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Chiral Discrimination in the Interactions between $[Co(en)_3]^{3+}$ and Cholesteric Liquid Crystals by ^{59}Co NMR Spectroscopy

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Chiral discrimination of $[Co(en)_3]^{3+}$ was investigated by using ^{59}Co NMR spectroscopy in liquid crystals comprising cesium N-dodecanoyl-L-(or D)-alaninate. The ^{59}Co quadrupole splitting was distinguishable by diastereomeric interactions while a change in the chemical shift was the same.

^{59}Co NMR spectra for intramolecular diastereomers such as $[Co(pn)_3]^{3+}$ (pn= propylenediamine) have been measured and both the chemical shift and linewidth are largely different between the enantiomers.1-3) On the other hand, there have been no studies on intermolecular diastereomers for the cobalt(III) complexes by using ^{59}Co NMR. We have been studying specific site bindings of cobalt(III) complex ions to surfactants in nematic lyotropic liquid crystals using ^{59}Co NMR4-5) and found that the quadrupole splitting of quadrupole nuclei in the probe ions is useful to get information concerning interactions between the ions and the surfactants.6-8) In the present work, we investigated selective interactions of the chiral (Δ– and Λ–) $[Co(en)_3]^{3+}$ with the mixed liquid crystal phases comprising tetradecyltrimethylammonium bromide (abbreviated as TDTMABr) and cesium N-dodecanoyl-L-(or D-) alaninate(abbreviated as L- or D-CsDDA). In order to reveal the chiral selectivity ^{59}Co quadrupole splittings and chemical shifts of $[Co(en)_3]^{3+}$ in the chiral liquid crystal systems were measured in comparison with non-chiral systems.

The enantiomers of $[Co(en)_3]Cl_3 \cdot H_2O$ were prepared by passing the corresponding iodide,9) through an ion-exchanger in Cl^- form. The $[\alpha]_D$ values are –157.2° and +154.7° (0.1 mol dm^{-3}, aqueous solutions) for Δ– and Λ–isomers, respectively. The preparation and the purification of the L-(or D-)CsDDA followed a standard method,10) and non-contamination of dodecanoate was confirmed using ^{13}C NMR spectrum. TDTMABr was obtained from Sigma Co., and was recrystallized twice from ethyl acetate-ethanol mixed solutions. The other reagents were guaranteed reagents of Wako Pure Chemical Industries, Ltd.. The basic composition of the liquid crystal is as follows: 1.29 mol kg^{-1} of mixed anionic and cationic surfactants (CsDDA and TDTMABr)/0.99 mol kg^{-1} CsCl/appropriate amounts of decanol. The details have been listed in Table 1 of Ref. 5. The composition of the liquid crystals will be described below only by that of the surfactant. The ^{59}Co NMR spectrum was measured with a JEOL GX-270 FT NMR spectrometer operating at 64.1 MHz. The temperature of the sample solution was controlled to 27±0.5 °C. The concentration of the $[Co(en)_3]^{3+}$ was adjusted to 5×10^{-3} mol dm^{-3} in all cases. The chemical shift was measured relative to a 5×10^{-3} mol dm^{-3} $[Co(en)_3]Cl_3$ solution.

Figure 1 shows a change in the quadrupole splittings ($\Delta\nu_Q$) for both the Δ– and Λ–isomers of

