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PREPARATION AND OPTICAL RESOLUTION OF COBALT(III) COMPLEXES WITH 2-SELENOLATOETHYLAMINE AND ITS DERIVATIVES

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Four optical isomers of Co(III) complexes with a coordinated selenium atom, $[Co(L)(en)_2]^{2+ \text{ or } 3+}$ (L = 2-selenolatoethylamine, 2-selenenatoethylamine, 2-seleninatoethylamine, and 2-(methylseleno)-ethylamine), were newly prepared and characterized on the basis of the electronic absorption and circular dichroism (CD) spectra.

Cobalt(III) complex with selenolato ligand has been reported with stereochemical interest.[1)] Selenium-bonded selenenato, seleninato, and selenoether complexes are derived from the selenolato complex. These complexes are remarked in connection with the spectrochemical and stereochemical features as in the case of thiolato,[2)] sulfenato,[3)] sulfinato,[4,5)] and thioether[6,7)] ones. This letter is concerned with the optical resolution of bis(ethylenediamine)(2-selenolatoethylamine)cobalt(III), $[Co(sea)(en)_2]^{2+}$, and with the syntheses of optically active $[Co(seea)(en)_2]^{2+}$, $[Co(siea)(en)_2]^{2+}$, and $[Co(msea)(en)_2]^{3+}$ isomers, which are derived from $(+)^{CD}_{500}$-$[Co(sea)(en)_2]^{2+}$, where seea, siea, and msea denote 2-selenenatoethylamine, 2-seleninatoethylamine, and 2-(methylseleno)ethylamine, respectively. Their electronic absorption and CD spectra are discussed in comparison with those of the corresponding Co(III) complexes with a coordinated sulfur atom.

$[Co(sea)(en)_2](NO_3)_2$ was prepared by the method of Deutsch et al.[1)] A solution of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ (1.0 g) in water (10 cm^3) was added with stirring to a solution of $[Co(sea)(en)_2](NO_3)_2$ (1.2 g) in water (40 cm^3) on water bath at 50°C. The solution was stirred for 5 min, though fine dark brown crystals began to appear soon. The crystals were collected by filtration and it was confirmed from the CD measurement that the dark brown crystals were $(+)^{CD}_{500}$ diastereomer containing a small amount of $(-)^{CD}_{500}$ one. When the crude $(+)^{CD}_{500}$ diastereomer was repeated several times to grind with a small volume of water and sodium perchlorate, the $(-)^{\mathrm{CD}}_{500}$ diastereomer contaminated was dissolved first. The remaining pure $(+)^{\mathrm{CD}}_{500}$ diastereomer was again dissolved by grinding in a mortar with water and sodium perchlorate, and the solution was concentrated with a rotary evaporator until the fine needle crystals of the selenolato complex appeared. After cooling in a refrigerator, $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}](\mathrm{ClO_4})_2$ was collected by filtration, and washed with ethanol and ether. *Anal.* Found: C, 14.81; H, 4.32; N, 13.96%. Calcd for $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}](\mathrm{ClO_4})_2$: C, 14.38; H, 4.42; N, 13.97%.

A calculated amount of 1% aqueous H_2O_2 (0.31 cm^3) was added dropwise to a solution of $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}](\mathrm{ClO_4})_2$ (0.05 g) in water (1 cm^3) and the mixture was stirred for 15 min. The orange-yellow crystals of the selenenato complex were obtained from the reaction solution by the addition of 2-propanol. *Anal.* Found: C, 13.96; H, 4.04; N, 13.35%. Calcd for $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(seea)(en)_2}](\mathrm{ClO_4})_2$: C, 13.93; H, 4.28; N, 13.54%.

An excess amount of 5% aqueous H_2O_2 (0.6 cm^3) was added to a solution of $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}](\mathrm{ClO_4})_2$ (0.05 g) in water (1 cm^3), followed by the addition of 30% $HClO_4$ (0.25 cm^3). The solution was stirred for 30 min and stood in a refrigerator overnight. The solution was concentrated with a rotary evaporator and the resultant seleninato complex was recrystallized from water by adding ethanol. *Anal.* Found: C, 13.21; H, 4.27; N, 12.94%. Calcd for $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(siea)(en)_2}](\mathrm{ClO_4})_2\cdot 0.5H_2O$: C, 13.29; H, 4.28; N, 12.92%.

To a solution of $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}](\mathrm{ClO_4})_2$ (0.05 g) in water (1 cm^3) was added dimethyl sulfate (1 cm^3). The mixture was allowed to stand in a refrigerator overnight and separated into two layers. The orange-red upper layer was poured onto a column containing QAE-Sephadex A-25 anion exchange resin (ClO_4^- form), and the column was eluated with water. The eluate was concentrated and the resultant crystals of the selenoether complex were collected by filtration. *Anal.* Found: C, 13.89; H, 3.94; N, 11.39%. Calcd for $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(msea)(en)_2}](\mathrm{ClO_4})_3$: C, 13.65; H, 4.09; N, 11.37%.

