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STEREOSELECTIVITY IN ION-PAIR FORMATION. I. ASSOCIATION CONSTANTS OF Λ- AND Δ-$[Co(en)_3]^{3+}$ WITH L- AND MESO-TARTRATES FROM CD MEASUREMENTS

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The ion association constants and the molar CD's were determined for the ion pairs, Λ- and Δ-$[Co(en)_3]^{3+}$ with L- and meso-tartrates, by utilizing CD measurements. The structures of these ion pairs were consistently interpreted in terms of the above two parameters. Furthermore, the results obtained here were compared with the chromatographic behaviors of these systems.

As a part of our structural studies on optical resolution, the crystal structures of Λ-$[Co(en)_3]Br(L\text{-}tart)\cdot 5H_2O$[1] and LiΛ-$[Cr(en)_3](L\text{-}tart)_2\cdot 3H_2O$[2] were determined by X-ray analysis. It was found that L-tartrate approaches the complex ion along the direction of C_3 axis forming the hydrogen bonds between its three oxygen atoms and the three axial N-H hydrogen atoms of the complex ion, and the conclusion was drawn that this structural feature plays an important role in the stereoselective formation of the above diastereoisomeric salts.

On the other hand, the difference in the association constants of L-tartrate with Λ- and Δ-$[Co(en)_3]^{3+}$ has been already detected in aqueous solution.[3] Fujita and Yamatera[4] have recently suggested from CD spectra that the structures of ion pairs of Λ- and Δ-$[Co(en)_3]^{3+}$ with L-tartrate are consistent with the result obtained from our X-ray analysis. Thus, the stereoselectivity in solution may be similar to that in crystal.

On the basis of this fact, we attempted to investigate the structures of these ion pairs and to get the information on the stereoselectivity in aqueous solution. The CD measurement is expected to serve as an effective mean for this purpose. However, the overall CD change consists of two contributions from both the concentration of an ion pair and its molar CD. Thus, the decisive conclusion can not be drawn as long as the overall CD change is not divided into these two contributions. Therefore, we have determined the association constants and the molar CD for the ion pairs, Λ- and Δ-$[Co(en)_3]^{3+}$ with L- and meso-tartrates, on the basis of CD measurements.

$[Co(en)_3]Br_3 \cdot 3H_2O$ was prepared and resolved into the enantiomers by a usual method. The specific rotations of the resolved enantiomers are in good agreement with those given in the literature. Measurements were made on a reference solution of the complex ion (0.002 M) and on a sample solution of the complex ion (0.002 M) containing the tartrate anion (2.5×10^{-3} M to 2.75×10^{-2} M). The ionic strength was set to 0.1 by the addition of an appropriate amount of sodium perchlorate. A JASCO J-40CS spectro polarimeter with a 2 cm cell was used for CD measurements. The cell was kept at 25.0 ± 0.2°C with a Haake Circulater Model FK. The data obtained from CD measurements were analyzed by using the following equation,[5)]

$$C_M(C_A-x)/\delta = (C_A-x)/(\Delta\varepsilon_{MX}-\Delta\varepsilon_M) + 1/K(\Delta\varepsilon_{MX}-\Delta\varepsilon_M)$$

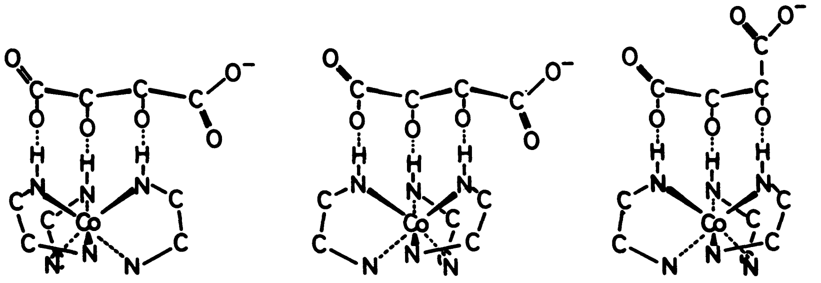
, where δ refers to the difference of the CD between a sample solution and a reference one, and $\Delta\varepsilon$ to the molar CD of the species indicated by the subscript.

The results obtained are given in Table 1. The measurements were made at 430 and 455 nm, corresponding to the CD peak for the A_2 component and to the maximum of the difference of the CD spectra between a sample solution and a reference solution, respectively.

