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ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF BIS(ETHYLENEDIAMINE) COBALT(III) COMPLEXES WITH 2-AMINOETHANESULFENIC OR 2-AMINOETHANESELENENIC ACID

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Optically active title complexes derived from $[Co(aese\ or\ seea)(en)_2]^{2+}$ (aese=2-aminoethanesulfenato and seea=2-aminoethaneselenenato) were obtained and their CD spectra were discussed in relation to the absolute configuration of the coordinated chalcogen atom. The Hseea isomer derived from the Λ(R) seea one exhibited the inversion on the chiral selenium atom.

The protonation on the oxygen atom of $[Co(seea)(en)_2]^{2+}$ generates the complex with a coordinated selenenic acid as the case of $[Co(aese)(en)_2]^{2+}$.[1,2] These complexes have a chiral chalcogen atom and their optically active complexes are remarked in connection with the spectrochemical and stereochemical features. This letter deals with the protonation reaction of $[Co(seea)(en)_2]^{2+}$, and electronic absorption and CD spectra of the optically active cobalt(III) complexes with a coordinated sulfenic acid, $[Co(Haese)(en)_2]^{3+}$, and a coordinated selenenic acid, $[Co(Hseea)(en)_2]^{3+}$, which are derived from Λ(R)- and Λ(S)-$[Co(aese)(en)_2]^{2+}$,[3,4] and Λ(R)-$[Co(seea)(en)_2]^{2+}$,[4] respectively. Their CD spectra are discussed in relation to the absolute configuration of the coordinated chalcogen atom.

The selenenato complex, $[Co(seea)(en)_2]^{2+}$, shows the instantaneous and reversible absorption spectral change with pH change of the solution and an isosbestic point is observed at 328 nm. The intensity of the characteristic selenenato band[4] at 27.55 x 10^3 cm^{-1} decreases with the increasing acid concentration ($HClO_4$), as in the case of the sulfenato complexes.[1,2] Accordingly, the Se-bonded selenenato ligand seems to be protonated on the pendant oxygen atom. The protonation constant (1/Ka) of (3.1 ± 0.5) x 10^3 mol^{-1} dm^3 at 25°C, μ = 1.0 mol dm^{-3} ($NaClO_4$) was determined spectrophotometrically at 305 nm. This value indicates that the selenenato ligand of $[Co(seea)(en)_2]^{2+}$ is at least 10^3-fold more basic than the sulfenato ligand of $[Co(aese)(en)_2]^{2+}$ (1/Ka = 1.4 ± 0.2 mol^{-1} dm^3, at 25°C, μ = 4.0 mol dm^{-3} ($LiClO_4$)).[1] Therefore, the seea and aese complexes give the protonated complexes, $[Co(Hseea)(en)_2]^{3+}$ and $[Co(Haese)(en)_2]^{3+}$, in 70% $HClO_4$ solution , respectively. Their absorption and CD spectra in 70% $HClO_4$ solution are shown in Fig. 1(a). The charge transfer band[4] at ca. 27.5 x 10^3 cm^{-1}, which is characteristic of the selenenato and sulfenato complexes, disappears in the protonated complexes, and the complexes show quite similar absorption spectra to those of the corresponding selenoether and thioether complexes.[4,5]

