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Molecular structure and stereoselective isomerization of $(-)^{\mathrm{CD}}_{504}$-*mer*-bis(ethylenediamine-*N*-acetato)cobalt(III) bromide

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Abstract

The crystal structure of the $(-)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]Br isomer (edma = ethylenediamine-*N*-acetate) has been determined by a single crystal X-ray diffraction technique. The crystal was orthorhombic with space group $P2_12_12_1$, $a = 8.507(1)$, $b = 18.363(2)$, $c = 8.499(1)$ Å, $V = 1327.6(3)$ Å^3, and $Z = 4$. The cobalt atom is surrounded octahedrally by *cis* two oxygen and four nitrogen atoms of the two edma ligands, which coordinate to the cobalt ion in the meridional form. The $(-)^{\mathrm{CD}}_{504}$ isomer has an $S(C_2)$ configuration and both of the asymmetric nitrogen donor atoms in the two edma ligands take an S configuration. The $(+)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]$^+$ isomer isomerized to the $(+)^{\mathrm{CD}}_{543}$-C_2-*trans*(O) and C_i-*trans*(O) isomers in a basic aqueous solution (pH 10.35) at 40 °C, and the formation ratio of these two isomers was *c.* 1:1. The isomerization mechanism of the $(+)^{\mathrm{CD}}_{504}$-*mer* isomer was discussed in relation to its absolute configuration.

Introduction

The *mer*-[Co(edma)$_2$]$^+$ isomer has been prepared and resolved into its optically active isomers by the chromatographic method [1]. Three pairs of enantiomers, $S(C_2)(\mathrm{N}_S,\mathrm{N}_S)$–$R(C_2)(\mathrm{N}_R,\mathrm{N}_R)$ (Fig. 1(1)), $S(C_2)(\mathrm{N}_S,\mathrm{N}_R)$–$R(C_2)(\mathrm{N}_R,\mathrm{N}_S)$ (2), and $S(C_2)$-$(\mathrm{N}_R,\mathrm{N}_R)$–$R(C_2)(\mathrm{N}_S,\mathrm{N}_S)$ (3), are possible for the *mer* isomer, with respect to the combination of the $S(C_2)$ or $R(C_2)$ configuration due to the skew pair of two unsymmetrical terdentate ligands as well as the *mer*-[Co(dipeptidato)$_2$] type complexes [2] and of the R or S configuration (N_R or N_S) due to the asymmetric nitrogen atom of the two edma ligands. However, it is quite difficult to decide their absolute configuration on the basis of the spectrochemical properties, therefore we determined herein the crystal structure of the $(-)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]Br isomer by X-ray crystal structure analysis.

The $(+)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]$^+$ isomer has stereoselectively isomerized to two isomers, $(+)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)- and achiral C_i-*trans*(O)-[Co(edma)$_2$]$^+$ [3]. However, the detailed isomerization mechanism of the $(+)^{\mathrm{CD}}_{504}$-*mer* isomer remains unknown [3], since the absolute configuration of the $(+)^{\mathrm{CD}}_{504}$-*mer* or $(-)^{\mathrm{CD}}_{504}$-*mer* isomer has not been determined. In this paper, the isomerization mechanism of the $(+)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]$^+$ isomer will be briefly discussed in connection with its molecular structure.

Experimental

Complex

The $(-)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]Br isomer was prepared and separated according to the method described in the previous paper [1]. The single crystals were obtained by gradual evaporation of an aqueous solution containing this isomer in a vacuum desiccator.

