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PREPARATION AND CRYSTAL STRUCTURE OF $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-((2D,9L)-DIAMINO-3,3,8,8-TETRAMETHYL-4,7-DITHIA-1,10-DECANDIOATO)COBALT(III) ION

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The crystal structure and absolute configuration of the title complex ion, $[\mathrm{Co(DL\text{-}ebp)}]^+$, were determined by an X-ray diffraction study of its $(+)_{546}$-(ethylenediaminetetraacetato)cobaltate(III) salt pentahydrate. The DL-ebp acts as sexidentate ligand. The $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis* isomer takes *S* configuration and the chiral sulfur donor atoms take selectively *R*(S),*R*(S) configuration.

The reaction of *cis·cis·cis*-$[\mathrm{Co(D\text{-}pen)(L\text{-}pen)}]^-$ (pen; penicillaminate)$^{1)}$ with 1,2-dibromoethane spanned with ethylene the thiolato type sulfur donor atoms in the D- and L-pen to give the title complex cation, *cis·cis·cis*-$[\mathrm{Co(DL\text{-}ebp)}]^+$. The resulting complex cation consists of the optical isomers, *R* and *S*,$^{2)}$ due to the arrangement of three kinds of the donor atoms, and each of them has another isomer with respect to the chirality, *R*(S) or *S*(S), due to the bridged sulfur atom. This letter is concerned with the preparation and resolution of the title complex cation, and also with the crystal structure and absolute configuration of the $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis* DL-ebp isomer determined by X-ray diffraction.

1,2-Dibromoethane (5 cm^3) was added to a solution containing of *cis·cis·cis*-$\mathrm{K[Co(D\text{-}pen)(L\text{-}pen)]\cdot 2H_2O}$$^{1)}$ (0.8 g) in 14 cm^3 of dimethyl sulfoxide. The mixture was stirred for a few minutes and was allowed to stand at room temperature for about a day. Dimethyl sulfoxide and unreacted 1,2-dibromoethane were extracted with ether for several times. To the remaining dark red solution was added a small amount of water and it was poured onto an SP-Sephadex C-25 column (Na^+ form, 4 x 25 cm). After sweeping the column with water, the adsorbed band was eluted with 0.05 mol dm^{-3} aqueous solution of NaBr. Only one red violet band was eluted. The eluate was concentrated to a small volume with a rotary evaporator. The deposited NaBr was filtered off and an appropriate amount of ethanol was added to the filtrate. The resulting red violet crystals were collected by filtration. Silver acetate (14 mg) and silver perchlorate (17 mg) were added to a solution containing the racemic *cis·cis·cis*-$[\mathrm{Co(DL\text{-}ebp)}]\mathrm{Br}$ (86 mg) and $(+)_{546}$-$\mathrm{K[Co(edta)]\cdot 2H_2O}$$^{3)}$ (32.4 mg) in a small amount of water. The silver bromide and potassium perchlorate precipitated were filtered off. After the filtrate had been concentrated to a small volume, the concentrated solution,

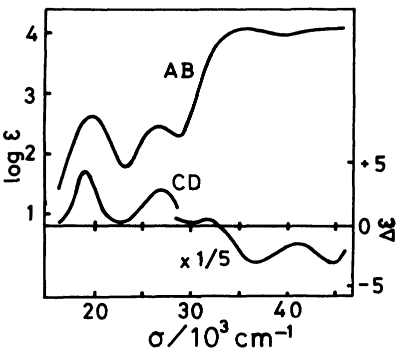

Fig. 1. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-$[\mathrm{Co(DL\text{-}ebp)}]\mathrm{Br}$.

which was added a small amount of ethanol, was kept in a refrigerator for 5 days. The less soluble diastereomer (violet needle crystals) was recrystallized from water by adding ethanol. By use of the anion exchange column (Br^- form), the diastereomer was converted into the bromide salt, $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-[Co(DL-ebp)]Br, which showed the absorption and CD spectra as in Fig. 1. The violet needle crystal (diastereomer) is orthorhombic with the space group $P2_12_12_1$; a = 13.215(5), b = 37.035(12), c = 6.527(2) Å, V = 3194.1(18) Å^3, and Z = 4. The observed density is 1.72 g cm^{-3} and the calculated one 1.70 g cm^{-3}. The crystal structure determination was based on the independent 2322 reflections with $|Fo| > 3\sigma(|Fo|)$ collected on a Rigaku-denki four circle diffractometer (AFC-5) by the ω-2θ scan technique up to $2\theta = 60°$, employing graphite-monochromated Mo Kα radiation. The structure was solved with the heavy atom method, and the full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms gave an R value of 0.088 (program RFINE by L.W.Finger was used).

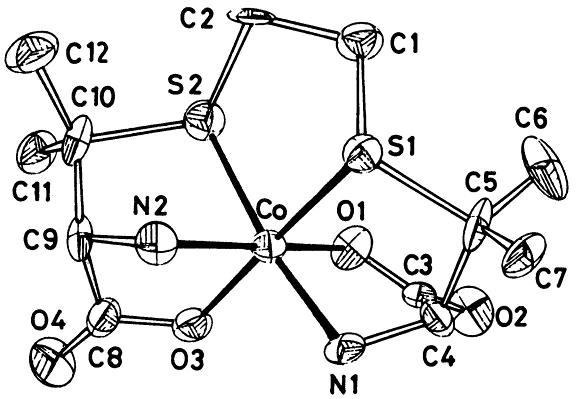

Fig. 2. Perspective view of $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-[Co(DL-ebp)]$^+$ ion.

The perspective drawing of the present complex cation is shown in Fig. 2. The cobalt atom is surrounded by two *cis* sulfur, two *cis* oxygen and two *cis* nitrogen atoms, and DL-ebp coordinates to cobalt atom as a sexidentate. The absolute configuration of the $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-[Co(DL-ebp)]$^+$ isomer was determined to *S* configuration$^{2)}$ (Fig. 2) on the basis of the known configuration, Δ, of the $(+)_{546}$-[Co(edta)]$^-$.$^{3)}$ Both of the chiral sulfur atoms take selectively *R*(S) configuration. The S,S-bridged five-membered chelate ring has a gauche form with λ conformation. The bond lengths and angles for the $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-[Co(DL-ebp)]$^+$ isomer are quite similar to those of the parent complex, *cis·cis·cis*-[Co(D-pen)(L-pen)]$^-$.$^{1)}$ These facts suggest that the S,S-bridged five-membered ring is fitted for the sulfur donor atoms of the parent complex anion without strain. It is noted that the Co-S bond lengths of 2.189 and 2.221 Å for the $(+)^{\mathrm{CD}}_{560}$-*cis·cis·cis*-[Co(DL-ebp)]$^+$ isomer are significantly shorter than those of the thioether type complexes such as *trans*(S)-bis(S-methyl-L-cysteinato)cobalt(III)$^{4)}$ and *trans*(O)-N,N'-ethylenebis(S-methyl-L-cysteinato)cobalt(III),$^{5)}$ which have a similar framework to the penicillaminate moiety of DL-ebp.

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