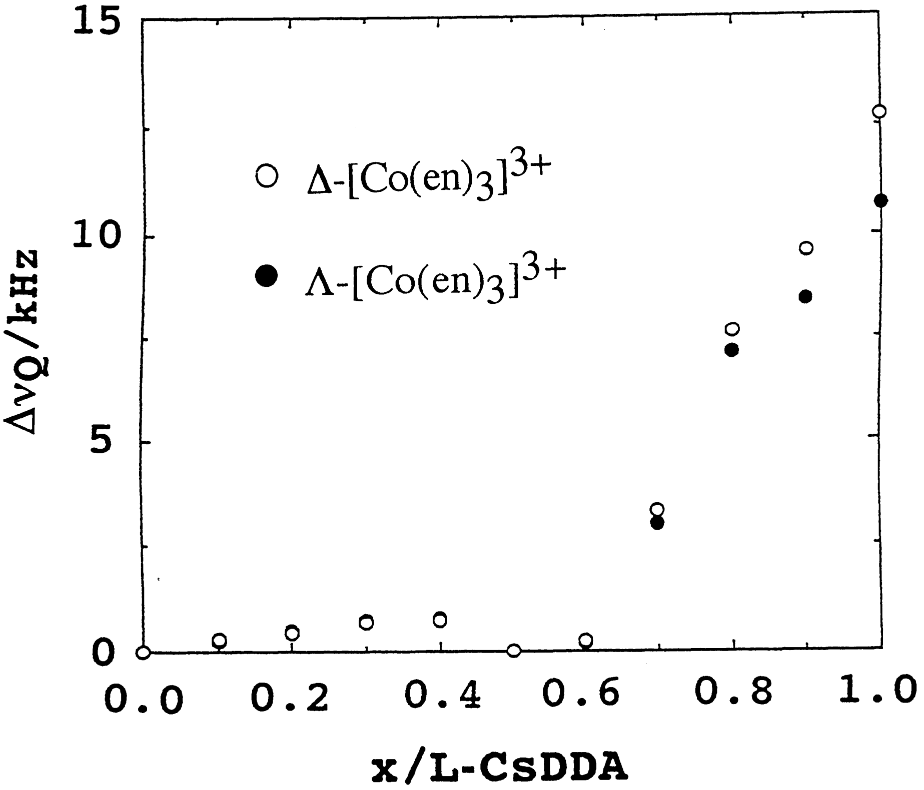

Fig.1. ^{59}Co quadrupole splittings of Λ-and Δ-$[Co(en)_3]^{3+}$ in the mixed TDTMABr/L-CsDDA liquid crystal system as a function of the mole fraction(x) of L-CsDDA.

Table 1. Quadrupole splittings($\Delta\nu_Q$/kHz) of ^{59}Co NMR spectra for optical isomers of $[Co(en)_3]Cl_3$ in the liquid crystals comprising CsDDA(1.29 mol/kg)

	$[Co(en)_3]Cl_3$		
	Δ	Λ	Racemic
L-CsDDA	12.6	10.7	11.4
D-CsDDA	10.8	12.6	11.7
DL-CsDDA	11.2	11.2	11.2

$[Co(en)_3]^{3+}$. The results show that in the higher x ranges there is a significant difference in the $\Delta\nu_Q$ values between the two enantiomers by the interaction with the L-CsDDA surfactant. Furthermore, the $\Delta\nu_Q$ values at x= 1.0 for all the combinations of optical active isomers including racemic ones were measured and the results are listed in Table 1. It shows that the Δ-isomer has a larger $\Delta\nu_Q$ with L-CsDDA than D-CsDDA while the reverse relationship holds for the Λ-isomer. Although the $\Delta\nu_Q$ values for the racemic isomers have larger ambiguities than those for the chiral system,$^{11)}$ it is significant that the $\Delta\nu_Q$ values are intermediate between those in the two optically isomeric systems. In order to directly compare the $\Delta\nu_Q$ values for each enantiomer of $[Co(en)_3]^{3+}$ under the same conditions, we used the same stock solutions of the liquid crystals for each isomer at the same x and furthermore the width at half-height ($\Delta\nu_{1/2}$) of the envelope of the proton spectra for each sample was confirmed to be the same between the samples having the same x values.$^{5)}$ The difference of the $\Delta\nu_Q$ values can therefore be due to those of the microscopic binding parameters, i.e. products of two factors, the extent of the binding ($p_b\chi_b$, where p_b is the fraction of the binding ions, χ_b the quadrupole coupling constant for the binding ions) and the order parameter(S_b) for the binding ion, since $\Delta\nu_Q$ can be expressed as 5,7,12)

$$\Delta\nu_Q \propto p_b\chi_b S_b = p_b(e^2 q_b Q/h)(3\cos^2\theta_{DE(i)} - 1)/2$$

where q_b is the electric field gradient at the nucleus of the binding ion, Q the nuclear electric quadrupole moment, and $\theta_{DE(i)}$ is the angle between the liquid crystal axis (director) and the electric field gradient (E.F.G.) from the polar group at site i as shown in Fig. 2. In this figure, the E.F.G. vector is the summation of the vectors for the individual polar group binding to the cobalt (III) complex. Although it is not easily determined which factor is dominating to differentiate the enantiomers, the difference in the conformation of the ion-binding may be more effective on the steric factor, S_b, in the above equation. As smaller $\theta_{DE(i)}$

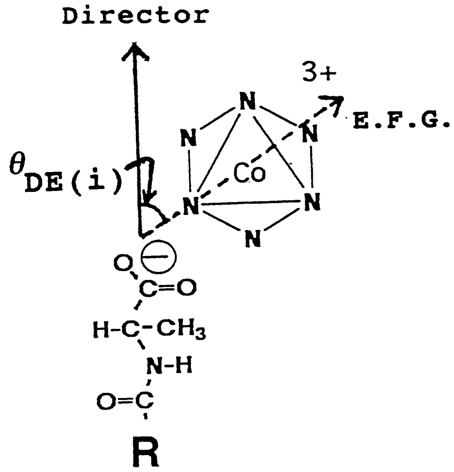

Fig.2. Schematic representation for the interaction between $[Co(en)_3]^{3+}$ and the alaninate polar group. ($R = C_{11}H_{23}$).