X-ray data collection

Unit cell parameters and intensity data for the single dark brown crystal (*c.* 0.38×0.40×0.40 mm) were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Unit cell parameters were determined by least-squares refinement from 25 reflections with $22 < 2\theta < 26°$. Crystal data:

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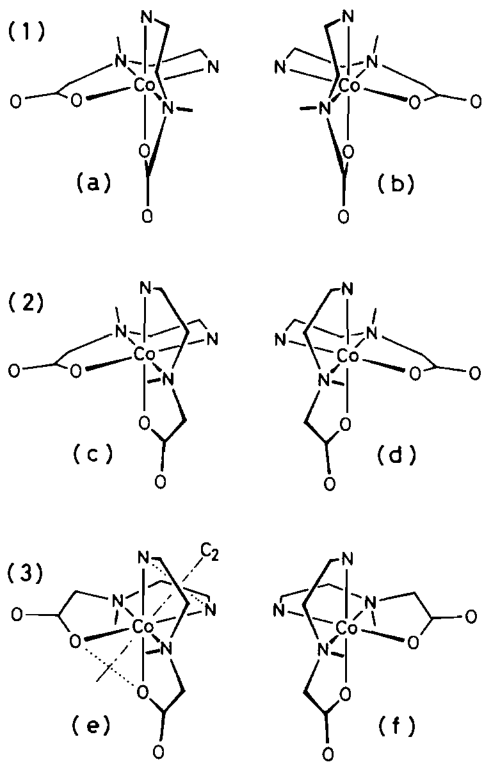


Fig. 1. Three possible pairs of enantiomers for the *mer*-[Co(edma)$_2$]$^+$ isomer: (1) (a) $S(C_2)(N_S,N_S)$ and (b) $R(C_2)(N_R,N_R)$; (2) (c) $S(C_2)(N_S,N_R)$ and (d) $R(C_2)(N_R,N_S)$ (pseudo-C_2 axis for these isomers); and (3) (e) $S(C_2)(N_R,N_R)$ and (f) $R(C_2)(N_S,N_S)$.

[Co($C_8H_{18}N_4O_4$)]Br, $M_r = 373.09$, orthorhombic, $P2_12_12_1$, $a = 8.507(1)$, $b = 18.363(2)$, $c = 8.499(1)$ Å, $V = 1327.6(3)$ Å^3, $Z = 4$, $D_x = 1.87$ g cm^{-3}, $\mu = 41.9$ cm^{-1}, $F(000) = 752$, and room temperature.

The intensity data were collected by the ω–2θ scan mode up to $2\theta \leqslant 60°$ ($0 \leqslant h \leqslant 11$, $0 \leqslant k \leqslant 25$, $0 \leqslant l \leqslant 11$) with scan width $(0.8 + 0.350 \tan \theta)°$ and scan rate varied from 1 to 5 ° min^{-1} (in omega). The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of psi-scans was applied. A total of 2002 independent reflections with $|F_o| > 3\sigma(|F_o|)$ of the measured 2231 reflections were considered as 'observed' and used for the structure determination.

Determination of crystal structure

The cobalt, two oxygen, and four nitrogen atom positions were determined from direct methods. The other non-hydrogen atom positions were determined from successive difference Fourier maps. The structure was refined by full-matrix least-squares using anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms of the ethylene in the edma ligands were included in the calculation, and these hydrogen atoms were fixed by geometrical constraints (C–H = 0.95 Å) and isotropic thermal parameters ($U = 0.05$ Å^2). The hydrogen atoms attached on the nitrogen atoms were not included in the calculation. The atomic scattering factors for all the atoms were taken from the literature [4]. The final residual values were $R = 0.036$ and $R_w = 0.042$; $w = 1.2590/(\sigma^2(F) + 0.001859(F)^2)$ and $S = 1.23$. The largest parameter shift was 0.002 times of e.s.d. and $|\Delta\rho|_{\max}$ in the final difference Fourier map is 1.08 e A^{-3} (this highest peak locates at the position close to the bromide atom). We attempted to determine the absolute configuration of the complex cation by an anomalous-scattering technique. When the refinements were carried out using a set of enantiomeric atomic parameters, the residual values converged to $R = 0.056$ and $R_w = 0.064$; $w = 2.5930/(\sigma^2(F) + 0.001013(F)^2)$ and $S = 3.25$. This indicates that the enantiomeric structure could be rejected at the 0.005 significant level by the Hamilton test [5]. These facts suggest, therefore, that the complex cation takes the $S(C_2)$ configuration and both of the asymmetric nitrogen donor atoms take an S configuration. All calculations were performed with MULTAN [6] and SHELX76 [7], and molecular illustrations were drawn using ORTEP [8] on the FACOM M780/20 computer at the University of Tsukuba. The final positional parameters are listed in Table 1.

