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Structure and Absolute Configuration of the $(-)^{CD}_{570}$-mer-(3-Azapentane-1,5-diamine)(N-methyliminodiacetato)cobalt(III) Ion

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The crystal structure and the absolute configuration of the title complex cation, $(-)^{CD}_{570}$-mer-$[Co(mida)(dien)]^+$, was determined by the X-ray diffraction study of its $(-)^{CD}_{580}$-(ethylenediaminetetraacetato)cobaltate(III) salt dihydrate. The relationship between the absolute configuration and the CD spectra for the mer isomers of the dien complexes with mida or iminodiacetate is also reported.

When two symmetrical terdentate ligands such as 3-azapentane-1,5-diamine (dien), iminodiacetate (ida), and N-methyliminodiacetate (mida) coordinate meridionally to a cobalt atom, a pair of enantiomers for each complex is possible as shown in Fig. 1,[1-5] where the isomers are designated as δ and λ spiral configurations[6] with respect to the arrangements of the trans N-H and $N-CH_3$ groups in the complex cation. The absolute configurations for the facial cobalt(III) complexes with the terdentate ligands have been extensively investigated on the basis of the CD spectral behavior[2,3,7] and the X-ray diffraction studies.[8,9] For the mer isomers, however, the relationship between the CD spectrum and the absolute configuration is not clear yet.[2-4] This letter is concerned with the absolute configuration of

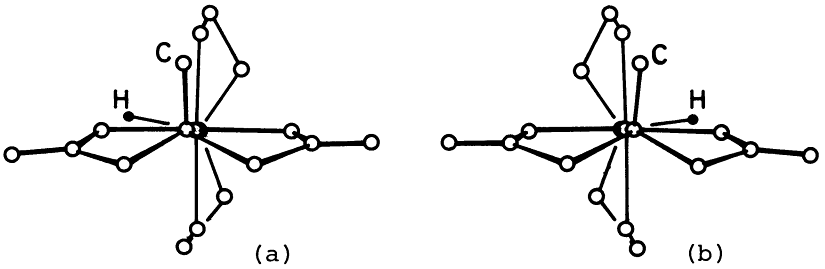

Fig. 1. Two possible isomers of mer-$[Co(mida)(dien)]^+$: δ (a) and λ (b) spiral configurations.

$(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]$^{+}$ determined by the X-ray diffraction study and with the CD spectra of the mer isomers for the dien cobalt(III) complexes with mida or ida.

The $(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]Cl·1.5H_2O isomer was obtained by the method of Koine et al.$^{5)}$ The dark-violet crystals, which were obtained as the less soluble diastereomer, $(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]·$(-)^{\mathrm{CD}}_{580}$-[Co(edta)]·2H_2O, were used for the X-ray diffraction study. The mer-[Co(ida)(dien)]Cl isomer was prepared by the method of Legg et al.,$^{1)}$ and the $(+)^{\mathrm{CD}}_{560}$-mer isomer was obtained by a procedure similar to that used for $(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]Cl. Found: C, 27.18; H, 5.95; N, 15.77%. Calcd for [Co(ida)(dien)]Cl·1.5H_2O = $C_8H_{21}N_4O_{5.5}ClCo$: C, 27.07; H, 5.95; N, 15.75%.

The dark-violet crystal (ca. 0.70 x 0.45 x 0.40 mm^3), $(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]·$(-)^{\mathrm{CD}}_{580}$-[Co(edta)]·2H_2O, is triclinic with the space group P1: $C_{19}H_{36}N_6O_{14}Co_2$, M.W. = 690.4, $a = 11.923(2)$, $b = 8.460(2)$, $c = 6.778(2)$ Å, $\alpha = 105.01(2)$, $\beta = 91.25(4)$, $\gamma = 82.29(2)°$, $V = 654.4(3)$ $\mathrm{Å}^3$, $d_m = 1.72\ \mathrm{g\ cm^{-3}}$, $d_x = 1.75\ \mathrm{g\ cm^{-3}}$, $Z = 1$, and $\mu(\mathrm{Mo}\ K\alpha) = 1.405\ \mathrm{mm^{-1}}$. The crystal structure determination was based on the independent 3768 reflections with $|Fo| > 3\sigma(|Fo|)$ collected on a Rigaku-denki four circle diffractometer (AFC-5) by the ω-2θ scan technique up to 60°, employing graphite-monochromatized Mo Kα radiation. The structure was solved with MULTAN$^{10)}$ and refined by a full-matrix least-squares refinements of the positional and anisotropic thermal parameters of all the non-hydrogen atoms (program RFINE$^{11)}$ was used). The final residual values were $R = 0.042$ and $Rw = 0.078$, respectively.

