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Circular Dichroism Spectrum of C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ Containing Chiral Methylene Formed by Stereospecific Deuteration

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Synopsis. C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ was prepared by way of the stereospecific deuteration of the facially coordinated edma (ethylenediamine-*N*-acetate) in $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(edma)$_2$]$^+$. The vicinal CD spectrum due to the C(*S*)-edma-d_1 in the C_i-*trans*(O) complex was investigated in connection with the D→H exchange in the ligands, suggesting a two-step mechanism.

Ethylenediamine-*N*-acetate (edma=$NH_2CH_2CH_2NHCH_2COO^-$) coordinates to cobalt(III) to form various geometrical and optical isomers.[1—5] Of these isomers, the one in which edma coordinated facially to cobalt(III) has been remarked because of the characteristic reactivity of the coordinated edma. In the course of our studies on stereochemistry of Co(III) complexes with edma and its derivatives, it was found that one of the methylene protons in the glycinate moiety (G-ring) of the facially coordinated edma is stereospecifically deuterated in a basic D_2O solution to form an asymmetric center; $NH_2CH_2CH_2NHC^*HDCOO^-$.[2] This note is concerned with the preparation of optically active edma (C(*S*)-edma-d_1) due to the stereospecific deuteration of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(edma)$_2$]$^+$,[6] and the preparation and CD spectrum of C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ [6] which has only the vicinal CD contribution arising from the asymmetric carbon atoms, -C*HD-, of the ligands.

Experimental

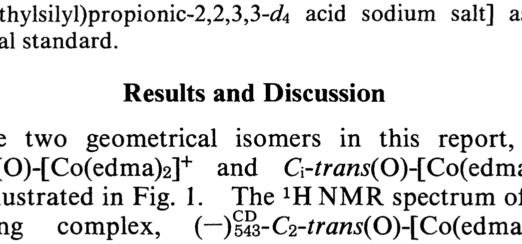
Preparation of Complexes. $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(edma)$_2$]Cl and C_i-*trans*(O)-[Co(edma)$_2$](ClO$_4$): These complexes were prepared according to the method described in the previous paper[2] and the absolute configuration of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(edma)$_2$]Cl has been determined as $\Delta\Lambda\Delta(N_R, N_R)$.[2]

C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$](ClO$_4$): A buffer solution (pH 10.30) was prepared by adding a few drops of 2 mol dm^{-3} DCl–D_2O to a solution containing 1.0 g of Na_2CO_3 in 20 cm^3 of D_2O. About 1.0 g of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O) isomer was dissolved into the buffer solution (20 cm^3), and the solution was kept at 40.0 °C for ca. 25 min in order to deuterate one of the two protons in the methylene of G-ring in the facially coordinated edma.[2] The deuteration of the G-ring $-CH_2-$ was confirmed by means of ^{1}H NMR measurements (Fig. 2). The solution was acidified to pH 6 with 2 mol dm^{-3} HCl to stop the reaction. Zinc powder (2 g) was added to the solution to reduce the central cobalt(III) to cobalt(II), and then the mixture was stirred for 5 min at room temperature (about 20 °C). After the excess of zinc was filtered off, lead dioxide (7 g) was added to the solution adjusted to pH 6. The mixture was stirred for 15 min at room temperature to reconstitute the cobalt(III) complex with the deuterated edma. After the reactant solution had been filtered, the filtrate was poured onto a column of SP-Sephadex (Na$^+$ form, 5.0 cm×60 cm) and then the adsorbed band was eluted with a 0.2 mol dm^{-3} NaCl aqueous solution. Three bands: brown (by-product), red, and another red (other geometrical isomers of deuterated [Co(edma)$_2$]$^+$), were eluted in this order.[1,2] After the earlier red band containing the deuterated C_2-*trans*(O) and C_i-*trans*(O) isomers was eluted out, two drops of 1 mol dm^{-3} acetic acid solution was added to the eluate and then the eluate was concentrated to ca. 50 cm^3 in a rotary evaporator under reduced pressure at 35 °C. Addition of about 1 cm^3 of saturated $NaClO_4$ solution to the concentrated solution gave the crude C_i-*trans*(O) isomer as fine yellowish orange crystals. The ClO_4^- salt of C_i-*trans*(O) is less soluble than that of C_2-*trans*(O) isomer. The crystals were quickly filtered and washed with a few milliliters of cold water. Recrystallization was carried out from a small amount of warm water by addition of five drops of saturated $NaClO_4$ solution. Found: C, 24.42; H, 4.61; N, 14.05%. Calcd for C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$](ClO$_4$) (F.W.=394.65): C, 24.35; H (1.008×18/F.W.), 4.60; N, 14.20%.[8]

