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# CIRCULAR DICHROISM SPECTRA OF COBALT(III) COMPLEXES CONTAINING AMINO ALCOHOL

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The complex $[Co(en)_2(L\text{-}praH)]Br_3$, where praH denotes 2-amino-1-propanol, was prepared and separated into two diastereoisomers, ΔL and ΛL. Their circular dichroism(CD) spectra changed remarkably by the change of pH of the solution. These changes were attributed to the dissociation of the alcoholic proton: $[Co(en)_2(L\text{-}praH)]^{3+} \rightleftharpoons [Co(en)_2(L\text{-}pra)]^{2+} + H^+$. The deprotonated $L\text{-}pra^-$ chelate gave an exceptionally large vicinal contribution to the optical activity. The CD spectra of optically active $[Co(en)_2(etaH)]Br_3$(etaH = aminoethanol) and $[Co(NH_3)_4(L\text{-}praH)]Br_3$ are also given.

Circular dichroism(CD) spectra of cobalt(III) complexes containing diamine or amino acid chelate rings have been studied extensively. However, there have been few studies on optically active complexes containing an amino alcohol chelate ring.[1) In this communication, we report CD spectra of $[Co(en)_2(etaH)]^{3+}$ and $[Co(en)_2(L\text{-}praH)]^{3+}$ where en = ethylenediamine, etaH = 2-aminoethanol and praH = 2-amino-1-propanol.

Experimental: The complex $[Co(en)_2(etaH)]Br_3 \cdot H_2O$ was prepared and resolved into enantiomers by the method reported by Buckingham et al.[2) By a similar procedure the complex $[Co(en)_2(L\text{-}praH)]Br_3 \cdot H_2O$ was synthesized. Calcd for $C_7H_{27}N_5O_2Br_3Co$: C, 16.42; H, 5.31; N, 13.68 %. Found: C, 16.52; H, 5.06; N, 13.62 %. The complex was separated into two diastereoisomers by use of SP-Sephadex C-25 column (3 x 50 cm)[3) with 0.07 M sodium L-tartrate. The dextrorotatory isomer was eluted first. Each eluate was concentrated under a reduced pressure at 40°C to dryness. The complex was extracted from the residue with a small amount of ethanol-water mixture, and passed through a Dowex-1 column in perchlorate form to remove tartrate.

Results and discussion: The CD and absorption spectra of $[Co(en)_2(etaH)]Br_3 \cdot H_2O$ in aqueous solution are given in Fig. 1. Both spectra show pH dependence in the pH range 2 to 5. The changes take place instantaneously and reversebly by the addition of sodium hydroxide or perchloric acid solutions. Three isosbestic points are observed in the CD spectra. These results indicate that the changes of CD and absorption spectra correspond to a protonation-deprotonation process. Buckingham et al.[2) reported that $[Co(en)_2(etaH)]^{3+}$ is an acid of $pK_a = 3.59$ ($\mu = 0.1$, 25°C), with the dissociation of the alcoholic proton to form $[Co(en)_2(eta)]^{2+}$. We have carried out the pH titration at $\mu = 0.04$, 25°C, and obtained a $pK_a$ value of 3.2. Using this value the CD and absorption spectra at various pH values could be explained as the sum of the two species [Co(en)$_2$(etaH)]$^{3+}$ and [Co(en)$_2$(eta)]$^{2+}$.

The absorption spectra of (+)$_D$- and (-)$_D$-L-praH complexes are similar to that of the etaH complex. Their CD spectra are shown in Figs. 2 and 3. These isomers exhibit also pH dependence but more remarkably than does the etaH complex. Three and two isosbestic points are observed for the (+)$_D$- and (-)$_D$-isomers, respectively. The CD and absorption spectra of these isomers can also be explained by considering the dissociation of alcoholic proton with a pK$_a$ value of 3.5 and 3.3 for the (+)$_D$- and the (-)$_D$-isomers, respectively. Thus a spectrum at pH above ~5 should be that of the deprotonated species, [Co(en)$_2$(amO)]$^{2+}$ and a spectrum at pH