The absolute configuration was determined by the anomalous scattering technique. The atomic scattering factors for all the non-hydrogen atoms were taken from the literature.$^{12)}$ 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 $R = 0.040$ and $Rw = 0.076$, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the λ spiral configuration) resulted in the residual values of $R = 0.045$ and $Rw = 0.081$, respectively. These facts indicate that the former is probably the correct choice, namely, the complex cation has the δ spiral configuration (Fig. 1(a)). This result was also confirmed by the determination on the basis of the known configuration of the $(-)^{\mathrm{CD}}_{580}$-[Co(edta)]$^{-}$ ($(+)_{546}$-Δ isomer).$^{13)}$

A perspective drawing of the present complex cation is shown in Fig. 2. The N-methyliminodiacetate and 3-azapentane-1,5-diamine coordinate meridionally to the cobalt atom as the terdentate ligands. The bond lengths and angles for dien coordinated to the cobalt atom coincide well with those of mer-[Co(dien)$_2$]$^{3+}$.4) One of the five-membered chelate rings of the dien, N2-C6-C7-N3, takes a δ conformation with an envelope form, as in the case of mer-[Co(dien)$_2$]$^{3+}$.4) On the contrary, the other fused chelate ring, N3-C8-C9-N4, takes a λ conformation with a gauche form; the C8 and C9 atoms are shifted by 0.478 and - 0.284 Å, respectively, from the plane formed by the cobalt and two ligating nitrogen atoms. For the mida coordinated meridionally to the cobalt atom, its bond lengths and angles are in good agreement with the results observed for the mida in u-fac-[Co(mida)$_2$]$^-$.14) The angle subtended by the two terminal oxygen atoms of the mida at the central cobalt atom is 173.0(2)°. The two five-membered chelate rings are almost symmetrical and they take a envelope form; the methylene carbon atoms in the mida are shifted by 0.657 Å (C2) and 0.733 Å (C4) from the plane formed by the cobalt and the ligating oxygen and nitrogen atoms.

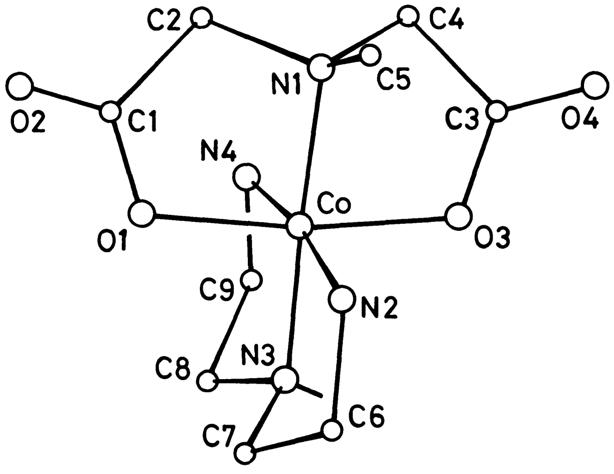

Fig. 2. Perspective view of the $(-)^{\mathrm{CD}}_{570}$-[Co(mida)(dien)]$^+$ ion.

The absorption and CD spectra of the mer isomers of [Co(mida)(dien)]$^+$ and [Co(ida)(dien)]$^+$ are shown in Fig. 3. The CD spectral pattern of $(+)^{\mathrm{CD}}_{560}$-mer-[Co(ida)(dien)]$^+$ can be superimposed in the whole region by the enantiomeric CD pattern of $(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]$^+$. For these two isomers, further, the rotational strength in the corresponding region also resemble each other. Accordingly, $(+)^{\mathrm{CD}}_{560}$-mer-[Co(ida)(dien)]$^+$ can be assigned to the λ spiral configuration as in Fig. 1(b). In the first d-d transition region, $(-)^{\mathrm{CD}}_{570}$-mer-[Co(mida)(dien)]$^+$ and $(+)^{\mathrm{CD}}_{560}$-mer-[Co(ida)(dien)]$^+$ exhibit three CD bands (Δε = + 0.214 mol^{-1} dm^3 cm^{-1} (17860 cm^{-1}), - 0.283 (19960), and + 0.102 (22730) for the ida isomer with the λ spiral configuration), while $(+)_{589}$-mer-[Co(dien)$_2$]$^{3+}$, which was determined to be the δ spiral configuration by the X-ray crystal structure analysis,4) has exhibited two CD bands (Δε = + 0.096 mol^{-1} dm^3 cm^{-1} (19500 cm^{-1}) and - 0.18 (21900)).3) These facts are different significantly from the results that the Δ configurations (or the Λ configurations) of the unsymmetrically facial isomer of [Co(L)(L')]-type (L and L'; ida, mida, and/or dien) exhibit similar CD spectral patterns in this region to one another.$^{3,8,9)}$ In the second d-d transition region, however, it is noted that the mida and ida isomers of the δ spiral configuration exhibit a positive and a negative CD bands from the lower energy, as in the case of $(+)_{589}$-mer-$[Co(dien)_2]^{3+}$ and $(+)_{589}$-mer-$[Co(dema)(dien)]^{3+}$ (dema; N-methylbis(2-aminoethyl)amine).$^{3)}$

