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OXIDATIVE SYNTHESIS, OPTICAL RESOLUTION, AND CHARACTERIZATION OF MIXED SULFENATO AND SULFINATO COBALT(III) COMPLEXES

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Five new complexes *fac*(*S*)-$[Co\{S(O)CH_2CH_2NH_2\}_n\{S(O)_2CH_2CH_2NH_2\}_{3-n}]$ (n = 3, 2, 1, and 0) prepared via H_2O_2 oxidation of *fac*(*S*)-$[Co(SCH_2CH_2NH_2)_3]$ have been isolated and optically resolved by means of column chromatography or preferential precipitation of a diastereomeric molecular compound with *d*-tartaric acid.

Successive oxidation of thiols coordinated to cobalt(III) generates several sulfur-bonded sulfenato and sulfinato complexes.$^{1)}$ These complexes are of interest in connection with their spectrochemical and stereochemical features. The present letter is concerned with the preparation and optical resolution of mixed sulfenato and sulfinato complexes, $[Co(aese)_n(aesi)_{3-n}]$ (n = 3, 2, 1, and 0), and the characterization of structures (aese = 2-aminoethanesulfenato(1-) ligand $NH_2CH_2CH_2SO^-$, and aesi = 2-aminoethanesulfinato(1-) ligand $NH_2CH_2CH_2SO_2^-$).

To a solution of 3.5 g (30 mmol) of 2-aminoethanethiol hydrochloride (Haet·HCl) in 30 cm^3 of water was gradually added 3.6 g (10 mmol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ and the mixture was stirred at 95 °C for an hour. The blue-green curdy precipitate of $[Co(aet)_3]$ was filtered and washed with water. A stoichiometric amount (21 mmol) of 2.86% aqueous H_2O_2 was added dropwise to a suspension of 2.0 g (7 mmol) of $[Co(aet)_3]$ in 25 cm^3 of water with stirring below 5 °C, leading to an orange-red solution. On addition of acetone (200 cm^3) and ether (200 cm^3), an orange precipitate was obtained. This was dissolved in a small amount of water, adsorbed on a column (2 × 100 cm) of anion-exchange resin (QAE-Sephadex A-25, *d*-tartrate form) and eluted with water. Five colored bands, orange (I), orange (II), orange (III), yellow-orange (IV), and orange-yellow (V), were eluted in this order. At this stage each of the bands was partially resolved and the fractions of bands II, III, IV and V showed negative CD (circular dichroism) at the longest wavelength region of the first d-d transition band.

The oxidation of eluate II or III by diluted H_2O_2 (ca. 2%) produced the bands IV and V after column chromatography. Similarly, the eluate IV generated the band V and a new yellow band VI, and the eluate V the single band VI. The sparingly soluble yellow complex VI could also be obtained via oxidation of eluate II, III, IV, or V by an excess of 30% H_2O_2. These results indicate that the oxidation process is stepwise in a series of (II or III)$\longrightarrow$ IV$\longrightarrow$ V$\longrightarrow$ VI (final product).

