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Absorption and CD Spectral Properties of Bis(ethylenediamine)cobalt(III) Complexes with *O*-Bonded Sulfoxide and Seleninate

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Synopsis. The absorption and CD spectral behavior of $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$ and $[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ was discussed. The *O*-bonded seleninato isomer, Λ-$(+)^{CD}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$, showed racemization at the chiral selenium atom in an aqueous solution and a shift of the equilibrium between the (*R*) and (*S*) configurations of the chiral selenium atom through the protonation on the pendant oxygen atom.

Several bis(diamine)cobalt(III) complexes containing a coordinated chiral sulfur or selenium atom have been investigated,[1–11] and some stereochemical differences between cobalt(III) complexes with a selenium-containing ligand and those with a sulfur-containing ligand have been reported.[8–10] Recently, the two diastereomers due to the non-coordinated chiral sulfur atom, $\Lambda(R)$ and $\Lambda(S)$,[12] have been isolated for the *O*-bonded sulfinato complex, $[\mathrm{Co\{OS(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$.[13] On the other hand, the single crystal X-ray analysis indicated that the chiral selenium atom in the corresponding *O*-bonded seleninato complex, $(-)^{CD}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$, selectively takes the (*S*) configuration in the crystal state.[14]

Here we report on the stereochemical behavior of Λ-$(+)^{CD}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ in solution, together with that of the newly prepared two diastereomers of the *O*-bonded sulfoxide complex, $\Lambda(R)$- and $\Lambda(S)$-$[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$. The absorption and CD spectra of the *O*-bonded seleninato complex are discussed in comparison with those of the corresponding *O*-bonded sulfinato and sulfoxide complexes.

Experimental

Complexes. (1) Λ-$(+)^{CD}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_2$. Fairly large crystals of this complex were prepared by the method described in a previous paper.[14]

(2) $\Lambda(S)$-$(-)^{CD}_{500}$-$[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}$ and $\Lambda(R)$-$(+)^{CD}_{500}$-$[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_3$. These isomers were prepared by a procedure similar to that used for $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$,[6,15] using $\Lambda(R)$- and $\Lambda(S)$-$[\mathrm{Co\{S(O)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_2$[9] instead of $[\mathrm{Co\{S(O)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_2$. To a dimethyl sulfoxide solution (3 cm^3) of $\Lambda(R)$- or $\Lambda(S)$-$[\mathrm{Co\{S(O)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_2$ (0.15 g) was added an excess amount of $\mathrm{CH_3I}$ (1.0 g); the mixture was then allowed to stand at room temperature for three days. After the excess $\mathrm{CH_3I}$ and dimethyl sulfoxide had been extracted with diethyl ether, to the remaining oily product was added a small amount of water, after which the solution was passed through a column (2.5 cm×25 cm) of QAE-Sephadex A-25 ($\mathrm{ClO_4^-}$ form) while being eluted with water. The reddish eluate was concentrated to a small volume with a rotary evaporator. The addition of a small amount of ethanol to the concentrate, followed by cooling in a refrigerator overnight, yielded crystals of the desired *O*-bonded sulfoxide isomer. The $(-)^{CD}_{500}$ and $(+)^{CD}_{500}$ isomers thus obtained showed the same absorption spectrum as the racemic $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$.[6,15] No CD spectral change was observed for the two isomers, at least for one day. Found for the $\Lambda(S)$ isomer: C, 13.97; H, 4.49; N, 11.67%. Calcd for $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_3\cdot\mathrm{H_2O}=\mathrm{C_7H_{27}N_5O_{14}SCl_3Co}$: C, 13.95; H, 4.52; N, 11.62%. Found for the $\Lambda(R)$ isomer: C, 14.45; H, 4.31; N, 11.98%. Calcd for $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_3=\mathrm{C_7H_{25}N_5O_{13}SCl_3Co}$: C, 14.38; H, 4.31; N, 11.97%. Attempts to prepare the corresponding selenoxide complex, $[\mathrm{Co\{OSe(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$, by the reaction of $\Lambda(R)$-$[\mathrm{Co\{Se(O)CH_2CH_2NH_2\}(en)_2}](\mathrm{ClO_4})_2$[9] (0.1 g) with $\mathrm{CH_3I}$ (0.7 g) were unsuccessful; instead, the selenide complex, $\Lambda(R)$-$[\mathrm{Co\{Se(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$,[9] was formed. An SP-Sephadex chromatographic investigation of the reaction solution (after ca. 10 min) revealed the formation of the selenolato complex, Λ-$[\mathrm{Co(SeCH_2CH_2NH_2)(en)_2}]^{2+}$,[9] besides the selenide complex.