Isomerization reaction of complex

The measurement of the isomerization reaction of the $(+)^{\mathrm{CD}}_{504}$-*mer*-[Co(edma)$_2$]$^+$ isomer has already been reported in the previous paper [3]. The reaction conditions were as follows: complex concentration, 4.66×10^{-3} mol dm^{-3}; pH, 10.35 ± 0.02 (Na_2CO_3–$NaHCO_3$ buffer); and temperature, 40.0 ± 0.1 °C.

Results and discussion

Description of the structure

A perspective drawing of the complex cation is shown in Fig. 2, together with its atomic numbering scheme. The bond distances and angles within the complex cation are summarized in Table 2. The cobalt atom is octahedrally surrounded by *cis* two oxygen and four nitrogen atoms. Both of the ethylenediamine-*N*-acetate ligands coordinate meridionally to the cobalt atom as a terdentate. For the *mer*-[Co(edma)$_2$]$^+$ isomer, three pairs of enantiomers, $S(C_2)(N_S,N_S)$-$R(C_2)(N_R,N_R)$, $S(C_2)(N_S,N_R)$-$R(C_2)(N_R,N_S)$ and $S(C_2)(N_R,N_R)$-$R(C_2)(N_S,N_S)$, are possible, with respect to the combination of the $S(C_2)$ or $R(C_2)$ configuration due to the skew pair of two unsymmetrical terdentates [2] and the R or S configuration due to the asymmetric nitrogen atom of

TABLE 1. Final atomic coordinates and equivalent isotropic thermal parameters (Å^2) for the non-H atoms

Atom	x	y	z	B_{eq}^{a}
Co	0.55692(6)	0.37496(3)	0.19301(6)	1.04(2)
O(1)	0.6786(4)	0.3025(2)	0.0860(4)	1.81(12)
O(2)	0.7060(6)	0.2526(2)	−0.1515(5)	3.83(19)
O(3)	0.6641(4)	0.4492(2)	0.0719(4)	1.74(12)
O(4)	0.9022(5)	0.4969(2)	0.0443(6)	3.63(18)
N(1)	0.4040(4)	0.3558(2)	0.0305(4)	1.41(12)
N(2)	0.4116(4)	0.4496(2)	0.2706(5)	1.53(13)
N(3)	0.7189(4)	0.3941(2)	0.3462(4)	1.39(12)
N(4)	0.4795(5)	0.3018(2)	0.3394(4)	1.53(13)
C(1)	0.6356(6)	0.2936(3)	−0.0573(6)	2.19(18)
C(2)	0.4909(6)	0.3338(3)	−0.1120(5)	1.91(17)
C(3)	0.2993(6)	0.4204(2)	0.0178(6)	1.95(17)
C(4)	0.2596(5)	0.4412(3)	0.1848(6)	1.78(15)
C(5)	0.8080(6)	0.4583(3)	0.1142(7)	2.15(18)
C(6)	0.8608(5)	0.4156(3)	0.2594(6)	1.86(17)
C(7)	0.7326(6)	0.3301(2)	0.4497(6)	1.87(16)
C(8)	0.5657(6)	0.3095(2)	0.4900(5)	1.74(15)
Br	0.66136(7)	0.12510(3)	0.41137(7)	2.78(2)

