The Structure of Ion-pairs of Λ- and Δ-$[Co(en)_3]^{3+}$ Ions with L-Tartrate and Related Anions as Deduced from Circular Dichroism Spectra*

Miho FUJITA** and Hideo YAMATERA
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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The circular dichroism (CD) spectra of optical antipodes of $[Co(en)_3]^{3+}$ and $[Co(pn)_3]^{3+}$ were measured in the presence of L-tartrate, L-tartranilate or related dicarboxylate ions. L-Tartrate(2−) ions gave a large and stereoselective effect on the CD spectra; the CD change was greater for the Λ-complex than for the Δ-complex. Hydrogen-L-tartrate(1−) and L-tartranilate(1−) ions also caused stereoselective CD changes. On the other hand, succinates-(2−) and L-malate(2−) ions gave small and non-stereoselective CD changes, and undissociated tartaric acid gave no CD change. From a comparison of the results, it was concluded that two hydroxyl and one carboxylate groups of the L-tartrate ion form hydrogen bonds with three N–H groups of the tris(diamine)cobalt(III) ion of the *lel* form.

In a previous papar,[1] we reported the stereoselective hydrogen-deuterium exchange rate of optically active $[Co(en)_3]^{3+}$ ions in D_2O solutions containing L-tartrate ions; the rate was faster for the Δ-isomer of the complex than for the Λ-isomer. The stereoselectivity of L-tartrate ions for optically active $[Co(en)_3]^{3+}$ ions has also been observed in optical rotatory dispersion, circular dichroism, UV absorption spectra,[2–4] and electrophoresis;[5] values have been obtained for the association constants of L-tartrate ions with Λ- and Δ-$[Co(en)_3]^{3+}$.[2,6]

However, neither the orgin of the stereoselective interaction nor the structure of the ion-pair seems to have been established. Ogino[2] suggested that two carboxylate groups of a L-tartrate ion participate in hydrogen-bonding with a $[Co(en)_3]^{3+}$ ion, and that the right-handed screw of $^-$COO–C–C–COO$^-$ in the gauche structure with two hydroxyl groups at *trans* position to each other is particularly important for the stereoselectivity. In contrast to this suggestion, our preliminary experiments on the hydrogen-deuterium exchange showed that hydroxyl groups may take a role as important as that of carboxylate groups.

Therefore, the present study was undertaken to investigate the role of each group of the L-tartrate ion in the stereoselective ion-paring with $[Co(en)_3]^{3+}$ or $[Co(pn)_3]^{3+}$ by a comparison of the effect of added dicarboxylate ions on the CD spectra.

Experimental

$[Co(en)_3]Br_3 \cdot H_2O$ was prepared by the usual method and resolved into the optical isomers by using silver L-tartrate and D-tartrate. The $[\alpha]_D$ values of the Λ- and Δ-$[Co(en)_3]Br_3 \cdot H_2O$ were +124° and −123°, respectively. $\Lambda(+)[Co\{(+)pn\}_3]Br_3$ and $\Delta(-)[Co\{(-)pn\}_3]Br_3$ were prepared according to the literature.[7] Their $[\alpha]_D$ values were +221° and −223°, respectively. L-Tartranilic acid was prepared in the same way as described by Montzka *et al.*[8] Found: C, 52.9; H, 4.89; N, 6.04%. Calcd for $C_4H_{11}NO_5$: C, 53.3; H, 4.92; N, 6.22%. The acids were neutralized with an equivalent amount of sodium hydroxide if necessary. Series of sample solutions, 0.01 M in either Λ- or Δ-$[Co(en)_3]Br_3$ and 0—0.1M in one of the dicarboxylates, were prepared by mixing solutions of the components. Sample solutions were made in pairs; two solutions of a pair were equivalent to each other except that each contained one antipode of the complex. Series of sample solutions of the optically active $[Co(pn)_3]Br_3$ were also prepared in the same way with sodium L-tartrate and with sodium succinate.

Circular dichroism spectra of these solutions were measured in the region of the first absorption band (600 nm—350 nm) with a JASCO ORD/UV5 spectrophotometer by using a 1 cm quartz cell at 25±1 °C.