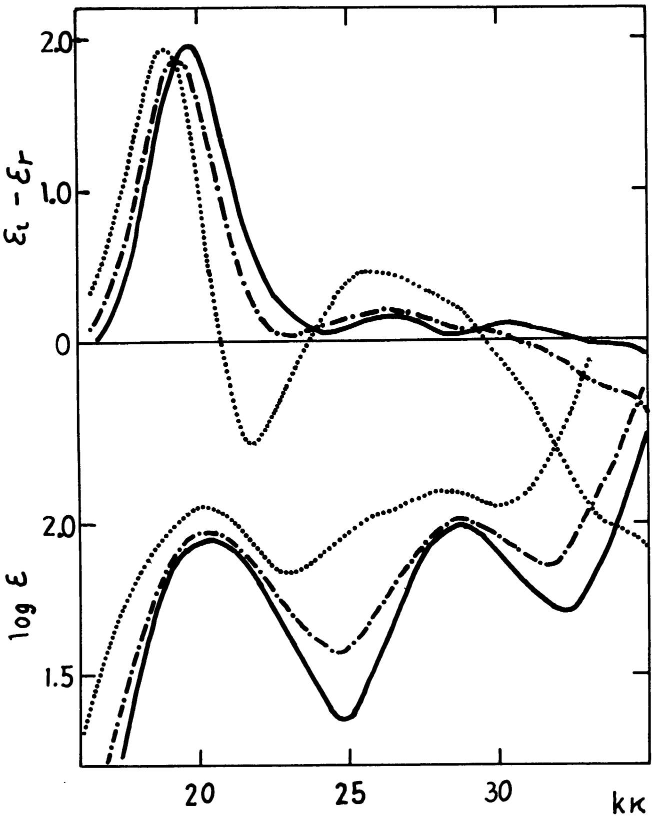

Fig. 1 The CD and absorption spectra of (+)$_D$-[Co(en)$_2$(etaH)]Br$_3$·H$_2$O at pH 1.4(——), pH 2.7(—·—·) and pH 9.7(·········).

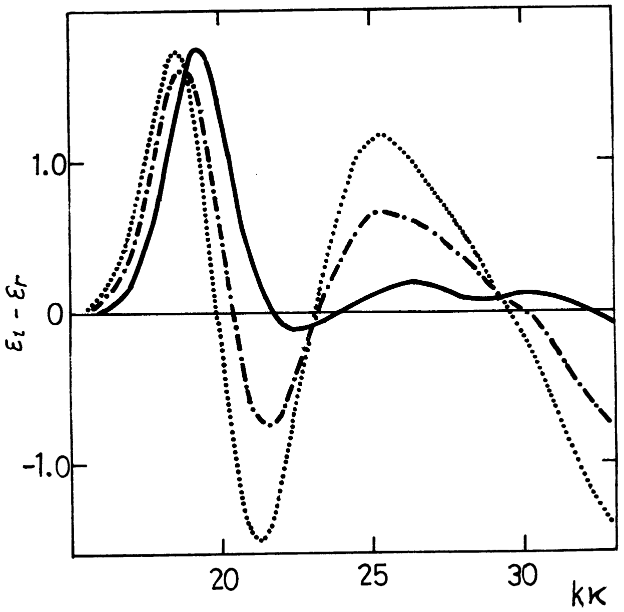

Fig. 2 The CD spectra of (+)$_D$-[Co(en)$_2$(L-praH)]$^{3+}$ at pH 1.8(——), pH 3.57(·—·—) and pH 5.1(·········).

