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Circular Dichroism of Copper(II) Complexes with Optically Active Tetradentate Ligands in Aqueous Solutions

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The circular dichroism(CD) spectra of copper(II) complexes containing the asymmetric tetradentate ligands, such as ethylenediamine-*N,N′*-di-L-α-propionate, ethylenediamine-*N,N′*-di-L-α-isovalerate, and ethylenediamine-*N,N′*-di-L-α-hydrocinnamate, were measured in an aqueous solution. Each of the CD curves can be resolved into four components in the d–d region by Gaussian analysis; these components are related to the four possible d–d transitions of the copper(II) ion. The visible CD spectrum profile of the complexes varies with the variation in ligands; this implies that the conformation of the complexes is affected appreciably by the bulkiness of the side chain in the ligand.

In the analyses of the absolute configurations of many metal complexes by means of CD measurements, the empirical rule, that the conformations of complexes containing similar ligands may be identical with each other when the CD spectra observed for these complexes resemble each other in shape and sign, has been very often employed. It has been reported that the copper(II) complexes containing a series of L-α-amino acids exhibit similar CD curves in an aqueous solution. Therefore, the conformations of these complexes seem to be identical with each other in an aqueous solution.[1–3]

In this study, we wish to report that the observed CD spectra of three copper(II) complexes containing optically active tetradentate ligands, prepared by joining the amino groups of identical amino acid with one ethylene group, are very different from each other, and that these complexes may adopt different conformations in an aqueous solution.

Experimental

The asymmetric tetradentate ligands used in this study are ethylenediamine-*N,N′*-di-L-α-propionic acid(abbreviated to $EDDPH_2$), ethylenediamine-*N,N′*-di-L-α-isovaleric acid ($EDDVH_2$), and ethylenediamine-*N,N′*-di-L-α-hydrocinnamic acid($EDDCH_2$), prepared from L-alanine, L-valine, and L-phenylalanine respectively by a method similar to that described in the literature.[4]

Each of the complex solutions for the spectral observation was prepared by mixing equimolar aliquots of an aqueous stock solution of copper(II) nitrate with the tetradentate acids. An equivalent quantity of a base (sodium hydroxide) was always added to assure the virtually complete formation of the complexes. The copper(II) solution was standardized by EDTA titration, using murexide as the metal-ion indicator.[5] The CD curves were obtained by means of a JASCO J-20A spectropolarimeter in the region from 200 to 1000 nm. The absorption measurements were made by means of a Hitachi EPS-3T spectrophotometer at room temperature.

Results and Discussion

The CD spectra of [Cu(EDDP)], [Cu(EDDV)], and [Cu(EDDC)] in an aqueous solution are shown in Fig. 1. The visible CD spectra are very different from each other. Especially, the main CD components of the two complexes, [Cu(EDDP)] and [Cu(EDDV)], are opposite in sign. Applying the "empirical rule" described above to the present case, it seems reasonable to expect that these complexes include different extents of some types of conformers in an aqueous solution.

By an examination of the molecular models, two conformations can be constructed for these complexes, as is illustrated in Fig. 2. In the (I) conformation the orientation of the ring substituent groups is equatorial,

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[1] T. Yasui, This Bulletin, **38**, 1746 (1965).

[2] C. J. Hawkins and C. L. Wong, *Aust. J. Chem.*, **23**, 2237 (1970).

[3] R. D. Gillard and S. H. Laurie, *J. Chem. Soc., A*, **1970**, 59 (1970).

[4] L. N. Schoenberg, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, **7**, 2386 (1968).

[5] G. Schwarzenbach, "Complexometric Titrations," Methuen, London, p. 82 (1957).

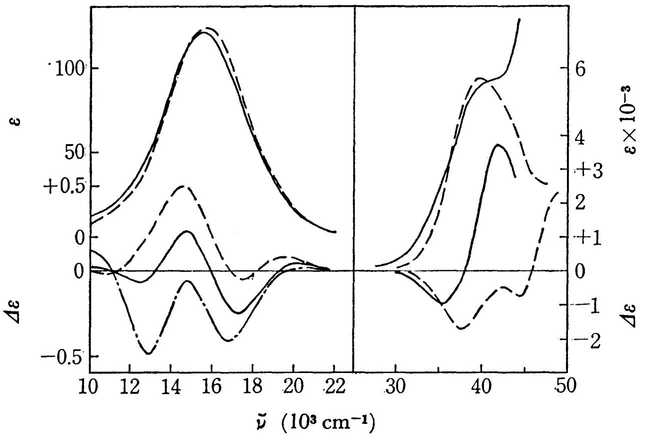

Fig. 1. Absorption and CD spectra of [Cu(EDDP)](— —), [Cu(EDDV)](—•—), and [Cu(EDDC)](——) in aqueous solution.