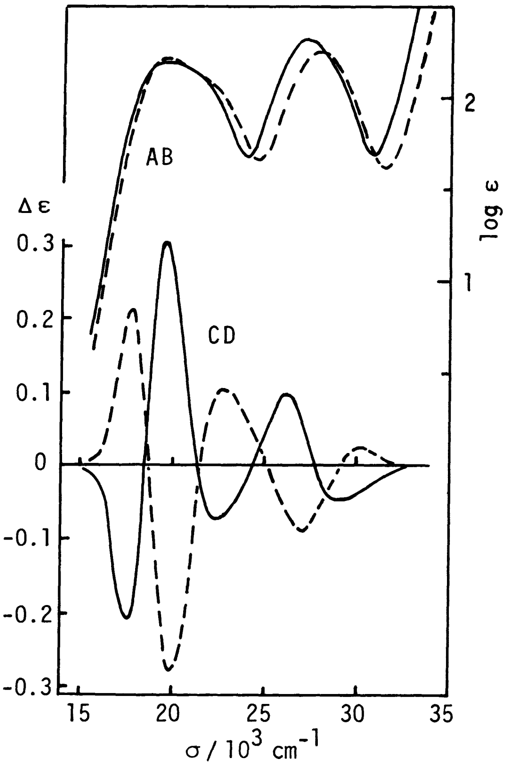

Fig. 3. Absorption and CD spectra of $(-)^{CD}_{570}$-mer-$[Co(mida)(dien)]^+$ (——) and $(+)^{CD}_{560}$-mer-$[Co(ida)(dien)]^+$ (----) in 0.01 mol dm^{-3} HCl.

References

1) J. I. Legg and D. W. Cooke, Inorg. Chem., 5, 594 (1966).

2) F. R. Keene and G. H. Searle, Inorg. Chem., 11, 148 (1972)

3) M. Kojima, M. Iwagaki, Y. Yoshikawa, and J. Fujita, Bull. Chem. Soc. Jpn., 50, 3216 (1977).

4) K. Okiyama, S. Sato, and Y. Saito, Acta Crystallogr., Sect. B, 35, 2389 (1979).

5) N. Koine, T. Tanigaki, J. Hidaka, and Y. Shimura, Chem. Lett., 1980, 871.

6) Inorg. Chem., 9, 1 (1970).

7) H. Kawaguchi, T. Ama, and T. Yasui, Bull. Chem. Soc. Jpn., 57, 2422 (1984), and references sited therein.

8) M. Konno, F. Marumo, and Y. Saito, Acta Crystallogr., Sect. B, 29, 739 (1973).

9) T. Yasui, K. Okamoto, J. Hidaka, T. Ama, and H. Kawaguchi, to be submitted in Bull. Chem. Soc. Jpn.

10) G. Germain, P. Main, and M. M. Woolfson, Acta Crystallogr., Sect. A, 27, 368 (1971).

11) L. W. Finger, RFINE-2, Geophisical Lab. Carnegie Institute, Washington, D.C. (1972).

12) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV; D. T. Cromer and J. B. Mann, Acta Crystallogr., Sect. A, 24, 321 (1966).

13) K. Okamoto, T. Tsukihara, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Jpn., 51, 3534 (1978).

14) Y. Kushi, T. Ideno, T. Yasui, and H. Yoneda, Bull. Chem. Soc. Jpn., 56, 2845 (1983).

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