Enantiomers of the Tris(trimethylenediamine)cobalt(III) Ion of 100% Optical Purity: Preparation and Circular Dichroism Study

By Miho Fujita*

(*Department of Chemistry, Nagoya City University, Mizuho, Nagoya* 467, *Japan*)

and Yuzo Yoshikawa and Hideo Yamatera

(*Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya* 464, *Japan*)

Summary Reaction of optically pure $[Co(tn)_3]^{3+}$ isomers (tn = $H_2NCH_2CH_2CH_2NH_2$) (in aqueous solutions), obtained by a new chromatographic technique, with L-tartrate ions resulted in stereoselective circular dichroism changes similar to those for $[Co(en)_3]^{3+}$, (en = $H_2NCH_2CH_2NH_2$), which implies the tris-*lel*-twist conformation† of the complex at least in the ion-pair.

Previously we prepared a new modification of Sephadex with D-$(-)_{589}$-tartrate groups of the ester type and successfully applied it to the column-chromatographic resolution of $[Co(en)_3]^{3+}$.[1]

A ϕ1·5 × 96 cm column of the Sephadex cation exchanger was used for the chromatographic resolution of $[Co(tn)_3]^{3+}$ with a 0·11 M sodium L-$(+)_{589}$-tartrate solution as the eluent. Figure 1 shows the elution curve in terms of the absorbance and the corresponding curve in terms of the apparent dissymmetry factor ($\Delta\epsilon_{485}/\epsilon_{490}$). The dotted lines are the elution curves for the $\Lambda(-)_{589}$- and $\Delta(+)_{589}$-isomers, deduced from the $\Delta\epsilon_{485}/\epsilon_{490}$ values on the assumption that

Table

$\nu_0/10^3$ cm^{-1}	$\Delta\epsilon_{max}$ This work	$\Delta\epsilon_{max}$ Ref. 2
18·7	−0·081	−0·062
20·9	+0·165	+0·124
28·0	+0·020	

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† See ref. 4 for the use of the term '*lel*'. In the *lel* form, the C–C–C plane of each chelate ring is approximately parallel to the C_3 axis of the complex ion.

the initial and final constant values of $\Delta\epsilon_{485}/\epsilon_{490}$ correspond to the $\Delta\epsilon_{485}/\epsilon_{490}$ values of 100% optical purity. The initial and final fractions of the eluted complex were collected to obtain pure Λ- and Δ-$[Co(tn)_3]Cl_3$ respectively as aqueous solutions; an ion-exchange technique was used for the anion conversion. The c.d. spectra of the isomers are entirely enatiomeric, as shown by the full lines of Figure 2. The $\Delta\epsilon$ values at the c.d. peaks are listed in Table and are compared with the values reported by Judkins *et al.*[2]

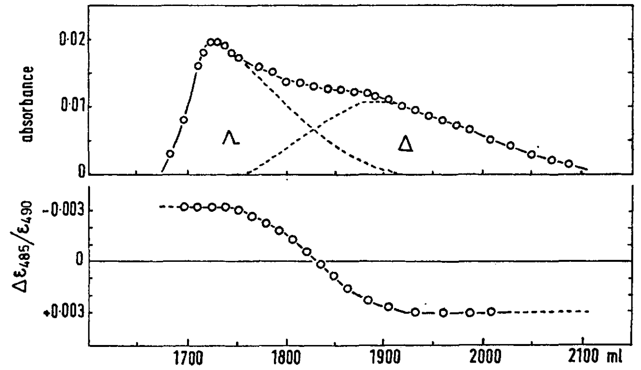

FIGURE 1. The elution curve of $[Co(tn)_3]^{3+}$ and the corresponding curve in terms of the apparent dissymmetric factor.

The broken lines in Figure 2 give the c.d. spectra of each isomer in the presence of a large excess of L-tartrate ions ([L-tartrate]/[complex] = *ca.* 280). The c.d. changes caused by the L-tartrate ions are stereoselective, especially in the high-wavenumbered component of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition (in the O_h approximation). This closely resembles the case of the $[Co(en)_3]^{3+}$ isomers.[3] Therefore, it seems reasonable to assume that $[Co(tn)_3]^{3+}$ forms an ion-pair of a structure similar to that of the $[Co(en)_3]^{3+}$–L-tartrate^{2-} ion-pair; thus Λ-$[Co(tn)_3]^{3+}$, at least in the ion-pair, adopts the tris-*lel*-twist conformation,[4] where three N–H bonds are nearly parallel with the C_3 axis of the complex.

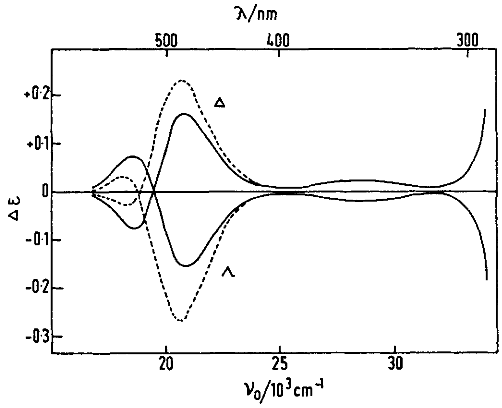

FIGURE 2. The c.d. spectra of Λ- and Δ-$[Co(tn)_3]Cl_3$ in water (——), and in the presence of a large excess of sodium L-tartrate (– – – –).

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[3] M. Fujita and H. Yamatera, unpublished work.
[4] P. G. Beddoe, S. F. Mason, and B. J. Peart, *Chem. Comm.*, 1971, 1283.