Results

A typical result is shown in Fig. 1. Λ-$[Co(en)_3]^{3+}$ shows a CD spectrum with two peaks in the region of the first absorption band (corresponding to the $T_{1g} \leftarrow A_{1g}$ transition in an octahedral ligand field). The positive peak at the larger wavelength has been assigned to the E component and the negative peak at the smaller wavelength to the A_2 component.[9] In the presence of L-tartrate(2−) ion, the CD spectrum was modified in such a way that the intensity of the E component decreased and that of the A_2 component increased, as

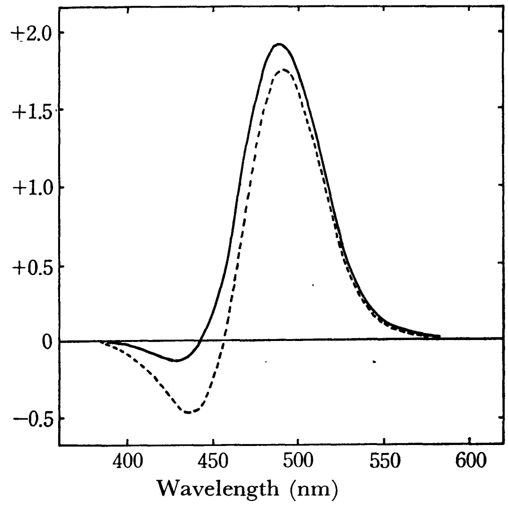

Fig. 1. CD spectra of 0.01 M Λ-$[Co(en)_3]Br_3 \cdot H_2O$ in the absence (—) and in the presence (---) of 0.15 M Na_2(L-tartrate) in the region of the first absorption band.

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[**] Present address: Department of Chemistry, Nagoya City University, Mizuho, Nagoya 467.

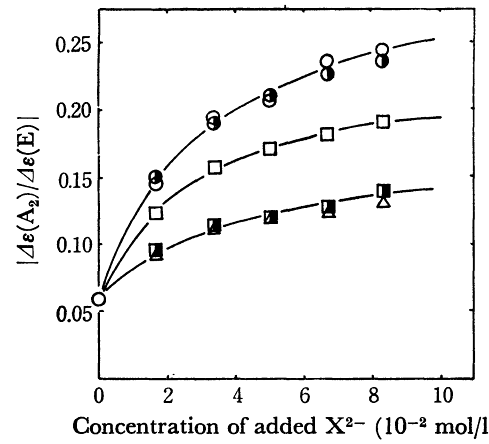

Fig. 2. Effects of the concentration of added dicarboxylate ions (X^{2-}) on the $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$ values of Λ- and Δ-$[Co(en)_3]^{3+}$ (0.01 M). ○: Λ-complex, X=L-tartrate, □: Δ-complex, X=L-tartrate. ◑: Λ- and Δ-complex, X=*meso*-tartrate. ◧: Λ- and Δ-complex, X=L-malate. △: Λ- and Δ-complex, X=succinate.

Table 1. Values of $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$ in the absence and presence of carboxylate and other anions (The concentrations are 0.01 M in the complexes and 0.084 M in the added anions.)

Anion	Λ-$[Co(en)_3]^{3+}$	Δ-$[Co(en)_3]^{3+}$
None	0.06	0.06
Bromide	0.06±0.01	0.06±0.01
Fumarate(2−)	0.09	0.09
Succinate(2−)	0.14	0.14
meso-Tartrate(2−)	0.23	0.23
L-Tartrate(2−)	0.24	0.19
H(L-Tartrate)(1−)	0.19	0.15
H_2(L-Tartrate)	0.06_7	0.07_0
L-Malate(2−)	0.14_8	0.14_8
L-Tartranilate(1−)	0.16	0.12
	Λ-$[Co\{(+)pn\}_3]^{3+}$	Δ-$[Co\{(-)pn\}_3]^{3+}$
None	0.30	0.30
Succinate(2−)	0.41	0.41
L-Tartrate(2−)	0.62	0.50

shown by the dotted line in Fig. 1. The same tendency was observed with all the carboxylates to some extent.

For ready comparison, the ratios of the CD intensity at the A_2 peak to that at the E peak (denoted by $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$) were plotted against the concentration of L-tartrate (Fig. 2). The effect of added L-tartrate was greater for the Λ-complex than for the Δ-complex. L-Tartaric acid, H_2 (L-tartrate), gave no change within the error of measurements and naturally showed no stereoselectivity. Nor did sodium bromide give appreciable effects.

