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STEREOSELECTIVITY IN ION-PAIR FORMATION. II.
THE ADDITIVITY OF INDUCED CIRCULAR DICHROISMS OF Λ-$[Co(en)_3]^{3+}$ BY THE ROTATIONAL ISOMERS OF L-MALATE ANION

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The changes in the CD spectrum of Λ-$[Co(en)_3]^{3+}$ have been observed upon the addition of some dicarboxylate anions (maleate, L-malate, and fumarate). The results demonstrated the additivity of circular dichroisms induced by the gauche and trans rotational isomers of the L-malate anion.

Several interesting studies[1)] have been reported on the stereoselective interactions between the chiral complex ions and the dicarboxylate anions by utilizing CD measurements. There are, however, only speculative discussions concerning the role of each rotational isomer (gauche and trans) of the dicarboxylate anions. Therefore, we have investigated the influence of each rotational isomer on the CD spectrum of Λ-$[Co(en)_3]^{3+}$ on the basis of the rotational isomer's population obtained from the PMR technique.

$[Co(en)_3]Br_3 \cdot 3H_2O$ was prepared and resolved into the optical isomers by a usual method. CD measurements were made on a reference solution of Λ-$[Co(en)_3]^{3+}$ (0.002 M) and on a sample solution of Λ-$[Co(en)_3]^{3+}$ (0.002 M) containing the dicarboxylate anion (0.0275 M). Difference CD spectra were obtained on a J-40CS spectropolarimeter with a 2 cm cell kept at 25.0 ± 0.2°C. PMR spectra were recorded on a Hitachi R-22 spectrometer operating at 90 MHz. The L-malate anion used for the PMR measurement was 0.1 M in a D_2O solution.

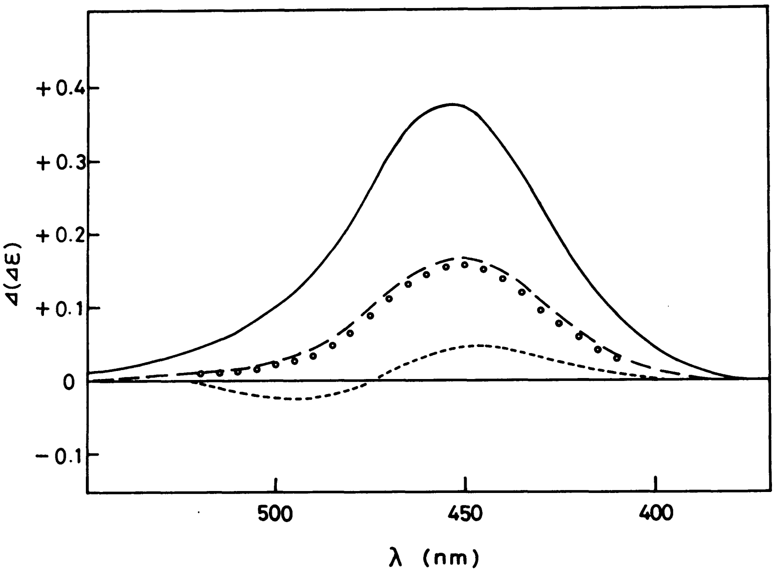


Fig. 1. The changes in the CD spectrum of Λ-$[Co(en)_3]^{3+}$ (0.002 M) upon the addition of the dicarboxylate anions (0.0275 M), $\mu = 0.1$ ($NaClO_4$).
(1) ———, maleate;
(2) – – – –, L-malate;
(3) ·········, fumarate;
(4) oooooo, calculated curve for L-malate anion.

$\Delta(\Delta\varepsilon) = \Delta\varepsilon_{sample} - \Delta\varepsilon_{reference}$.

The pattern of the CD change for the fumarate anion is similar to those usually observed for singly charged anions.[2)]

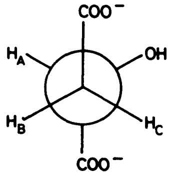
Figure 1 shows the changes in the CD spectrum of Λ-$[Co(en)_3]^{3+}$ in the presence of the maleate, L-malate, and fumarate anions. This figure indicates that the CD change for the L-malate anion (gauche or trans conformation) is smaller than that for the maleate anion (cis) and is larger than that for the fumarate anion (trans). Thus, the CD change seems to be largely dependent on the relative position of two carboxyl groups.

Table 1. The fractional populations(%) of the L-malate anion (0.1 M).

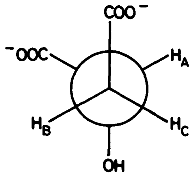
	(A)	(B)	(C)	(D)
p_I	71	65	66	63
p_{II}	9	11	10	15
p_{III}	20	24	24	22
J_{AC}	10.1	9.4	9.5	9.2
J_{AB}	3.1	3.3	3.2	3.7

(A): This work. (B): Ref. 3. (C): Recalcd. in ref. 4. (D): This work; in the presence of $[Co(NH_3)_6]^{3+}$ (0.2 M). The fractional populations of rotational isomers (I) to (III) were obtained by $p_I = (J_{AC}-J_g)/(J_t-J_g)$, $p_{II} = (J_{AB}-J_g)/(J_t-J_g)$, and $p_{III} = 1 - p_I - p_{II}$, in which J_t = 13.4 Hz and J_g = 2.0 Hz.

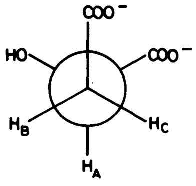
Of these anions, the L-malate anion consists of the following three rotational isomers,



(I)



(II)



(III)

, where two carboxyl groups are trans in the rotational isomer (I), and are gauche in the rotational isomers (II) and (III). Therefore, the change in the CD spectrum of Λ-$[Co(en)_3]^{3+}$ upon the addition of the L-malate anion is attributed to the contributions of these three isomers, one trans and two gauche forms.

On the other hand, the populations of above rotational isomers can be determined by the PMR technique.3),4) The data obtained are summarized in Table 1. The fractional populations of these three isomers are found to be 67%, 10%, and 23% (trans: 67%, gauche: 33%) on the average in the absence of the complex ion. The changes in these populations upon the addition of the complex ion are negligible (see Table 1, where $[Co(NH_3)_6]^{3+}$ is used in place of $[Co(en)_3]^{3+}$ because the methylene signals in $[Co(en)_3]^{3+}$ unfortunately overlaps with those in the L-malate anion).

Assuming that the contributions of the gauche and trans rotational isomers of the L-malate anion are equal to those of the maleate and fumarate anions respectively, the CD change for the L-malate anion is estimated by the following equation,

$$\Delta(\Delta\varepsilon)_{malate} = 0.33 \times \Delta(\Delta\varepsilon)_{maleate} + 0.67 \times \Delta(\Delta\varepsilon)_{fumarate}$$

, where Δ(Δε) refers to the CD change at each wavelength. The spectrum thus calculated is in good agreement with the observed one as shown in Fig. 1. This result demonstrates the additivity of the induced circular dichroisms by the gauche and trans rotational isomers, and suggests that each rotational isomer interacts independently with Λ-$[Co(en)_3]^{3+}$ through the carboxyl group.

Reference

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