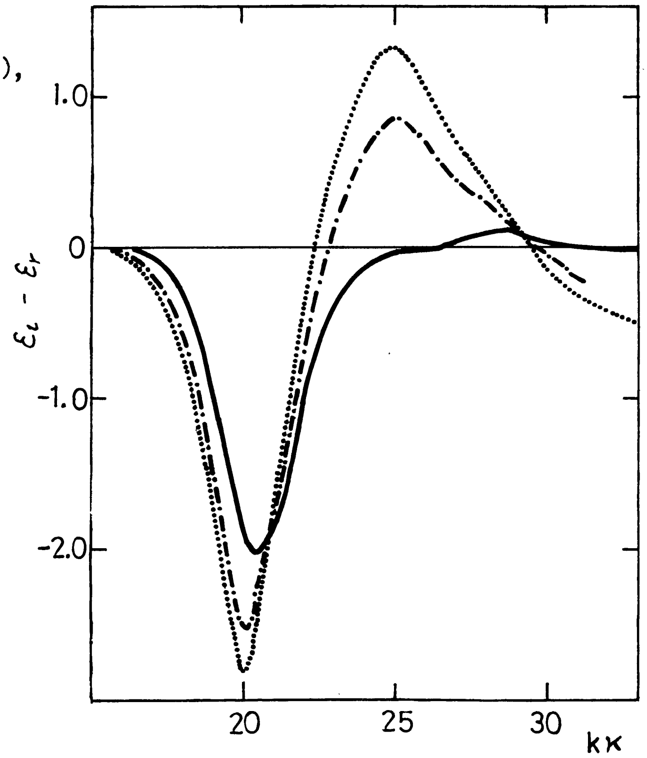

Fig. 3 The CD spectra of (-)$_D$-[Co(en)$_2$(L-praH)]$^{3+}$ at pH 1.8(——), pH 3.24(—·—·) and pH 6.1(·········).

below 2, that of the protonated species, $[Co(en)_2(amOH)]^{3+}$, where amO and amOH denote amino alcoholate anion and amino alcohol, respectively.

The CD spectra of $[Co(en)_2(amOH)]^{3+}$ complexes are similar to those of $[Co(diamine)_3]^{3+}$ 4,5) and $[Co(en)_2(aminoacid)]^{2+}$ 6) complexes; an intense CD band is seen in the first absorption band region and a weak band in the second absorption band region. From the sign of the main CD band at ca. 20000 $cm^{-1}$ the absolute configurations of $(+)_D$-$[Co(en)_2(etaH)]^{3+}$ and $(+)_D$-$[Co(en)_2(L\text{-}praH)]^{3+}$ are assigned to $\Lambda$, and that of $(-)_D$-$[Co(en)_2(L\text{-}praH)]^{3+}$ to $\Delta$. An amino alcohol chelate ring would have a puckered structure similar to that of a diamine chelate ring. Thus chelated L-praH will take the $\delta$-gauche conformation with an equatorial methyl group. It is known that the contributions of the configurational and the vicinal effects are additive in the CD spectra of a series of cobalt(III) complexes containing five-membered chelate rings.4-6) Assuming such an additivity for the CD spectra of $\Delta$- and $\Lambda$-$[Co(en)_2(L\text{-}praH)]^{3+}$ the configurational and the vicinal effect curves are obtained as shown in Fig. 4. Though there is some difference in intensity, the vicinal effect curve obtained from $[Co(en)_2(L\text{-}praH)]^{3+}$ complexes is similar to the CD spectrum of $[Co(NH_3)_4(L\text{-}praH)]^{3+}$.7) The result indicates that the vicinal contribution of an L-praH chelate ring is analogous to that of a L-1,2-diaminopropane chelate ring.4,5)

The CD spectrum of the deprotonated species $[Co(en)_2(L\text{-}pra)]^{2+}$ is quite different from that of the protonated complex. The higher wave-number component of the first absorption band is enhanced and an intense CD band is observed at ca. 25000 $cm^{-1}$. Such a difference is less pronounced between the CD spectra of $[Co(en)_2(etaH)]^{3+}$ and $[Co(en)_2(eta)]^{2+}$. Fig. 5 shows the configurational and the vicinal effect curves