Table 1 summarizes the $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$ values measured for several kinds of dicarboxylate ions which have carbon skeletons similar to a L-tartrate ion. Optically active L-malate(2−) gave only a small CD change, similar to that due to succinate(2−), and showed no stereoselectivity. On the other hand, *meso*-tartrate(2−) gave an effect almost identical to that of L-tartrate, but without any stereoselectivity. The L-tartranilate(1−) ion, in which a carboxylate group of the L-tartrate(2−) ion is replaced by an acid-anilide group, showed a distinct stereoselectivity. As is seen from Table 1, however, the magnitude of CD change due to L-tartranilate was smaller than that due to L-tartrate at the same carboxylate concentration. This can be ascribed to the difference in the charge between the L-tartranilate(1−) and L-tartrate(2−) ions. If the difference in the ionic charge is taken into account, L-tartranilate seems to be comparable to L-tartrate in the stereoselectivity for the optically active $[Co(en)_3]^{3+}$ ions. A similar result was observed with the monohydrogen-L-tartrate(1−) ion, H(L-tartrate)⁻.

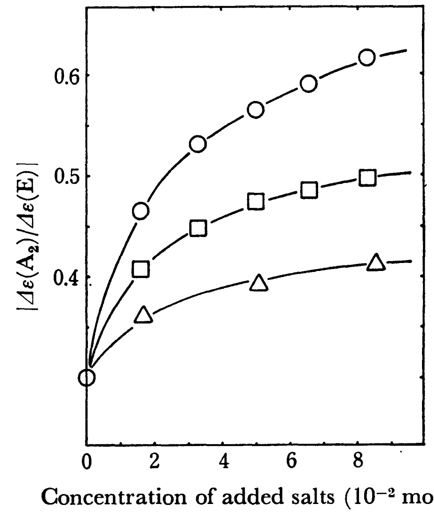

Fig. 3. Effects of the concentration of added L-tartrate and succinate ions on $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$ values of Λ-$[Co\{(+)pn\}_3]^{3+}$ and Δ-$[Co\{(-)pn\}_3]^{3+}$ (0.01 M). ○: Λ-complex, L-tartrate. □: Δ-complexes, L-tartrate. △: Λ- and Δ-complex, succinate.

Measurements on the optically active $[Co(pn)_3]^{3+}$, Λ-$[Co\{(+)pn\}_3]^{3+}$ and Δ-$[Co\{(-)pn\}_3]^{3+}$, resulted in nearly the same pattern of CD changes as those of Λ-$[Co(en)_3]^{3+}$ and Δ-$[Co(en)_3]^{3+}$, respectively. Figure 3 shows the relationship between the $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$ value and the concentration of L-tartrate (and of succinate, as a reference). The $|\Delta\varepsilon(A_2)/\Delta\varepsilon(E)|$ values at the same concentration of different carboxylates are compared in Table 1. A comparison of Fig. 3 with Fig. 2 shows that the stereoselectivity of L-tartrate for the optically active $[Co(pn)_3]^{3+}$ ion corresponds to that for the optically active $[Co(en)_3]^{3+}$ ion.

Discussion

The Λ-$[Co\{(+)pn\}_3]^{3+}$ ion is known to have the *lel* conformation and one of two N–H bonds at each end of the propylenediamine lies nearly parallel to the C_3 (or quasi-C_3) axis of the complex. Thus a set of three N–H hydrogens at each end of the complex can be conveniently used for hydrogen bonding with anions approaching the complex ion along the C_3 axis. This is also the case with the *lel* form of $[Co(en)_3]^{3+}$, which predominates over the *ob* form in aqueous solutions.

Thus the formation of an ion-pair between tris(diamine)-cobalt(III) and phosphate ions with a set of three N–H···O hydrogen bonds was proposed by Mason and Norman in order to explain the marked changes in the CD spectrum of the complex observed in the presence of phosphate ions.$^{10)}$

A tartrate ion has two carboxylate and two hydroxyl groups which can be used for hydrogen bonding with the N–H groups of the complex ion. In analogy with Mason's model, it is very probable that three of these four groups participate in the hydrogen bonding. The two possibilities for the formation of three hydrogen bonds, with two carboxylate and one hydroxyl groups or with two hydroxyl and one carboxylate groups, will be discussed in connection with the experimental results.