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra with a JASCO J-20 spectropolarimeter in an aqueous solution at room temperature. The ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-FX-100 or -FX-90Q NMR spectrometer in a $\mathrm{D_2O}$ or $\mathrm{HClO_4}$-$\mathrm{D_2O}$ solution at room temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference.

Results and Discussion

The two isomers of the *O*-bonded sulfoxide complex, $(-)^{CD}_{500}$- and $(+)^{CD}_{500}$-$[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$, were prepared by the reaction of $\Lambda(R)$- and $\Lambda(S)$-$[\mathrm{Co\{S(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ respectively with $\mathrm{CH_3I}$. As shown in Fig. 1 their absorption spectra show an intense shoulder at ca. 37.0×10^3 cm^{-1} besides the first absorption band (ca. 19.5×10^3 cm^{-1}) and the second absorption band (ca. 27.5×10^3 cm^{-1}). In the first absorption band region, the CD patterns of the *O*-bonded sulfoxide isomers coincide well with those of the parental $\Lambda(R)$ and $\Lambda(S)$ sulfenato isomers[9] (Fig. 1), suggesting that the isomers retain the Λ configuration of the parental sulfenato isomers. The $(-)^{CD}_{500}$ isomer derived from the $\Lambda(R)$ sulfenato isomer exhibits a sharp ^{1}H NMR peak arising from the methyl group of the ligand at 2.93 ppm, while the $(+)^{CD}_{500}$ isomer derived from the $\Lambda(S)$ isomer exhibits a peak at 2.83 ppm. Furthermore, the methylation of $[\mathrm{Co\{S(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ to $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$ is known to proceed with a retention of the absolute configuration at the chiral sulfur atom.[15,16] Taking these facts into consideration, it is probable that the methylation reaction of the $\Lambda(S)$ and $\Lambda(R)$ sulfenato isomers produce the $\Lambda(R)$ and $\Lambda(S)$ *O*-bonded sulfoxide isomers respectively. The $\Lambda(R)$ and $\Lambda(S)$ isomers of $[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$

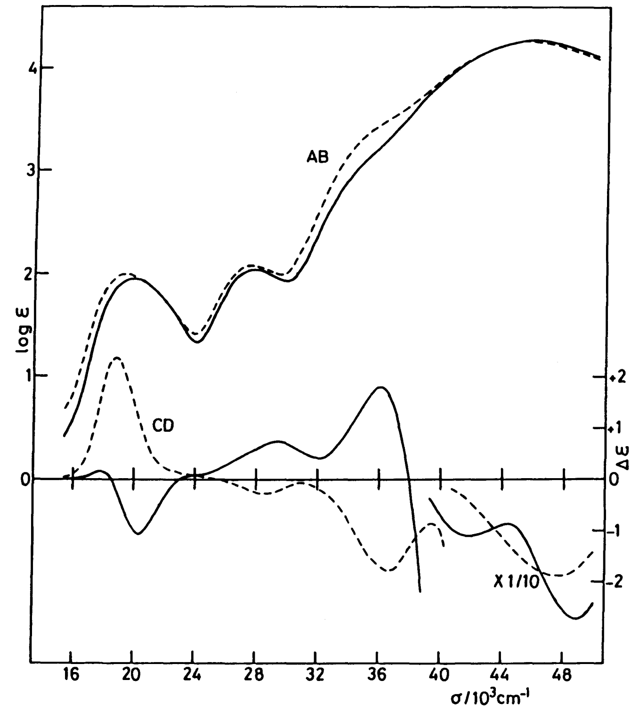

Fig. 1. Absorption and CD spectra of $\Lambda(S)$-[Co{OS(CH$_3$)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ (——) and $\Lambda(R)$-[Co{OS(CH$_3$)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ (----).