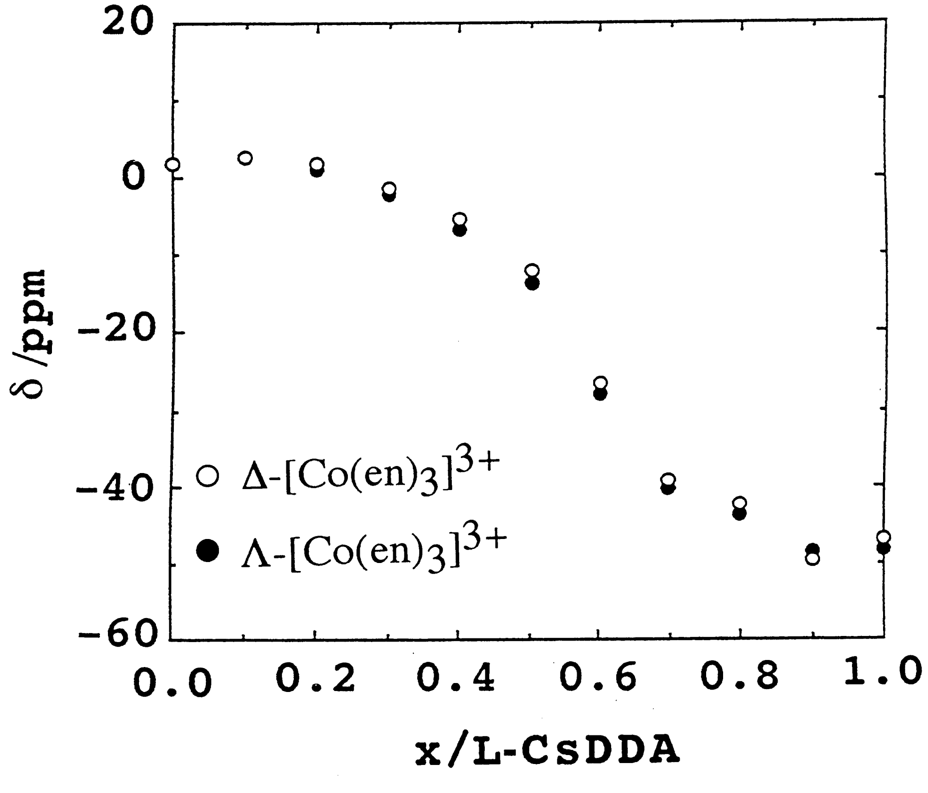

Fig.3. Changes in ^{59}Co chemical shifts for the chiral $[Co(en)_3]^{3+}$ in the mixed TDTMABr/L-CsDDA liquid crystal system as a function of the mole fraction (x) of L-CsDDA.

gives larger quadrupole splitting, $\theta_{DE(i)}$ may be smaller in the Δ-L and Λ-D systems than those in the Δ-D and Λ-L ones.

Chemical shifts also generally monitor an extent of the interaction between molecules; we thus measured them for the central peak of the ^{59}Co splitted spectra by changing the composition of the surfactants in the liquid crystal phases. Figure 3 is the result. Although they show an upfield shift with an increase in the interaction, the difference in the chemical shifts could not be distinguished between the enantiomers of $[Co(en)_3]^{3+}$ interacting with L-CsDDA. In the present solutions, the line-widths of the ^{59}Co NMR spectra are larger than in the usual aqueous solutions due to their higher viscosities and so their chemical shifts have larger ambiguities (nearly ±2 ppm) than in the usual solutions. However, it is clear that the ^{59}Co quadrupole splitting has higher sensitivity to the selectivity of the chiral cobalt(III) complex with the chiral surfactant in the liquid crystalline system than their chemical shift. Although both the quadrupole splitting and the chemical shift are represented by a second-rank tensor and there is a linear relationship between them as a first approximation,13) this relationship does not seem to hold in the lyotropic liquid crystalline systems as previously reported by us.4)

It was revealed that the ^{59}Co quadrupole splitting is more sensitive to discriminate the enantiomers of $[Co(en)_3]^{3+}$ than the chemical shift in the cholesteric liquid crystalline systems which strongly interact with the cobalt (III) complexes.

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11) As the ^{59}Co NMR spectra for the racemic systems consist of the mixtures of the signals due to the two enantiomers, the quadrupole splittings may contain larger errors than those for the chiral systems.
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