Figure 1 shows the electronic absorption spectra of the complexes. No thiolato

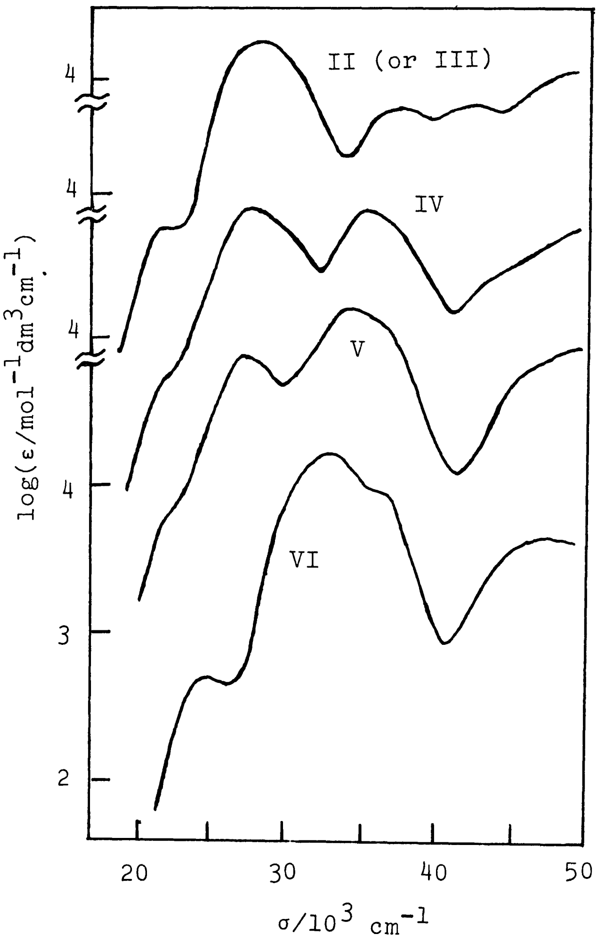

Fig. 1. Absorption spectra

group remains in the present oxidation products because a 600 nm absorption band characteristic to the coordinated thiols[2] did not occur. The intense absorption bands which appeared in the near-ultraviolet region for all the complexes indicate that the coordination of sulfenato and/or sulfinato groups occurs through the sulfur atoms.[3] The complexes II and III, both of which are the precursors of complexes IV, V, and VI in the oxidation reaction, gave the same absorption spectra, exhibiting the most intense band of the sulfenato groups at ca. 360 nm, and can be identified to the isomers of a $[Co(aese)_3]$ complex. The absorption spectra and the following elemental analyses confirm that the complexes II (and III), IV, V, and VI correspond to n = 3, 2, 1, and 0 of $[Co(aese)_n(aesi)_{3-n}]$, respectively, though the first orange band (I) could not be identified. Found for II: C, 21.08; H, 5.56; N, 12.25%. Calcd for $[Co(aese)_3]\cdot 0.5H_2O = C_6H_{19}N_3O_{3.5}S_3Co$: C, 20.93; H, 5.56; N, 12.20%. Found for III: C, 19.08; H, 6.12; N, 11.22%. Calcd for $[Co(aese)_3]\cdot 2.5H_2O = C_6H_{23}N_3O_{5.5}S_3Co$: C, 18.94; H, 6.09; N, 11.05%. Found for IV: C, 18.39; H, 5.62; N, 10.79%. Calcd for $[Co(aese)_2(aesi)]\cdot 2H_2O = C_6H_{22}N_3O_6S_3Co$: C, 18.61; H, 5.72; N, 10.48%. Found for V: C, 18.50; H, 5.17; N, 10.84%. Calcd for $[Co(aese)(aesi)_2]\cdot H_2O = C_6H_{20}N_3O_6S_3Co$: C, 18.70; H, 5.23; N, 10.90%. Found for VI: C, 18.80; H, 4.80; N, 10.90%. Calcd for $[Co(aesi)_3] = C_6H_{18}N_3O_6S_3Co$: C, 18.80; H, 4.73; N, 10.96%.

The optical resolution of III-$[Co(aese)_3]$ was achieved using *d*-tartaric acid (*d*-H_4tart) as a resolving agent. The racemate III-$[Co(aese)_3]\cdot 2.5H_2O$ (1.0 g, 2.76 mmol) was dissolved in an ethanol-water (2:1) mixture and then *d*-H_4tart (0.42 g, 2.76 mmol) was added to the solution. After a few minutes, an orange-red diastereomeric molecular compound, $(+)^{CD}_{500}$-III-$[Co(aese)_3]$(*d*-H_4tart)$\cdot H_2O$ began to deposit. This was filtered and washed with ethanol. Found: C, 23.72; H, 5.22; N, 8.35%. Calcd for $(+)^{CD}_{500}$-III-$[Co(aese)_3]$(*d*-H_4tart)$\cdot H_2O = C_{10}H_{26}N_3O_{10}S_3Co$: C, 23.86; H, 5.21; N, 8.35%. The diastereomer was converted to $(+)^{CD}_{500}$-III-$[Co(aese)_3]$ by treating with an equimolar amount of $Ca(OH)_2$.

Pure optically active complexes corresponding to the bands IV, V, and VI were prepared by the oxidation of $(+)^{CD}_{500}$-III-$[Co(aese)_3]$. The oxidation products of $(+)^{CD}_{500}$-II-$[Co(aese)_3]$ resolved by the column chromatographic technique were the same

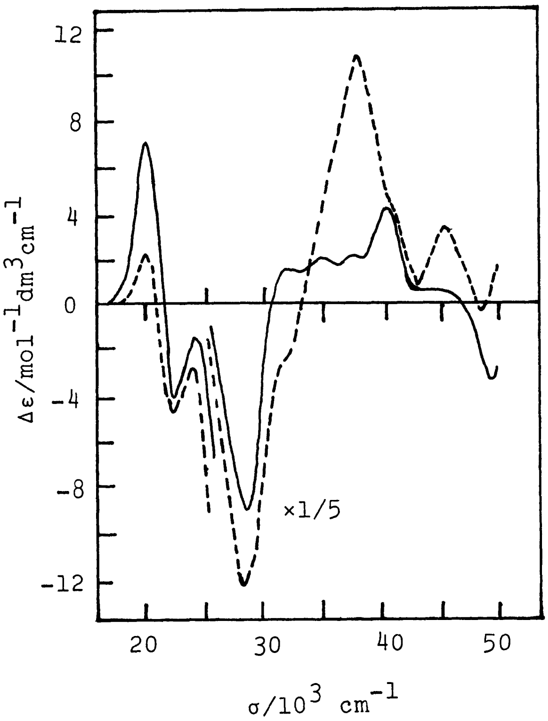

Fig. 2. CD spectra of $(+)^{CD}_{500}$-II (——) and $(+)^{CD}_{500}$-III (---) complexes