The absorption spectra of four Co(III) complexes which belong to $[\mathrm{Co(N)_5(Se)}]$ type are generally similar to those of the corresponding $[\mathrm{Co(N)_5(S)}]$ type complexes (Fig. 1). The intense absorption bands at around $32\text{-}36\times10^3$ cm^{-1} are assigned to the charge transfer ones due to the coordinated selenium atom, which correspond to the sulfur-to-metal charge transfer bands.[2,3] Of the present complexes, the selenenato complex, $[\mathrm{Co(seea)(en)_2}]^{2+}$, shows another intense band at 27.55×10^3 cm^{-1} in addition to the shoulder at 32.3×10^3 cm^{-1}. Similar absorption spectral behavior was also observed for the sulfenato complexes[3)] and the band at 27.55×10^3 cm^{-1} seems to be characteristic for the selenenato complex. The first absorption bands of the present complexes commonly shift to the lower energy side than those of the corresponding Co(III) complexes with a coordinated sulfur atom. The ligand field strength of a coordinated sulfur atom increased with the order of thiolato, sulfenato and sulfinato,[3,4)] while this order is discounted for the present case. That is, the seleninato group locates at lower energy side than the selenenato one (Fig. 1).

In the first absorption band region, $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}]^{2+}$ exhibits three CD bands, (+), (+) and (-) from the lower energy side (Fig 1a). This CD pattern is similar to that of Λ-$[\mathrm{Co(aet)(en)_2}]^{2+}$ (Haet = 2-aminoethanethiol)[2)] and suggests that the $(+)^{\mathrm{CD}}_{500}$ sea complex takes Λ configuration. The seleninato complex, $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(siea)(en)_2}]^{2+}$,