Measurements. The absorption and CD spectra were measured by a JASCO UVIDEC 670-type spectrophotometer and JASCO J-22 and J-600 spectropolarimeters, respectively. The ^{1}H NMR spectra were recorded on a Hitachi R-90H Fourier Transform NMR spectrometer, using TSP [3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt] as an internal standard.

Results and Discussion

The two geometrical isomers in this report, C_2-*trans*(O)-[Co(edma)$_2$]$^+$ and C_i-*trans*(O)-[Co(edma)$_2$]$^+$ are illustrated in Fig. 1. The ^{1}H NMR spectrum of the starting complex, $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(edma)$_2$]$^+$, right after dissolving in basic D_2O solution shows an AB quartet signal (at δ=ca. 3—4) due to the methylene protons of G-ring (Fig. 2(a)). The two higher-field and two lower-field peaks of this AB quartet have been assigned to the inside methylene proton (H_a in Fig. 3(a)) and the outside one (H_b in Fig. 3(a)), respectively.[2] Moreover, it has been known that one of the G-ring methylene protons in $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(edma)$_2$]$^+$ is stereospecifically deuterated in a basic D_2O solution, namely, the outside proton (H_b) is deuterated faster than the inside one (H_a).[2] In fact, the lower-field peaks (H_b) disappeared and the higher-field ones (H_a) turned out to the singlet one, twenty-five minutes after dissolving in the solution (Fig. 2(b)). This spectral behavior indi-



C₂-trans(O)   Ci-trans(O)

Fig. 1. Two geometrical isomers, C_2-*trans*(O)- and C_i-*trans*(O)-[Co(edma)$_2$]$^+$.

cates that one of the G-ring methylene protons in $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$ was deuterated to form asymmetric centers, -C*HD-. Here, it is to be noted that the G-ring methylene carbons are regulated to C(*S*) configuration, because both the secondary nitrogen atoms of the facially coordinated ligands in $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$ take N(*R*) configuration (Fig. 3(b)). $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ thus obtained was converted into C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ (Fig. 3(c)) as described in experimental section.

The absorption and CD spectra in the d-d transition band region of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ and the converted complex are shown in Fig. 4. The absorption spectral pattern of the latter differs significantly from that of the former and then, coincides with that of the C_i-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$,[2] suggesting that the converted complex takes a C_i-*trans*(O) geometry. When the formation of this C_i-*trans*(O) complex proceeded with retention of the configuration of C(*S*)-edma-d_1, the secondary nitrogen atoms of the coordinated ligands should take N(*R*) configuration for C(*S*)edma-d_1 having inside proton and N(*S*) configuration for C(*S*)-edma-d_1 having outside proton, as shown in Fig. 3(c). This is confirmed from the comparison with ^{1}H NMR spectra (Figs. 5(a) and (b)) of C_i-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$ and the converted C_i-*trans*(O) complex, in line with the assignment of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$ and the deuterated one. Namely, two singlet peaks (at δ=ca. 4.1 and ca. 3.3) due to two G-ring -C*HD- are observed for the spectrum of the converted C_i-*trans*(O) complex (Fig. 5(b)), and the signal peak at δ=ca. 4.1 is assigned to the outside proton and the peak at δ=ca. 3.3 to the inside one. Thus, the converted C_i-

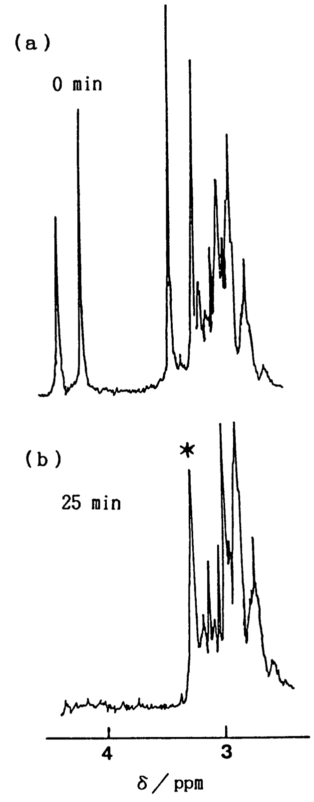


Fig. 2. ^{1}H NMR spectral change with time of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$ in basic D_2O solution. Asterisked peak: G-ring -C*HD-.

