline solution was reported to yield only *cis*-[Co(NH$_2$CH$_2$CH$_2$SO$_3^-$-*N*)(OH)(en)$_2$]$^+$, which shows the low coordination ability of an oxygen atom of the sulfonate ligand.[6] However, the absorption and CD spectra of the present complex remained unchanged for 4 days at room temperature. To our knowledge, this is the first stable sulfonato cobalt(III) complex. The stability of the *O,N*-chelate is interesting when compared with the above report.

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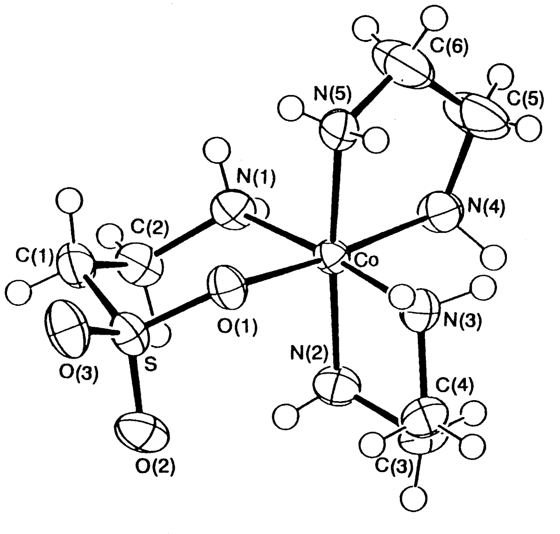

Figure 2. An ORTEP drawing for the complex cation, $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*O,N*}(en)$_2$]$^{2+}$. Selected bond distances (Å) and angles(°): Co-O(1) 1.944(2), Co-N(1) 1.978(3), Co-N(2) 1.965(2), Co-N(3) 1.952(3), Co-N(4) 1.952(3), Co-N(5) 1.944(2), S-O(1) 1.482(2), S-O(2) 1.446(2), S-O(3) 1.439(2), S-C(1) 1.767(4), N(1)-C(2) 1.492(4), C(1)-C(2) 1.491(5), O(1)-Co-N(1) 91.0(1), O(1)-S-C(1) 104.6(2), Co-N(1)-C(2) 118.7(2), Co-O(1)-S 128.5(1), S-C(1)-C(2) 111.6(3), N(1)-C(2)-C(1) 112.5(3).

References and Notes

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4 Crystal data for $(-)_{589}$-Δ-[Co{OS(O)$_2$CH$_2$CH$_2$NH$_2$-*O,N*}(en)$_2$](ClO$_4$)$_2$: $C_6H_{22}CoCl_2N_5O_{11}S$, FW 502.17, monoclinic, $P2_1$, a = 9.075(1), b = 11.282(2), c = 9.191(1) Å, β = 108.37(1) °, V = 893.2(2) Å^3, Z = 2, D_x = 1.867 g·cm^{-3}, μ = 1.44 mm^{-1} for Mo $K\alpha$ radiation (λ = 0.71069 Å). Intensity measurements were carried out on a Rigaku AFC-5R diffractometer. Among 4343 reflections measured in the range $-11 \le h \le 11$, $-14 \le k \le 14$, $0 \le l \le 11$, those of 3740 had $Io > 3\sigma(Io)$. The structure was solved by a direct method and refined by a full-matrix least squares procedure including anomalous scattering terms of Co, Cl, and S atoms to R = 0.029 and Rw = 0.028. Full details of the X-ray structure determination will be published separately.

5 The absolute configuration was determined by using the anomalous dispersion effect. When the Λ-configuration was assumed, the refinement resulted in R = 0.045 and Rw = 0.048, which were significantly larger than those for the Δ configuration. Furthermore, the inequality relationship was checked for 21 pairs of reflections with $\{|Fo(hkl)| - |Fo(\bar{h}\bar{k}\bar{l})|\}$ larger than $10\sigma(Fo)$. The relationship held without exception for the Δ-configuration, but was reversed for the Λ-configuration. Thus the absolute configuration of the slower eluted isomer was determined to be Δ.

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