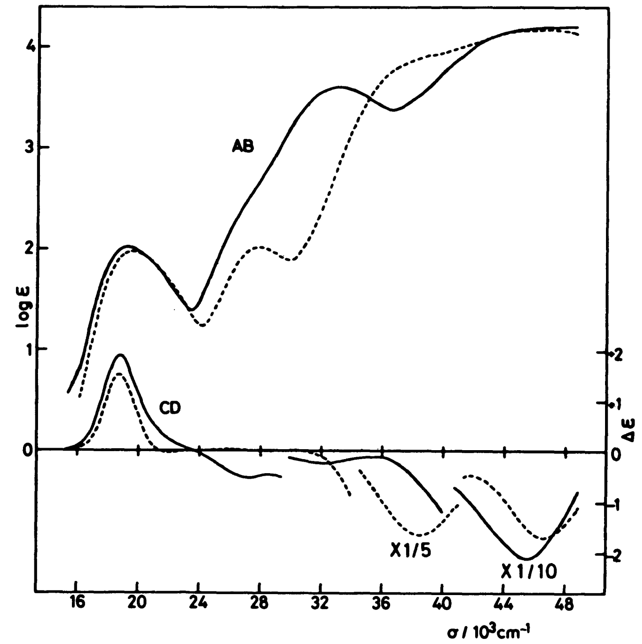

Fig. 2. Absorption and CD spectra of Λ-$(+)^{\rm CD}_{500}$-[Co{OSe(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ in water (——) and Λ-$(+)^{\rm CD}_{500}$-[Co{OSe(OH)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ in 6% HClO$_4$ (----).

show almost enantiomeric CD spectra in the region of 18—38×10^3 cm^{-1} (Fig. 1), indicating that the non-coordinated chiral sulfur atom in the sulfoxide complex contributes significantly to the CD spectrum, just as in the case of the coordinated chiral sulfur atoms in [Co{S(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$,[9] and [Co{S(OH)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$.[8] The methylation of the selenenato complex, $\Lambda(R)$-[Co{Se(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$, produced the selenide complex, $\Lambda(R)$-[Co{Se(CH$_3$)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$; no selenoxide complex was detected. The presence of the selenolato complex, Λ-[Co(SeCH$_2$CH$_2$NH$_2$)(en)$_2$]$^{2+}$, in the reaction solution (after ca. 10 min) besides the selenide complex suggests that the selenide complex was formed via the intermediate, Λ-[Co(SeCH$_2$CH$_2$NH$_2$)(en)$_2$]$^{2+}$, which retained the Λ configuration of $\Lambda(R)$-[Co{Se(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$.

The *O*-bonded seleninato complex, [Co{OSe(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$, shows an instantaneous and reversible absorption spectral change with the pH change in an aqueous solution. The pK_a value for this complex at 25 °C and μ=1.0 mol dm^{-3} (NaClO$_4$) has been determined to be 1.91±0.05 in a previous paper.[14] For the *O*-bonded seleninato complex, there are three possible protonation sites: the coordinated oxygen atom, the pendant oxygen atom, and the selenium atom. As shown in Fig. 2 the first absorption band of the protonated complex is quite similar to that of the parental *O*-bonded seleninato complex, suggesting that the coordinated oxygen atom is not protonated. The charge-transfer band at ca. 33×10^3 cm^{-1} characteristic of the *O*-bonded seleninato complex[14] disappears in the protonated complex. Furthermore, the protonated complex exhibits a new intense shoulder at ca. 39×10^3 cm^{-1} and the second absorption band at 27.86×10^3 cm^{-1}. This absorption spectral behavior of the protonated complex is in good agreement with that of the corresponding *O*-bonded sulfoxide complex, [Co{OS(CH$_3$)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ (Figs. 1 and 2). Taking account of the fact that the absorption spectra of [Co{Se(OH)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ and [Co{S(CH$_3$)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$ behave quite similarly to each other,[8] it is probable to consider that the protonation of the *O*-bonded seleninato complex occurs on the pendant oxygen atom to form [Co{OSe(OH)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{3+}$.

In the crystal state, the chiral selenium atom in the *O*-bonded seleninato isomer, Δ-$(-)^{\rm CD}_{500}$-[Co{OSe(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$, takes selectively the (*S*) configuration with the axial pendant oxygen atom.[14] Thus, the Λ-$(+)^{\rm CD}_{500}$ isomer should have the (*R*) configurational selenium atom in the crystal state. When the Λ-$(+)^{\rm CD}_{500}$ isomer was dissolved in water, a slight intensity change in the CD spectrum (ca. 12% decrease at 500 nm) was observed and the solution attained equilibrium after ca. 10 min. No change in the absorption spectrum was observed during the CD measurement. The ^{13}C NMR spectrum of Λ-$(+)^{\rm CD}_{500}$-[Co{OSe(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$ in a D$_2$O solution exhibits ten peaks for the six carbon atoms of the complex (Fig. 3(a)). This ^{13}C NMR spectral behavior is similar to that of a mixture of the $\Lambda(R)$ and $\Lambda(S)$ isomers of the corresponding *O*-bonded sulfinato complex, [Co{OS(O)CH$_2$CH$_2$NH$_2$}(en)$_2$]$^{2+}$; the peaks at 32.94, 45.45, 46.86, 47.08, and 51.09 ppm correspond to those for the $\Lambda(R)$ *O*-bonded sulfinato isomer, and