$^aB_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

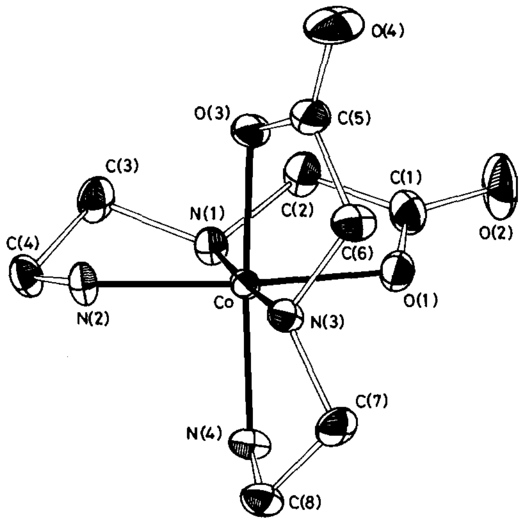


Fig. 2. A perspective drawing of the $(-)_{504}^{\mathrm{CD}}$-*mer*-[Co(edma)$_2$]$^+$ isomer (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

the two edma ligands (Fig. 1). The absolute configuration of the present complex cation was determined to be an $S(C_2)$ configuration and those of the two asymmetric nitrogen donor atoms to be an S configuration (Figs. 1(1a) and 2). This seems to indicate that one of three pairs of enantiomers, the $S(C_2)(\mathrm{N}_S,\mathrm{N}_S)$ and $R(C_2)(\mathrm{N}_R,\mathrm{N}_R)$ isomers (Fig. 1(1)), was selectively formed in the crystalline state, because the other isomers may have a significantly intramolecular steric interaction between the amino groups in the edma ligand and the two methylene groups in the other edma one. A similar trend was also observed for the *mer*-[Co(edma)(dien)]$^{2+}$ isomer [9].

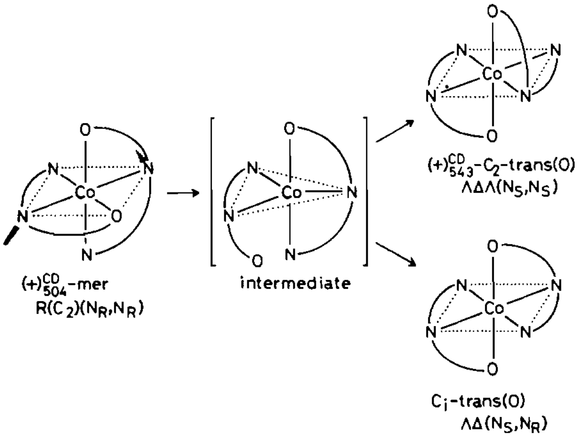
The bond distances and angles for the coordinating edma ligand are almost similar to those for the *mer*-[Co(edma)(dien)]$^{2+}$ isomer [9] and the *cis*(O)*trans*-(NH)-[Co(edma)$_2$]$^+$ one [1]. The Co–N distances (1.946(3) and 1.960(3) Å) for the terminal nitrogen atoms are somewhat longer than those (1.928(4) and 1.930(4) Å) for the central imino nitrogen atoms. The O–Co–N angles (170.5(1) and 170.2(1)°) for the meridionally coordinated edma ligands are of a reasonable value, summing up the formed two five-membered chelate rings. The conformations for the chelate rings in the edma ligands are also quite similar to those in the *mer*-[Co(edma)(dien)]$^{2+}$ isomer [9].