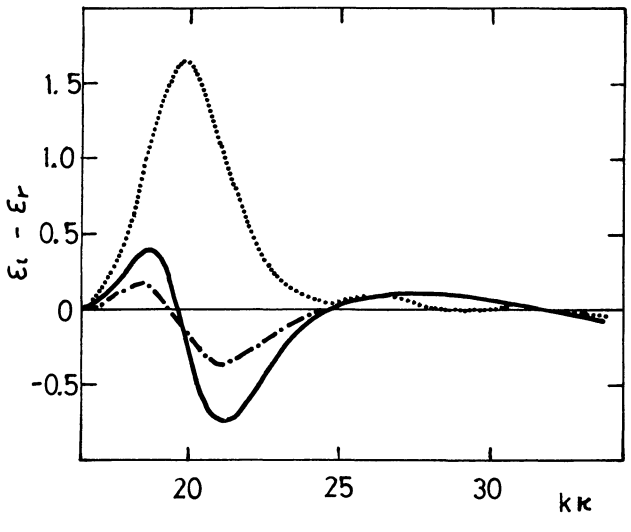

Fig. 4 Vicinal(——) and configurational (········) effect curves of $[Co(en)_2(L\text{-}praH)]^{3+}$. The CD spectrum of $[Co(NH_3)_4(L\text{-}praH)]^{3+}$ is given for comparison(-·-·-·).

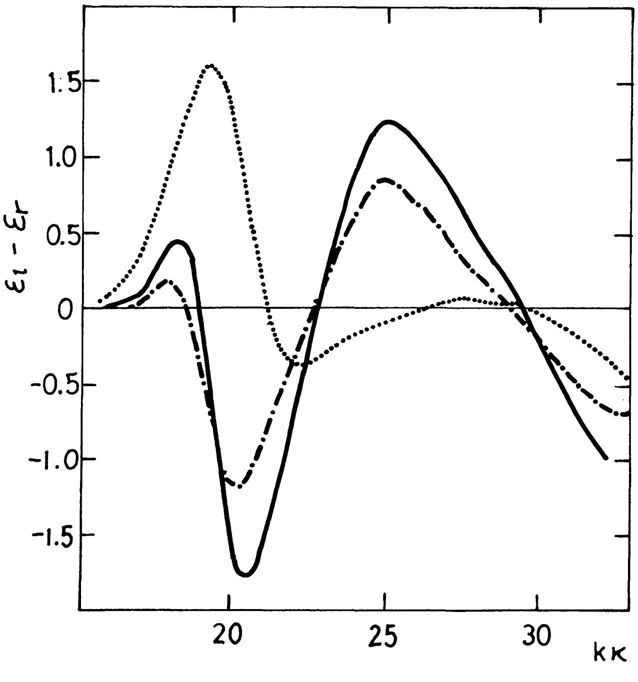

Fig. 5 Vicinal(——) and configurational (········) effect curves of $[Co(en)_2(L\text{-}pra)]^{2+}$. The CD spectrum of $[Co(NH_3)_4(L\text{-}pra)]^{2+}$ is given for comparison(-·-·-·).

of $[Co(en)_2(L\text{-}pra)]^{2+}$ obtained in a similar way to those of the L-praH complexes. While the configurational effect of the $pra^-$ complex is similar to that of $[Co(en)_2(L\text{-}praH)]^{3+}$, the vicinal effect is different considerably from that of the protonated species. Comparison of the CD curves in Figs. 2, 3 and 5 reveals that the characteristics of the CD spectrum of $[Co(en)_2(L\text{-}pra)]^{2+}$ can be attributed to the vicinal effect of L-$pra^-$ chelate ring. The $[Co(NH_3)_4(L\text{-}pra)]^{2+}$ complex$^{7)}$ exhibits also a CD spectrum similar to that of the vicinal effect of Δ- and Λ-$[Co(en)_2(L\text{-}pra)]^{2+}$ complex.

In the absorption spectra of $[Co(en)_2(amO)]^{2+}$ complexes, a shoulder band is observed at ca. 25000 $cm^{-1}$. These shoulder bands may be related to the intense CD bands at ca. 25000 $cm^{-1}$ observed for the deprotonated L-$pra^-$ complexes. The nature of the shoulder bands is not obvious at this stage. However, the entire absence of these bands in the spectra of protonated species implies that the presence of two nonbonding electron pairs on the coordinating oxygen atom in amino alcoholate complexes may be responsible for the abnormal CD curve. Further study on other complexes containing amino alcohol is in progress.

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