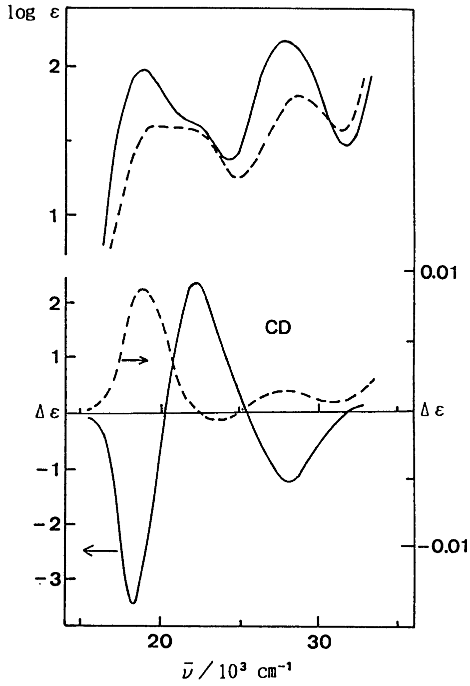


Fig. 4. Absorption and CD spectra of C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ (-----) and $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ (——).

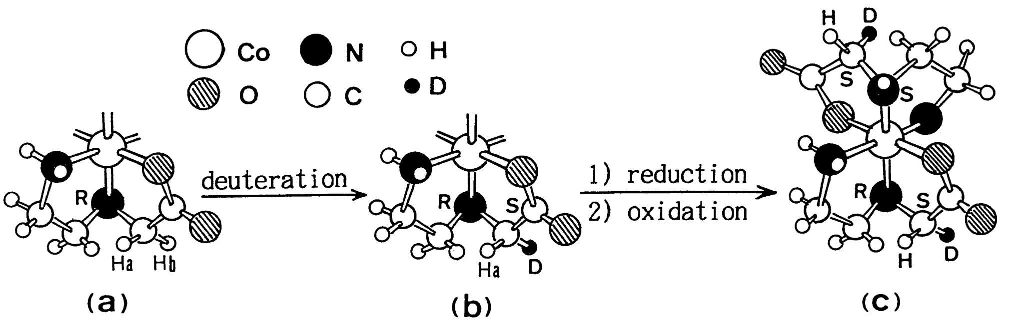


Fig. 3. Stereoselective deuteration on the G-ring -CH$_2$- of the facially coordinated edma. (a): Undeuterated edma; (b) stereospecifically deuterated edma; and (c): C_i-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$ converted from $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-[Co(C(*S*)-edma-d_1)$_2$]$^+$.

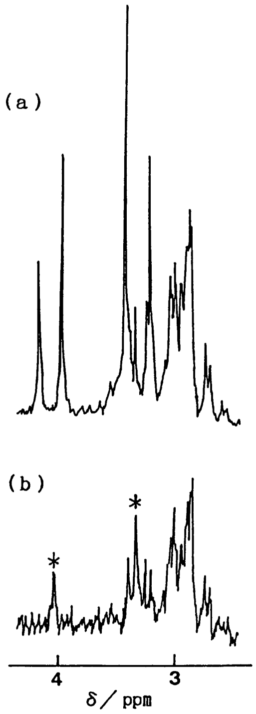


Fig. 5. ^{1}H NMR spectra of C_i-*trans*(O)-$[\mathrm{Co(edma)_2}]^+$. (a) Undeuterated complex and (b) deuterated complex. Asterisked peaks: G-ring -C*HD-.