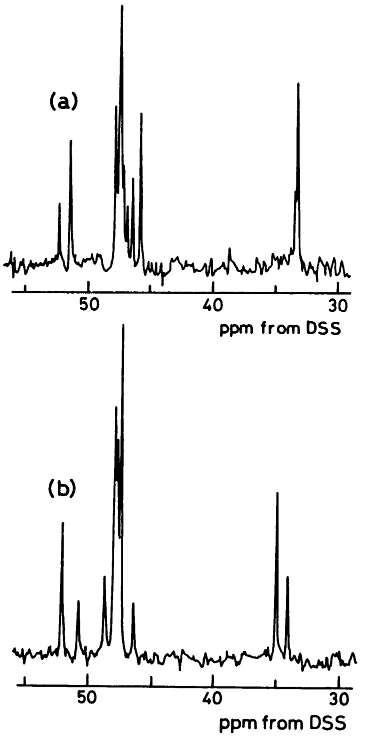

Fig. 3. ^{13}C NMR spectra of Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ in D_2O (a) and Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(OH)CH_2CH_2NH\}(en)_2}]^{3+}$ in 6% $\mathrm{HClO_4}$–D_2O (b).

the peaks at 33.10, 46.10, 46.53, 47.51, and 51.95 ppm to those for the $\Lambda(S)$ isomer.[13] These facts mean that Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ exists in a mixture of the $\Lambda(R)$ and $\Lambda(S)$ isomers in an aqueous solution because of the inversion at the chiral selenium atom. The $\Lambda(R)$ isomer seems to be dominant in the mixture, considering the intensity of the ^{13}C NMR peaks for the two isomers. In order to confirm the presence of the two isomers, the SP-Sephadex column chromatographic separation was attempted for Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$. However, only one absorbed band appeared, and all of its fractions showed the same CD spectra, though the corresponding *O*-bonded sulfinato isomers, $\Lambda(R)$- and $\Lambda(S)$-$[\mathrm{Co\{OS(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$, have been separated by the use of an SP-Sephadex column.[13] These facts indicate that the inversion at the chiral selenium atom in $[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ is faster than that at the chiral sulfur atom in $[\mathrm{Co\{OS(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$.

The Λ-$(+)^{\mathrm{CD}}_{500}$ *O*-bonded seleninato isomer shows an instantaneous and reversible CD spectral change with the pH change corresponding to the absorption spectral change. The positive CD band at 18.76×10^3 $\mathrm{cm^{-1}}$ in the first absorption band region of the protonated $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(OH)CH_2CH_2NH_2\}(en)_2}]^{3+}$ suggests that the protonation reaction proceeds with a retention of the Λ configuration (Fig. 2). The ^{13}C NMR spectrum of Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(OH)CH_2CH_2NH_2\}(en)_2}]^{3+}$ exhibits nine peaks for the six carbon atoms of the complex (Fig. 3(b)). This ^{13}C NMR spectral behavior indicates the coexistence of the $\Lambda(R)$ and $\Lambda(S)$ isomers as the parental Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$. For each pair of peaks at ca. 34 and 51 ppm, however, the peak at the higher magnetic field appears weaker than that at the lower one, in contrast with the case of the parental Λ-$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(O)CH_2CH_2NH_2\}(en)_2}]^{2+}$ (Fig. 3). Furthermore, the CD spectrum of $\Lambda(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co\{OSe(OH)CH_2CH_2NH_2\}(en)_2}]^{3+}$is quite similar to that of $\Lambda(R)$-$[\mathrm{Co\{OS(CH_3)CH_2CH_2NH_2\}(en)_2}]^{3+}$ (Figs. 1 and 2), where the (R) configuration of the latter complex corresponds to the (S) configuration of the former one.[16] The ^{13}C NMR and CD spectral behavior suggests that a shift of the equilibrium between the (R) and (S) configurations taskes place through the protonation reaction and that the protonated Λ-$(+)^{\mathrm{CD}}_{500}$ isomer takes the (S) configuration dominantly.

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