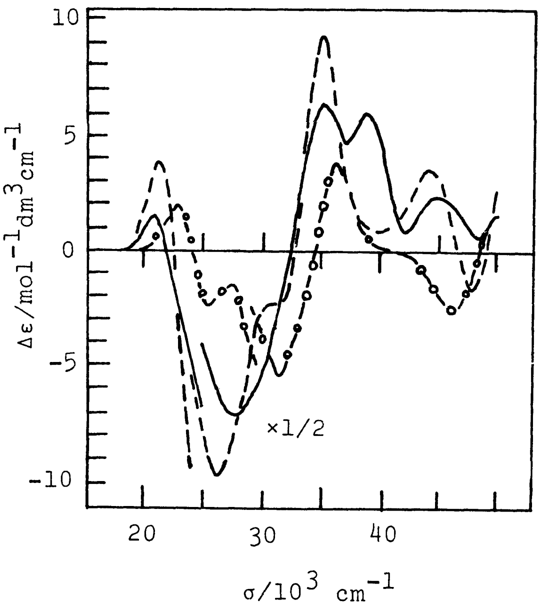

Fig. 3. CD spectra of $(+)^{CD}_{485}$-IV (——), $(+)^{CD}_{468}$-V (---), and $(+)^{CD}_{440}$-VI (-o-o-) complexes

as those of $(+)^{CD}_{500}$-III-[Co(aese)$_3$].

The unsymmetrical nature of 2-aminoethanethiol leads to the possibility of two geometrical isomers, *fac* and *mer*, for the [Co(aet)$_3$] complex. However, it has been shown that this complex exists only in the facial form despite several efforts in synthetic routes,$^{4)}$ and this conclusion has been supported by the recent investigations of trinuclear derivatives.$^{5)}$ Therefore, we assume that the present oxidation products of *fac*(*S*)-[Co(aet)$_3$] retain the *fac*(*S*) geometry.

The CD spectra of the complexes are shown in Figs. 2 and 3. The complexes except VI have two CD contributions, one from the configurational chirality based on the skew pair of chelate rings and the other from the chirality based on the asymmetric sulfur donor atoms of sulfenato groups. It has been reported that the oxidation of Λ-[Co(L-cysteinato-*N*,*S*)(en)$_2$]$^{2+}$ produced two sulfenato complexes arising from the chirality of the sulfur donor atom (*R*) or (*S*).$^{6)}$ These Λ-complexes showed a positive CD band at the longest wavelength region in the first d-d transition band, though the almost enantiomeric CD patterns were seen in the remaining regions. Accordingly, the complexes of $(+)^{CD}_{500}$-II, $(+)^{CD}_{500}$-III, $(+)^{CD}_{485}$-IV, $(+)^{CD}_{468}$-V, and $(+)^{CD}_{440}$-VI are tentatively assigned to Λ-configuration on the basis of the sign of the longest wavelength CD band. The absolute configuration of the sulfur center can be characterized on the basis of the CD sign in the sulfenato absorption band region at ca. 360 nm (28 × 10^3 cm^{-1}); (*R*) and (*S*) configuration correspond to a negative and a positive band, respectively.$^{6)}$ Since the negative band at 360 nm is more intense in Λ-III than in Λ-II, the Λ-(*R*,*R*,*R*) configuration can be assigned for Λ-III and Λ-(R,R,S) one for Λ-II. The ^{13}C NMR spectrum of III showed only two resonances (52.07 and 42.12 ppm)7) in agreement with the above assignment. The fact that the oxidation of $(+)^{CD}_{500}$-II-Λ-(R,R,S) and $(+)^{CD}_{500}$-III-Λ-(R,R,R) generated the same products leads to an unequivocal assignment of the IV and V complexes; $(+)^{CD}_{485}$-IV and $(+)^{CD}_{468}$-V have Λ-(R,R) and Λ-(R) configuration, respectively. These assignments were supported by the single crystal X-ray structure analysis of $(+)^{CD}_{500}$-III-$[Co(aese)_3](d\text{-}H_4tart)\cdot H_2O$ in which the cobalt(III) complex has the *fac*(S)-Λ-(R,R,R) structure.8)

References and Notes

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7) In D_2O containing 1,4-dioxane (δ = 67.40) as an internal standard.

8) The present authors, to be published shortly.

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