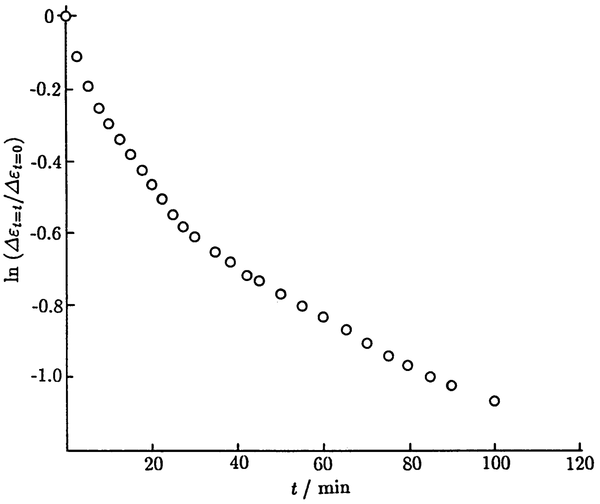


Fig. 6. The time-course change of CD intensity for C_i-*trans*(O)-$[\mathrm{Co(C(}S\mathrm{)\text{-}edma\text{-}}d_1)_2]^+$ which was kept in a buffered aqueous solution (pH 10.33) at 40.1 °C.

trans(O) complex is assigned to C_i-*trans*(O)-$[\mathrm{Co(C(}S\mathrm{)\text{-}edma\text{-}}d_1)_2]^+$.

In the d-d transition band region, C_i-*trans*(O)-$[\mathrm{Co(C(}S\mathrm{)\text{-}edma\text{-}}d_1)_2]^+$ shows extremely weak CD bands ($\Delta\varepsilon$: +0.0084 at 19000 cm^{-1} and +0.0018 at 27500 cm^{-1}) whose sign pattern differs obviously from that of $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O)-$[\mathrm{Co(C(}S\mathrm{)\text{-}edma\text{-}}d_1)_2]^+$ (Fig. 4). This reflects that the optical activity of the C_i-*trans*(O) complex arises only from the asymmetric carbon atoms, -C*HD-, of the ligands, while that of the $(-)^{\mathrm{CD}}_{543}$-C_2-*trans*(O) complex is contributed from the configuration Δ of complex and asymmetric nitrogen atoms, N(*R*)N(*R*), besides that from -C*HD- of the ligands. In general, the vicinal CD contribution arising from the asymmetric carbon atom of coordinated ligand is very weak in intensity compared with the CD contribution from the configurational chirality, for example, $[\mathrm{Co(L\text{-}ala)(NH_3)_4}]^{2+}$ shows weak CD bands ($\Delta\varepsilon$: ca. −0.02, +0.07, and −0.22 at 18300, 19500, and 20200 cm^{-1}, respectively) in the d-d transition region.$^{7)}$ In the corresponding region, C_i-*trans*(O)-$[\mathrm{Co(C(}S\mathrm{)\text{-}edma\text{-}}d_1)_2]^+$ shows much weaker CD intensity than $[\mathrm{Co(L\text{-}ala)(NH_3)_4}]^{2+}$ (Fig. 4). This may be ascribed to the difference between the substituents on the methylene carbon of the ligands, namely, -C*H(CH$_3$)- and -C*HD-.

C_i-*trans*(O)-$[\mathrm{Co(C(}S\mathrm{)\text{-}edma\text{-}}d_1)_2]^+$ loses its optical activity by D→H exchange of the ligands in an aqueous solution and the CD change with time at 525 nm is shown in Fig. 6. The exchange seems to proceed with two steps and the two $t_{1/2}$ values are roughly estimated from the figure as 8.8 and 130 min. Taking into consideration that the outside proton (H$_b$) exchanges more easily than the inside one (H$_a$) in the deuteration,$^{2)}$ it is probable that the earlier step results from the exchange of outside D with H on C(*S*)-edma-d_1 having N(*R*) configuration and the later step from the exchange of inside D on C(*S*)-edma-d_1 having N(*S*) configuration. The ratio of the exchange rates of the outer and inner D is about 15.

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6) The prefixes C_2 and C_i denote that the *trans*(O) complex ion has a C_2 axis or inversion center.

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8) A TCD cell-type C,H,N-Analyzer which was normalized to natural H was used for the present elemental analysis. Accordingly, atomic weight of D in the analyzed gas can be regarded to 1.01 as within the experimental error. However, weighing the sample, the atomic weight of D should be regarded to 2.01.