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Crystal Structure of $(-)^{CD}_{500}$-mer-(3-Azapentane-1,5-diamine)(ethylenediamine-N-acetato)cobalt(III) Bromide

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The crystal structure and absolute configuration of the title complex, $(-)^{CD}_{500}$-mer-[Co(edma)(dien)]Br_2, was determined by X-ray diffraction study. There are three crystallographically independent complex cations in an asymmetric unit. All of them, in which the terdentate ligands coordinate meridionally, have a δ spiral configuration and the asymmetric nitrogen donor atoms of the edma take an S configuration.

Three facial and one meridional isomers of (3-azapentane-1,5-diamine)(ethylenediamine-N-acetato)cobalt(III), fac- and mer-$[Co(edma)(dien)]^{2+}$, have been prepared and resolved chromatographically.[1)] Of these isomers ($[Co(O)(N)_5]$-type), the fac isomers have been spectrochemically investigated in detail.[1)] However, it is fairly difficult to distinguish accurately the present mer isomer on the basis of the spectrochemical behaviors,[1)] because two pairs of enantiomers are possible for the mer isomer as shown in Fig. 1, where the isomers are designated by the combination of the R and S configurations due to the asymmetric nitrogen donor atoms of the edma and the δ and λ spiral configurations due to the arrangements of the two trans N-H groups as in the case of mer-$[Co(mida)(dien)]^+$ (mida; N-methyliminodiacetate).[2)] So we attempted to determine the crystal structure of $(-)^{CD}_{500}$-mer-$[Co(edma)(dien)]^{2+}$. This letter deals with the crystal structure of the $(-)^{CD}_{500}$-mer isomer and also with the absolute configuration determined by the X-ray diffraction method.

The single crystal (ca. 0.30 × 0.32 × 0.63 mm^3), $(-)^{CD}_{500}$-mer-[Co(edma)(dien)]-$Br_2 \cdot 2/3CH_3OH \cdot 2/3H_2O$, is triclinic with the space group P1: $C_{8.67}H_{26}N_5O_{3.33}Br_2Co$, M.W.=472.4, a=13.824(8), b=13.814(8), c=8.055(3)Å, α=101.18(6), β=101.17(6), γ=116.32(5)°, V=1282(2)$Å^3$, d_m=1.82 g/dm^3 (by flotation), d_x=1.835 g/dm^3, Z=3, and μ(Mo Kα)=6.008 mm^{-1}. The crystal structure determination was based on the independent 5001 reflections with |Fo| >

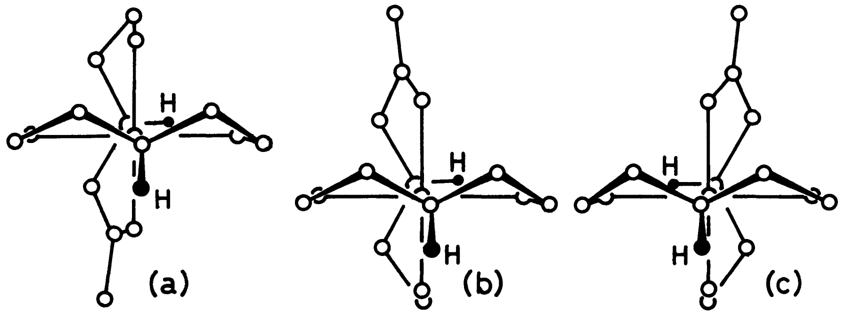

Fig. 1. Possible isomers of mer-$[Co(edma)(dien)]^{2+}$: (a) R(δ spiral), (b) S(δ spiral), and (c) R(λ spiral) configurations.

$3\sigma(|Fo|)$ collected on a Rigaku-denki four circle diffractometer (AFC-5) by the ω-2θ scan technique up to $2\theta = 60°$, employing graphite monochromatized Mo Kα radiation. The positions of three cobalt and six bromide atoms were obtained from MALTUN[3] and the difference Fourier maps, based on these positions, revealed all the non-hydrogen atoms. The structure was refined by a full-matrix least-squares method on the atomic parameters for all the non-hydrogen atoms (program RFINE[4,5] was used). The final residual values were R=0.049 and Rw=0.058, respectively.

The absolute configuration was determined by the anomalous scattering technique. When the refinements were carried out by use of a set of the atomic parameters containing the δ spiral configuration of the complex cation, the residual values converged to R= 0.047 and Rw=0.056, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the λ spiral configuration) resulted in the residual values of R=0.054 and Rw=0.062, respectively. These facts indicate that the δ spiral configuration is probably the correct choice (Fig. 1(b)). A similar treatment was reported for the determination of the absolute configuration of the cobalt(III) complexes,[2,6] which comprise the internal reference of the known configuration and their systematic errors are nearly the same as those of the present work.

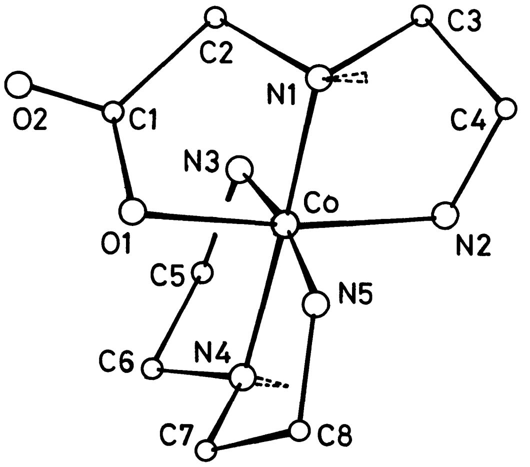

Fig. 2. Perspective view of the $(-)^{CD}_{500}$-mer-$[Co(edma)(dien)]^{2+}$ ion.

There are three crystallographically independent complex cations in an asymmetric unit, although their shapes and sizes remarkably resemble one another. A perspective drawing of the typical complex cation (one species) is shown in Fig. 2. The edma and the dien coordinate meridionally to the cobalt atom as terdentate ligands. The bond lengths and angles for the dien coordinated coincide with those of mer-$[Co(mida)(dien)]^{+}$[2] and mer-$[Co(dien)_2]^{3+}$.[7] The absolute configuration of the asymmetric nitrogen donor atom in $(-)^{CD}_{500}$-mer-$[Co(edma)(dien)]^{2+}$, which has the δ spiral configuration, was determined to be an S configuration (Figs. 1(b) and 2). Namely, of two possible isomers R and S for the δ spiral configuration (Fig. 1 (a) and (b)), the S(δ spiral) isomer was selectively formed. This suggests that the R(δ spiral) isomer has a significantly intramolecular steric interaction between the amine group in the edma and the two methylene groups in the dien, and thus the S(δ spiral) isomer is more preferable than the R(δ spiral) one.

References

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