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The CD Spectra of (L-Aspartato) (L-2,4-diaminobutyrato) cobalt (III) Complexes

Masatoshi WATABE and Sadao YOSHIKAWA*

General Education Department, Kogakuin University, Hachioji, Tokyo 193
**The Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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Systematic correlations in CD spectra are found when the CD spectra of the isomers of the [Co(L-aspartato)-(L-2,4-diaminobutyrato)] complex, the $[Co(N)_3(O)_3]$ type, are compared with those of the isomers of the [Co-(L-2,4-diaminobutyrato)$_2$]$^+$, the $[Co(N)_4(O)_2]$ type, and those of the isomers of the [Co(L-aspartato)$_2$]$^-$, the $[Co(N)_2(O)_4]$ type.

The coordination of two optically active tridentate ions such as aspartate (=asp) or 2,4-diaminobutyrate (=2,4-dba), with cobalt(III) can result in three geometric isomers. One of these isomers has been easily characterized, without ambiguity, on the basis of the electronic absorption spectra. The assignment of the other two isomers has been attempted by using the CD spectra, but no distinct characterization has yet been established.[1-5] The CD spectra of these complexes are different from those of the complexes containing bidentate and tetradentate ligands. The two *cis*(*N*) isomers of the [Co(L-2,3-dpa)$_2$]$^+$(L-2,3-dpa= L-2,3-diaminopropionate ion)[2] were assigned by using X-ray analysis, while the isomers of the [Co(L-2,4-dba)$_2$]$^+$ were characterized by using the PMR spectra in comparison with those of the [Co(L-2,3-dpa)$_2$]$^+$. The CD spectra of the complexes containing asp, dba, and dpa did not show any distinct relation between the sign of the CD components and the absolute configuration of these isomers. Legg and Neal, by comparing these CD spectra with those of the [Co(EDDS)]$^-$-(EDDS=ethylenediaminedisuccinate) and the [Co(EDDAMS)]$^-$(EDDAMS=ethylenediamine-*N*,*N*-diacetic-*N'*-monosuccinate),[6] proposed that the assignment done by Douglas[4] for the configuration of the two *cis*(*N*) isomers of the [Co(L-asp)$_2$]$^-$ had better be reversed.

We ourselves have previously reported the preparation and the separation of the isomers of the [Co(L- or D-asp)(L-2,4-dba)] complex.[7] These isomers have been characterized by using the PMR spectra. They have the same membered chelate rings as the [Co(L-2,4-dba)$_2$]$^+$ and the [Co(L-asp)$_2$]$^-$. This paper will describe whether the CD spectra of the isomers of the [Co(L-asp)(L-2,4-dba)] join those of the [Co(L-asp)$_2$]$^-$ and those of the [Co(L-2,4-dba)$_2$]$^+$.

Experimental

The preparation and the separation of the isomers were reported in a previous paper.[7] Three geometrical isomers were obtained for the [Co(L-asp)(L-2,4-dba)], they were designated L1, L2, and L3 in the order of elution in the ion-exchange chromatography. The electronic absorption spectra and the CD spectra were measured with a JASCO J-20 spectrophotometer. The measurements were carried for an aqueous solution except for the L1 isomer, the solution of which contains *ca.* 50% H_2SO_4.

Results and Discussion

Figure 1 shows the possible geometric isomers of the [Co(L-asp)(L-2,4-dba)]. The facial isomer (L3) can easily be distinguished from meridional isomers by comparing the electronic spectra of the three isomers of the [Co(L-asp) (L-2,4-dba)].

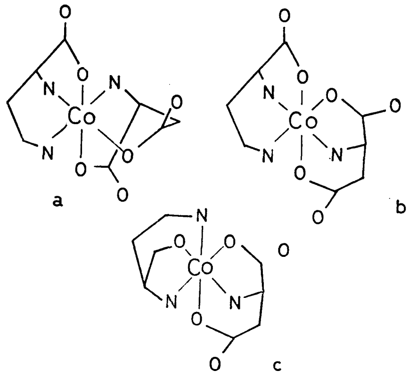

Fig. 1. The three possible geometrical isomers of the [Co(L-asp)(L-2,4-dba)] a: *trans*(*O*)*cis*(*N*), b: *cis*(*O*) *trans*(*N*), c: *cis*(*O*)*cis*(*N*). The isomers are named by considering 5-membered N and O atoms.

CD Spectra. The L-2,4-dba and the L-asp coordinated have 5-membered, 6-membered, and 7-membered chelate rings. When γ-amine nitrogen atoms of the L-2,4-dba for the [Co(L-2,4-dba)$_2$]$^+$ are replaced by oxygen atoms, one by one, the [Co(L-2,4-dba)$_2$]$^+$ may change to the [Co(L-asp)(L-2,4-dba)], and then to the [Co(L-asp)$_2$]$^-$. At this time, the relative positions of the 5-, 6-, and 7-membered chelate rings are not changed. The observed CD spectra may be classified into three groups (the A, B, and C rows in Fig. 2) by assuming that: (1) the difference between the N and O atoms coordinated may be disregarded, (2) the $\gamma_{\max}$ of the CD spectra varies with the change in the number of X and Y for the $[Co(N)_x(O)_y]$ system, and (3) the additivity of the vicinal effect holds for these nine isomers. Each of the three groups is composed of three isomers containing a different $[Co(N)_x(O)_y]$ type. In each series, one exact geometrical configuration is revealed by the electronic absorption spectra, ***trans*(*O*)-*cis*(*N*)** for [Co(L-2,4-dba)$_2$]$^+$, ***cis*(*O*)*cis*(*N*)** for [Co(L-asp)(L-2,4-dba)], and ***cis*(*O*)*trans*(*N*)** for [Co(L-asp)$_2$]$^-$ (see Fig. 2). The CD spectrum of the α isomer (the