Table 1. Association constants and $\Delta(\Delta\varepsilon)$ values at 25°C (μ=0.1). $\Delta(\Delta\varepsilon) = \Delta\varepsilon_{MX}-\Delta\varepsilon_M$.

	nm		meso-tart^{2-}	L-tart^{2-}	D-(-)-malate^{2-}
Λ-$[Co(en)_3]^{3+}$	430	K	39.6 ± 0.8	13.0 ± 0.1	10.9 ± 0.4
		$\Delta(\Delta\varepsilon)$	0.55 ± 0.01	0.85 ± 0.01	0.46 ± 0.02
	455	K	39.5 ± 0.5	13.6 ± 0.2	11.0 ± 0.5
		$\Delta(\Delta\varepsilon)$	0.89 ± 0.01	1.33 ± 0.02	0.68 ± 0.03
Δ-$[Co(en)_3]^{3+}$	430	K	40.3 ± 0.7	10.5 ± 0.4	11.1 ± 0.5
		$\Delta(\Delta\varepsilon)$	0.53 ± 0.01	0.66 ± 0.03	0.46 ± 0.02
	455	K	39.8 ± 0.6	11.7 ± 0.4	11.2 ± 0.6
		$\Delta(\Delta\varepsilon)$	0.88 ± 0.01	0.98 ± 0.04	0.67 ± 0.04

Fig. 1.



(I) $\Lambda\cdot$L-tart^{2-} (II) $\Delta\cdot$L-tart^{2-} (III) $\Delta\cdot$meso-tart^{2-}

It is clear from Table 1 that the association constant for meso-tartrate is about three times as large as that for L-tartrate, irrespective of the wavelength employed for the measurement. It is surprising that the association constants for meso- and L-tartrates, which are similar in structure and in charge type, are considerably different from each other. Thus, this fact seems to be due to the difference in the structures of both ion pairs, and to be explicable in the following manner.

If the structural feature obtained by our X-ray analysis is applied to the ion pairs, Λ-[Co(en)$_3$]$^{3+}\cdot$L-tart^{2-}, Δ-[Co(en)$_3$]$^{3+}\cdot$L-tart^{2-}, and Δ-[Co(en)$_3$]$^{3+}\cdot$meso-tart^{2-}, they can be represented as shown in Fig. 1. According to these molecular models, it is clear that the difference between the ion pairs for L-tartrate [(I) and (II)] and that for meso-tartrate (III) is in the positions of the COO$^-$ groups free from the hydrogen bonding to the complex ions. That is, the COO$^-$ group is close to the complex ion in the ion pairs [(I) and (II)] and is apart from the complex ion in the ion pair (III).

Therefore, the observed difference in the association constants between L- and meso-tartrate ion pairs seems to be caused by the difference in the position of the free COO$^-$ group. In these systems, the electrostatic contribution to the association constant is almost equal for each pair with the same charge. If the interaction between the free COO$^-$ group and the complex ion is not attractive but repulsive, little steric repulsion is expected for the meso-tartrate ion pair. Then, the more smooth association occurs in the meso-tartrate ion pair than in the L-tartrate ion pair with greater steric repulsion. This is in good agreement with our results (Table 1). In contrast, the difference in the steric interaction seems to be small between the ion pairs (I) and (II). In fact, our results show that the difference is small between the association constants for (I) and (II) systems (Table 1). It is also important to note that D-(-)-malate, which cannot form the ion pair like that for tartrate, does not show any stereoselectivity at all (Table 1).

Therefore, we conclude that the structural feature mentioned above is essential to the stereoselectivity in aqueous solution, and the steric repulsion which is caused by the free COO^- group seems to play an important role in the preferential or stereoselective association, in these systems. This idea is also supported by the information obtained from the molar CD for each ion pair. If $\Delta(\Delta\varepsilon)$ values for $[Co(en)_3]^{3+}\cdot$meso-tart^{2-} and $[Co(en)_3]^{3+}\cdot$L-tart^{2-} are related to the degree of the distortion of the complex ion (or steric repulsion), the large $\Delta(\Delta\varepsilon)$ value for the L-tartrate ion pair and the small $\Delta(\Delta\varepsilon)$ value for the meso-tartrate ion pair are expected. The order of $\Delta(\Delta\varepsilon)$ values obtained here is; L-tartrate ion pair $>$ meso-tartrate ion pair, and is in accordance with our expectation. Therefore, the model proposed above seems to be confirmed.

Furthermore, the difference in association constant should be related to the elution order in the column chromatography. Table 2 shows the elution data for $[Co(en)_3]^{3+}$ with meso- or L-tartrates as the eluents. These data support the result that the complex ion associates to a higher extent with meso-tartrate than with L-tartrate. ($[Co(en)_3]^{3+}$ did not separate into Λ- and Δ-forms under this condition.)

Table 2. The elution order of $[Co(en)_3]^{3+}$ with L- or meso-tartrates.

Resin : SP-Sephadex
Column : 5mm x 435mm
Sample : $[Co(en)_3]Br_3\cdot 3H_2O$ (1 mg)
Eluent : Na_2L-tart (0.15 M) or Na_2meso-tart (0.15 M)

eluent	10 ml (volume of effluent)		15 ml (volume of effluent)	
Na_2L-tart	9.5 cm	distance of flow	14.5 cm	distance of flow
Na_2meso-tart	16.5 cm		25.5 cm	

References and Notes

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5) See ref. 3b) as to the meanings of C_M, C_A, M, MX, and x.

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