From the fact that sodium bromide and tartaric acid (the fully protonated tartrate) caused only slight CD changes, the free carboxylate group seems to play an important role in causing CD changes. The fumarate-(2−) ion, of which only one of the two carboxylate groups can be used for hydrogen bonding with a tris(diamine)-cobalt(III) ion, caused only a small CD change, whereas the succinate ion capable of forming hydrogen bonds through two carboxylate groups caused greater CD changes. The L-malate ion which has two carboxylate and one hydroxyl groups caused a CD change similar to that caused by the succinate ion. These experimental results might be taken as an indication that carboxylate groups play a principal role in the CD changes of the tris(diamine)cobalt(III) ions. However, this is not likely to be the case, since further greater CD changes were caused by the hydrogen-L-tartrate(1−) ion which has only one free carboxylate group. The greatest CD changes were observed when the L-tartrate-(2−) ion was added to solutions containing tris(diamine)-cobalt(III) ions, especially of the Λ-form. Considering that introduction of the second hydroxyl group into the malate(2−) ion gives the tartrate(2−) ion, the second hydroxyl group seems to play an important role in the ion association and thus in the great CD changes.

Thus we propose a model of the ion-pair in which two hydroxyl and one carboxylate groups form hydrogen bonds with three N–H groups of tris(diamine)cobalt(III) ion of the *lel* form. This model of the ion-pair can also give a satisfactory explanation of the stereoselective CD changes, as can be seen from Fig. 4, which shows a schematic representation of the structures of tartrate and related ions. The clockwise arrangement of the COO^-, OH, and OH groups are characteristic of the isomers causing greater CD changes for the Λ-complexes. Thus the hydrogen-L-tartrate and L-tartranilate ions, which have the same configuration as that of L-tartrate as far as one carboxylate and two hydroxyl groups are concerned, caused stereoselective CD changes, which are large considering the lower ionic charge. The *meso*-tartrate ion has two asymmetric carbons of the *R* and *S* chiralities, and differs from the L-tartrate in that the carboxylate and hydrogen attached to the *S* carbon are interchanged. This appears to explain why meso-tartrate causes great CD changes in the CD spectra of both isomers of the complex.

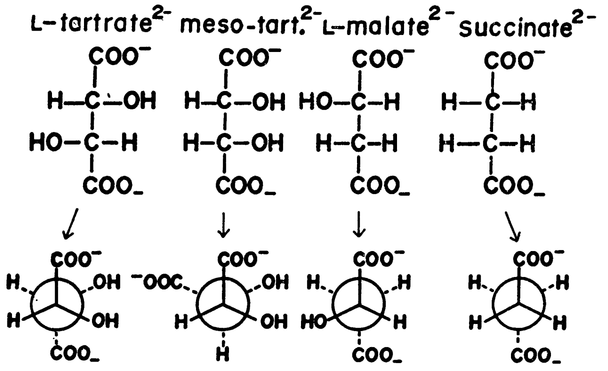

Fig. 4. Schematical representation of the structures of tartrate and related ions.

During the preparation of this manuscript, an X-ray analysis was carried out on a crystal of $\Lambda(+)[Co(en)_3]Br(\text{L-tartrate})\cdot 5H_2O$ by Kushi *et al.*$^{11)}$ Their result seems to confirm our model for the ion-pair described above. In addition, we recently prepared two types of optically active Sephadex cation exchangers with L-tartrate groups, and applied them to a direct column-chromatographic resolution of $[Co(en)_3]^{3+}$.$^{12)}$ The exchanger with tartrate groups of the ester type showed higher efficiency than that with tartrate groups of the ether type. This is also a support for our model.

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References

1) H. Yamatera and M. Fujita, *Bull. Chem. Soc. Jpn.*, **42**, 3043 (1969).

2) K. Ogino and U. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 826 (1967).

3) K. Ogino, *Bull. Chem. Soc. Jpn.*, **42**, 447 (1969).

4) B. Norden, *Acta Chem. Scand.*, **26**, 111 (1972).

5) H. Yoneda and T. Miura, *Bull. Chem. Soc. Jpn.*, **43**, 574 (1970); **45**, 2126 (1972).

6) M. Fujita and H. Yamatera, Presented at the 21st Symposium on Coordination Chemistry of the Chemical Society of Japan, Nagoya, 1971.

7) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

8) T. A. Montzka, T. L. Pindell, and J. D. Matiskella, *J. Org. Chem.*, **33**, 3993 (1968).

9) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

10) S. F. Mason and B. J. Norman, *J. Chem. Soc., A*, **1966**, 307.

11) Y. Kushi, M. Kuramoto, and H. Yoneda, *Chem. Lett.*, **1976**, 135.

12) M. Fujita, Y. Yoshikawa, and H. Yamatera, *Chem. Lett.*, **1974**, 1515; **1975**, 473.