Isomerization

The $(+)_{504}^{\mathrm{CD}}$-*mer*-[Co(edma)$_2$]$^+$ isomer has slowly isomerized over a period of 53 h under the condition of pH 10.35 at 40 °C to form stereoselectively two isomers, $(+)_{543}^{\mathrm{CD}}$-C_2-*trans*(O)- and C_i-*trans*(O)-[Co(edma)$_2$]$^+$, whose molar ratio was *c*. 1:1, and the racemization of the $(+)_{504}^{\mathrm{CD}}$-*mer* isomer was almost negligible throughout the reaction [3]. In this reaction, it is noted that the isomerization from the *mer* isomer to the two *fac*-type isomers must be attended with the rearrangement of the oxygen atoms from *cis* to *trans*, and with the inversion at one (N_S,N_R for the C_i-*trans*(O) isomer) or both (N_S,N_S for the $(+)_{543}^{\mathrm{CD}}$-C_2-*trans*(O) isomer) of the two *sec*-N chiral centers (Scheme 1). The configuration of the asymmetric

TABLE 2. Bond distances (Å) and angles (°)

Co–O(1)	1.916(3)
Co–O(3)	1.936(3)
Co–N(1)	1.930(4)
Co–N(2)	1.960(3)
Co–N(3)	1.928(4)
Co–N(4)	1.946(3)
O(1)–C(1)	1.282(6)
O(2)–C(1)	1.251(6)
O(3)–C(5)	1.287(6)
O(4)–C(5)	1.223(6)
N(1)–C(2)	1.475(6)
N(1)–C(3)	1.488(6)
N(2)–C(4)	1.492(5)
N(3)–C(6)	1.469(5)
N(3)–C(7)	1.474(5)
N(4)–C(8)	1.482(5)
C(1)–C(2)	1.509(7)
C(3)–C(4)	1.508(7)
C(5)–C(6)	1.529(7)
C(7)–C(8)	1.509(7)
O(1)–Co–O(3)	88.9(1)
O(1)–Co–N(1)	84.1(1)
O(3)–Co–N(1)	93.8(1)
O(1)–Co–N(2)	170.5(1)
O(3)–Co–N(2)	89.1(1)
N(1)–Co–N(2)	86.8(1)
O(1)–Co–N(3)	93.5(1)
O(3)–Co–N(3)	83.9(1)
N(1)–Co–N(3)	176.7(2)
N(2)–Co–N(3)	95.5(1)
O(1)–Co–N(4)	90.4(1)
O(3)–Co–N(4)	170.2(1)
N(1)–Co–N(4)	95.9(1)
N(2)–Co–N(4)	93.1(2)
N(3)–Co–N(4)	86.3(1)
Co–O(1)–C(1)	112.7(3)
Co–O(3)–C(5)	113.0(3)
Co–N(1)–C(2)	107.4(3)
Co–N(1)–C(3)	108.1(3)
C(2)–N(1)–C(3)	117.3(3)
Co–N(2)–C(4)	108.0(3)
Co–N(3)–C(6)	107.3(3)
Co–N(3)–C(7)	108.3(3)
C(6)–N(3)–C(7)	116.7(3)
Co–N(4)–C(8)	108.6(3)
O(1)–C(1)–O(2)	123.2(5)
O(1)–C(1)–C(2)	117.5(4)
O(2)–C(1)–C(2)	119.2(4)
N(1)–C(2)–C(1)	106.9(4)
N(1)–C(3)–C(4)	105.5(4)
N(2)–C(4)–C(3)	107.0(4)
O(3)–C(5)–O(4)	124.2(5)
O(3)–C(5)–C(6)	116.0(4)
O(4)–C(5)–C(6)	119.8(4)
N(3)–C(6)–C(5)	107.6(4)
N(3)–C(7)–C(8)	105.1(3)
N(4)–C(8)–C(7)	107.1(3)



Scheme 1.