The optically active isomers of $[Co(Haese)(en)_2]^{3+}$ derived from Λ(R) and Λ(S) aese isomers show almost enantiomeric CD bands in the sulfur-to-metal charge transfer band region (ca. 35 x 10^3 cm^{-1}) (Fig. 1(a)). In the first absorption band region, the CD pattern for each of the Haese isomers coincides well with that of the parental aese isomers.[3,4] Furthermore, the CD spectral change for each of the two aese isomers is instantaneous and reversible with pH change as well as the absorption spectral one. No inversion occurs for the aese isomers during this protonation reaction, namely, the two Haese isomers take the same absolute configurations as the parental aese isomers. $\Lambda(S)$-$[Co(Haese)(en)_2]^{3+}$ exhibits a similar CD spectrum to the $\Lambda(R)$ isomers of $[Co(Y(CH_3)CH_2CH_2NH_2)(en)_2]^{3+}$ (Y = S or Se)[4,5] (Fig. 1(a)), namely, (S)-sulfur atom in the former corresponds configurationally to (R)-sulfur or -selenium atom in the latter. This is also supported from the result that the vicinal CD curve of (S)-sulfur atom calculated from $\Lambda(R)$- and $\Lambda(S)$-$[Co(Haese)(en)_2]^{3+}$ (Fig. 1(b)) is similar to the CD spectral pattern of trans(tertiary amine N, Se)-$[Co(Se(CH_3)CH_2CH_2NH_2)(N(CH_2CH_2NH_2)_3)]^{3+}$ whose CD contribution is due to the coordinated (R)-selenium atom.[6]

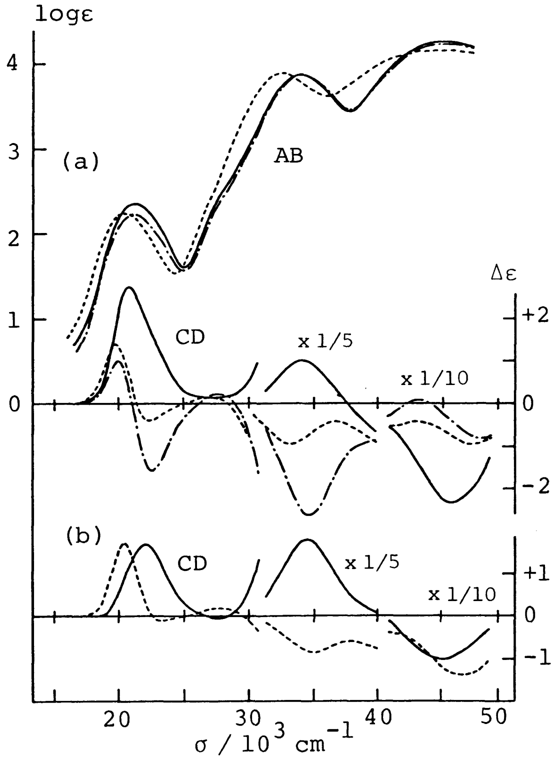

Fig. 1. (a): Absorption and CD spectra of $\Lambda(S)$-$[Co(Haese)(en)_2]^{3+}$ (———), $\Lambda(R)$-$[Co(Haese)(en)_2]^{3+}$ (—•—•—), and Λ-$[Co(Hseea)(en)_2]^{3+}$ (-----). (b): Calculated CD curves of $[Co(Haese)(en)_2]^{3+}$; $1/2\{\Delta\varepsilon(\Lambda(S) - \Delta\varepsilon(\Lambda(R)\}$ (——) and $1/2\{\Delta\varepsilon(\Lambda(S) + \Delta\varepsilon(\Lambda(R)\}$ (---).

Similar instantaneous and reversible CD spectral change is also observed for $\Lambda(R)$-$[Co(seea)(en)_2]^{2+}$. However, the CD spectrum of the Hseea isomer derived from the $\Lambda(R)$ seea one differs significantly from that of $\Lambda(R)$-$[Co(Haese)(en)_2]^{3+}$ (Fig. 1(a)), though the parental $\Lambda(R)$ seea and $\Lambda(R)$ aese isomers show quite similar CD spectra to each other.[4,5] The CD spectrum of the Hseea isomer agrees well with the Λ configurational CD curve calculated from $\Lambda(R)$- and $\Lambda(S)$-$[Co(Haese)(en)_2]^{3+}$ (Fig. 1(b)), and furthermore, with the CD spectrum of Λ-$[Co(aesi)(en)_2]^{2+}$ (aesi = 2-aminoethanesulfinato)[7] which has no chirality due to the sulfur donor atom. This suggests that an inversion occurs on the chiral selenium atom, namely, the Hseea isomer takes a mixture of $\Lambda(R)$ and $\Lambda(S)$ configurations in $HClO_4$ solution.

References

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