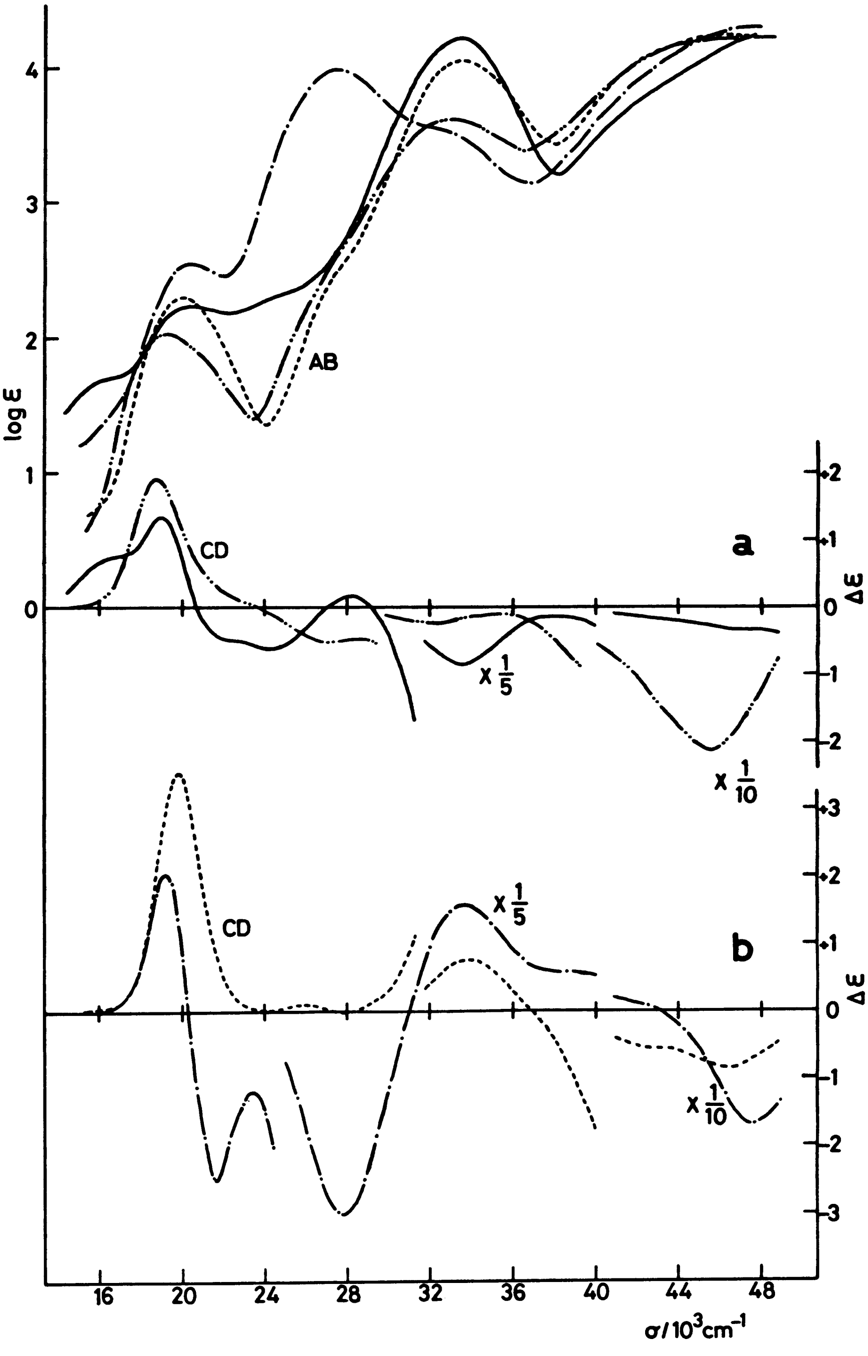

Fig. 1. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(sea)(en)_2}]^{2+}$ (————), $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(seea)(en)_2}]^{2+}$ (—·—·—), $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(siea)(en)_2}]^{2+}$ (—··—··—), and $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(msea)(en)_2}]^{3+}$ (-------).

can be assigned to Λ configuration from the fact that a positive CD band appears in the first absorption band region (Fig. 1a), as in the case of Λ-[Co(mea)(en)$_2$]$^{3+}$ (mea = 2-(methylthio)ethylamine).[2)]

For each of $(+)^{CD}_{500}$-[Co(seea)(en)$_2$]$^{2+}$ and $(+)^{CD}_{500}$-[Co(msea)(en)$_2$]$^{3+}$ complexes, R or S configuration with respect to a coordinated selenium atom is expected. In the CD spectra of Λ(R)- and Λ(S)-[Co(L-cysteinesulfenato-N,S)(en)$_2$]$^{+}$,[8)] the lowest energy CD band in the first absorption band region has a positive sign for both isomers, but the CD band in the sulfenato charge transfer band region (ca. 27x10^3 cm^{-1}) has a negative sign for the Λ(R) isomer and a positive for the Λ(S) one. This CD spectral behavior is also recognized for the Λ(R) and Λ(S) isomers of [Co(aese)-(en)$_2$]$^{2+}$ (aese = 2-aminoethanesulfenato).[9)] The CD spectral pattern of $(+)^{CD}_{500}$-[Co-(seea)(en)$_2$]$^{2+}$ is quite similar to that of Λ(R)-[Co(L-cysteinesulfenato-N,S)(en)$_2$]$^{+}$ (Fig. 1b), and it is suggested that the $(+)^{CD}_{500}$ seea isomer takes Λ(R) configuration. The $(+)^{CD}_{500}$-[Co(msea)(en)$_2$]$^{3+}$ complex shows a positive CD band in the first absorption band region (Fig. 1b). From the comparison with the CD spectrum of Λ-[Co(mea)(en)$_2$]$^{3+}$,[2)] it is possible to suggest that the $(+)^{CD}_{500}$ msea isomer takes Λ configuration. The ^{13}C NMR and ^{1}H NMR spectra of the $(+)^{CD}_{500}$ msea isomer in D_2O show only one methyl signal and suggest that the isomer is either Λ(R) or Λ(S) in solution. Molecular model constructions reveal that the Λ(R) is preferable. An X-ray analysis of $(+)^{CD}_{500}$-[Co(msea)(en)$_2$](ClO$_4$)$_3$ is in progress in order to elucidate its structure clearly.

References

1) C. A. Stein, P. E. Ellis, Jr., R. C. Elder, and E. Deutsch, Inorg. Chem., 15, 1618 (1976).
2) K. Yamanari, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Jpn., 50, 2299 (1977).
3) I. K. Adzamli, K. Libson, J. D. Lydon, R. C. Elder, and E. Deutsch, Inorg. Chem., 18, 303 (1979).
4) C. P. Sloan and J. H. Krueger, Inorg. Chem., 14, 1481 (1975).
5) M. Kita, K. Yamanari, and Y. Shimura, Chem. Lett., 1980, 275.
6) T. Isago, K. Igi, and J. Hidaka, Bull. Chem. Soc. Jpn., 52, 407 (1979).
7) K. Okamoto, K. Wakayama, M. Ohmasa, and J. Hidaka, Chem. Lett., 1981, 453.
8) D. L. Herting, C. P. Sloan, A. W. Cabral, and J. H. Krueger, Inorg. Chem., 17, 1649 (1978).
9) The present authors, to be published later.

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