sec-N donor atom in the *fac*-type isomers of the $[\mathrm{Co(edma)_2}]^+$ complex is regulated by the absolute configuration (Δ or Λ) around the cobalt(III) ion, but that of the *mer*-type ones is not. For example, the *sec*-N donor atoms in the $(+)^{\mathrm{CD}}_{543}$-ΛΔΛ-C_2-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$ isomer is restricted to the N_S configurations, and the C_i-*trans*(O) isomer is achiral, ΛΔ(N_S,N_R). In contrast with the *fac*-type isomers, the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer*-$[\mathrm{Co(edma)_2}]^+$ isomer can take the three possible configurations, (N_R,N_R), (N_R,N_S) and (N_S,N_S) (Fig. 1), although the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* isomer takes only the (N_R,N_R) configuration in the crystalline state. Judging from the rate of the inversion at the *sec*-N atom of the edma ligand in the $(-)^{\mathrm{CD}}_{500}$-*mer*-$[\mathrm{Co(edma)(dien)}]^{2+}$ isomer [9], it is probable that the inversion at the *sec*-N atoms in the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* isomer occurs very rapidly in a basic aqueous solution, that is, equilibration of $(\mathrm{N}_R,\mathrm{N}_R) \rightleftharpoons (\mathrm{N}_R,\mathrm{N}_S) \rightleftharpoons (\mathrm{N}_S,\mathrm{N}_S)$ is rapidly attained. Therefore, it is reasonable to consider that the stereoselectivity in the isomerization reaction of the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer*-$[\mathrm{Co(edma)_2}]^+$ isomer does not depend on the chirality of the *sec*-N atom, but on the '$R(C_2)$' configuration.

In the present results for the $[\mathrm{Co(edma)_2}]^+$ complex, the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* → $(+)^{\mathrm{CD}}_{543}$-ΛΔΛ(N_S,N_S)-C_2-*trans*(O) change can be explained by both the twist and bond-rupture mechanisms, by which intramolecular coordination site exchanges can occur in octahedral complexes, while the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* → ΛΔ(N_S,N_R)-C_i-*trans*(O) change does not occur by the twist mechanism. Therefore, the isomerization reaction of the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer*-$[\mathrm{Co(edma)_2}]^+$ isomer seems to proceed with a mechanism (Scheme 1) occurring through a transient five-coordinate intermediate formed by the Co–O bond rupture, as in the case of the *fac*-type isomers of the

$[\mathrm{Co(edma)_2}]^+$ complex [3]. In this mechanism, the isomerization of the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* isomer is expected to take place in three stages: (1) the fission of the Co–O bond, (2) intermediate of the Co–O bond-ruptured state, and (3) the recombination of the 'bond-ruptured O' atom. In stage (3), the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* configuration is retained, when the 'bond-ruptured O' atom rejoins at the trigonal plane. When the 'bond-ruptured O' atom rejoins at the terminal N coordination site of the other edma and the terminal N donor atom is accompanied with the simultaneous shift to the trigonal plane, the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* isomer forms stereoselectively the $(+)^{\mathrm{CD}}_{543}$-$\Lambda\Delta\Lambda(\mathrm{N}_S,\mathrm{N}_S)$-$C_2$-*trans*(O) and $\Lambda\Delta(\mathrm{N}_S,\mathrm{N}_R)$-$C_i$-*trans*(O) isomers with the molar ratio of 1:1. If the 'bond-ruptured O' atom rejoins at the oxygen coordination site as well as the terminal N one and the oxygen donor atom is accompanied with the simultaneous shift to the trigonal plane, the $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer* isomer would isomerize to the *cis*(O) isomers. Taking the formation of the *trans*(O) isomers into consideration, the result indicates that the 'bond-ruptured O' atom tends to move toward the 'N-side' rather than the 'O-side'.

The *mer*-[Co(edma)(ida)] isomer mainly isomerizes to the *mer*(O)-type isomer rather than the *fac*(O) one [10]. This stereoselectivity is also explained by the same idea as used for the present $(+)^{\mathrm{CD}}_{504}$-$R(C_2)$-*mer*-$[\mathrm{Co(edma)_2}]^+$ isomer.

Supplementary material

Observed and calculated structure factors, anisotropic thermal parameters, and H-atom coordinates are available from Dr K. Okamoto on request.

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