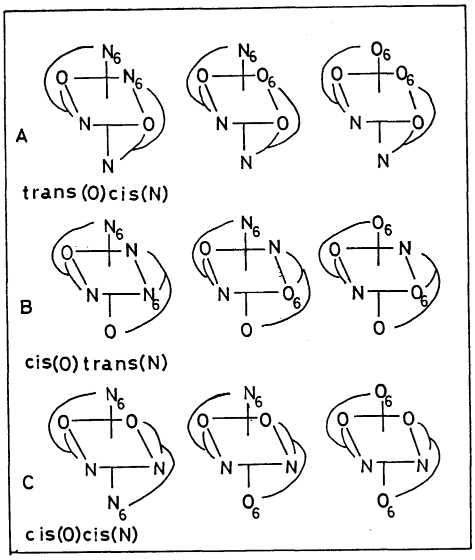

Fig. 2. Configurational analogies of the [Co(L-2,4-dba)$_2$]$^+$ (left), the [Co(L-asp)(L-2,4-dba)] (middle), and the [Co(L-asp)$_2$]$^-$ complexes (right).

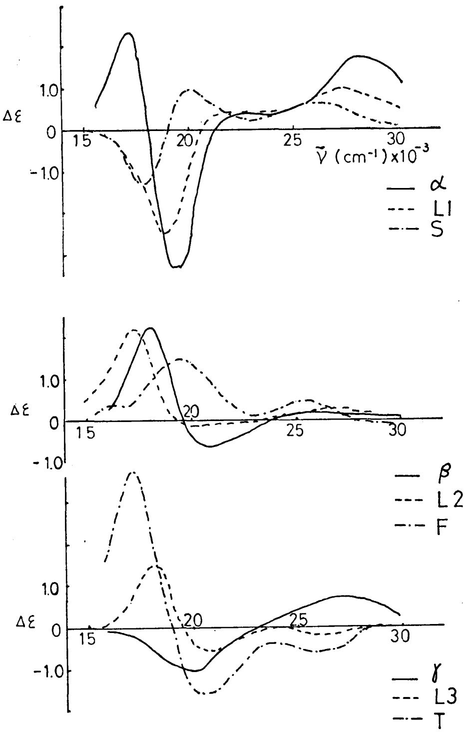

Fig. 3. CD spectra of the [Co(L-asp)$_2$]$^-$, the [Co(L-asp)-(L-2,4-dba)], and the [Co(L-2,4-dba)$_2$]$^+$.

three isomers obtained for the [Co(L-2,4-dba)$_2$]$^+$ are named α, β, and γ in the order of elution in ion-exchange chromatography), the configuration of which has the *trans*(*O*) geometry, resembles that of L1 of the [Co(L-asp)(L-2,4-dba)] rather than that of L2 (Fig. 3). The L1 isomer is assigned to the *trans*(*O*)*cis*(*N*) according to the above assumption (Fig. 2-A). Since the CD spectrum of L1 resembles that of the S isomer (the three isomers obtained are named F, S, and T in the order of elution in ion-exchange chromatography) of the [Co(L-asp)$_2$]$^-$, S must have the *trans*(*O*)*cis*(*N*) configuration. This last assignment, while not consistent with that of Douglas *et al.*,[4] agrees with that done by Legg and Neal.[6] When these three CD spectra are compared with each other in the order of [Co(L-2,4-dba)$_2$]$^+$→[Co(L-asp)(L-2,4-dba)]→[Co(L-asp)$_2$]$^-$, the value of the large negative peak at about 18×10^3 cm^{-1} is found to decrease gradually and the ν_{max} is found to shift to the longer wavelength side. The intensities of these CD spectra in the second absorption band region are also aligned in the order of α>L1>S. The β isomer for the [Co(L-2,4-dba)$_2$]$^+$ has the *cis*(*O*)*trans*(*N*) configuration.[3] The *cis*(*O*)*trans*(*N*) of [Co(L-asp)(L-2,4-dba)] lies in the same series as the *cis*(*O*)*trans*(*N*) isomer of the [Co(L-2,4-dba)$_2$]$^+$ (Fig. 2-B), and the CD spectrum of the L2 isomer considerably resembles that of the β isomer (Fig. 3). The configuration of the L2 isomer must be *cis*(*O*)*trans*(*N*). The *cis*(*O*)*trans*(*N*) of the [Co(L-asp)$_2$]$^-$ lies also in the same series, and the CD spectrum of the F isomer resembles those of both the β isomer and the L2 isomer, especially by having the same $\Delta\varepsilon$ in the second absorption region, except for the large splitting in the first absorption band as a result of the *trans*(*N*) configuration. In the last series, the CD spectrum of the L3 isomer resembles that of the T isomer, but neither resembles that of the γ isomer. However, the CD intensities in the second absorption region of these complexes are aligned in the order of γ>L3>T. This indicates a gradual change in the vicinal effect.

We have also confirmed the alternative assignment of the two *cis*(N) isomers of the [Co(L-asp)$_2$]$^-$ and the [Co(L-asp)(ida)]$^-$, first identified by Legg and Neal.[6]

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