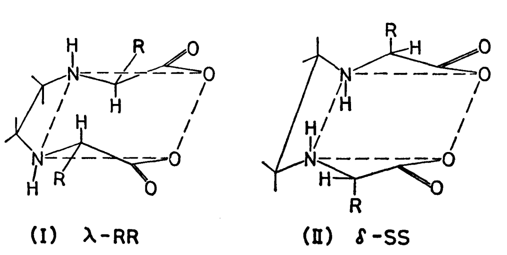

Fig. 2. The two possible conformers. The symbols δ and λ represent the conformations of the central en-type chelate ring, and R and S the configurations of the asymmetric donor nitrogen.

whereas in the (II) conformation the orientation is axial. In general, it is accepted that the equatorial orientation is more stable than the axial orientation in most chelate complexes. However, the energy difference between the two types of orientations of the substituent groups in the amino acid chelate portions of the present tetradentate ligands is much smaller than that in the en-type chelate ring, since, in the en-type chelate ring, the *gauche* structure discriminates greatly between the two orientations, whereas in the amino acid chelate ring this is not the case because of its planarity.[6] Furthermore, the energy difference between the two orientations in square-planar complexes can be expected to be much smaller than that in octahedral complexes. In square-planar complexes, the interaction of the axially-oriented substituent group with the molecules occupying the apical positions may be small.[7] Therefore, the energy difference between the two conformers, (I) and (II), in Fig. 2 seems to be not so large that an equilibrium may exist between the two conformers in an aqueous solution. The equilibrium distribution between the two conformers should vary with the bulkiness of the substituents; hence, these three complexes are speculated to have different equilibrium constants in (I)$\rightleftharpoons$(II). Thus, we seem to be able to account convincingly for the spectral results observed here in terms of the equilibrium.

If there is such an equilibrium in the complexes, an appreciable change in the CD curves of these complexes would be expected with a variation in the temperature because of the temperature dependence of the equilibrium. In practice, the CD curves observed for these complexes change considerably with a variation in the temperature, despite the limited temperature range. For example, the temperature dependence of the CD curve in the EDDV complex is shown in Fig. 3.

As the origins of the temperature dependence of the CD spectra, vibronic effects or an equilibrium between some conformers may be expected. Since it has been suggested that the magnitudes of the CD bands of metal complexes are only weakly influenced by the vibronic effects,[8] the temperature dependence may be mainly due to the existence of an equilibrium. Furthermore, the presence of an isosbestic point in Fig. 3 indicates the binary equilibrium. Thus, the temperature dependence observed here may be attributed to the equilibrium between the two conformers, (I) and (II), in Fig. 2.

It is clear that the visible CD spectra in Fig. 1 are composed of some d-d transition components. The observed shapes of the CD curves depend essentially on the relative magnitudes of these components, which should subsequently change with the variation in the equilibrium distribution described above. Therefore, it seemed that it would be worthwhile to resolve each of the CD spectra into their transition components.

Each of the visible CD spectra in Fig. 1 can be apparently resolved into four CD bands, although these four bands may not correspond exactly to the four com-

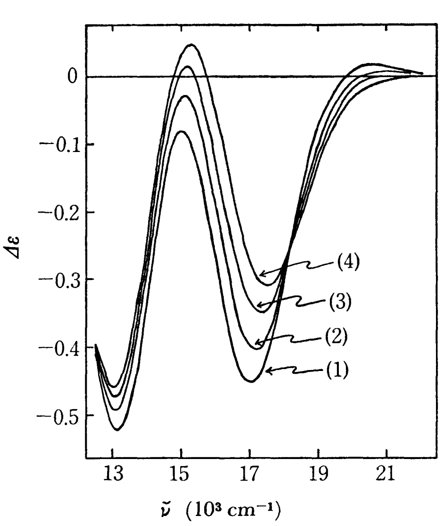

Fig. 3. CD variation with the temperature in the EDDV complex; (1) 3°±1 °C, (2) 27.5°±0.2 °C, (3) 51.2°±0.2 °C, (4) 72.0°±0.3 °C

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[6] Equatorial and axial orientations in these tetradentate ligands are somewhat different from the so-called 'quasi'-equatorial and 'quasi'-axial orientations in amino acid chelates. By the examination of the molecular models, the *gauche* structure of the N–C–C–N skeleton may be responsible for the orientation of the substituents, and the energy difference between the two orientations seems to be larger than that in the amino acid chelates.

[7] C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, p. 203 (1971).

[8] F. S. Richardson, *J. Phys. Chem.*, **75**, 692 (1971), and references therein.

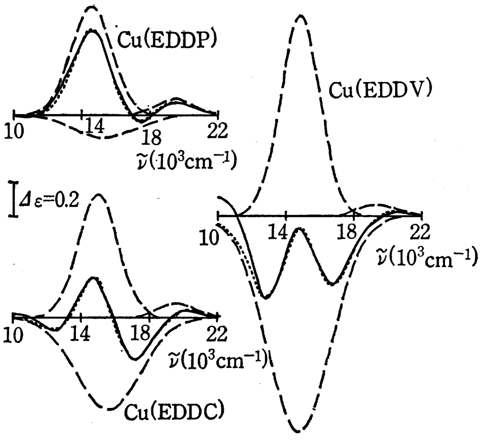

Fig. 4. Gaussian analyses of the CD spectra observed at room temperature: The solid curves are measured spectra; the dashed curves are the Gaussian components; the dotted curves represent the Gaussian summations.

ponents of the d-d transitions. From a comparison of the CD shapes in the 12000—18000 cm^{-1} region, it can be anticipated that each of the CD curves in this region is composed of two components, each of which has one peak near 15000 cm^{-1} with an opposite sign. In the CD spectrum of the EDDV complex at room temperature, the positive one of the two components is not observed in any appreciable amount (Fig. 1). However, the positive component emerges at the higher temperature, as is shown in Fig. 3. Moreover, small positive CD bands appear at about 10000 and 20000 cm^{-1}, and finally these CD curves could be composed of four components.

In order to support the view that these CD curves are composed of four components, we attempted to resolve the CD spectra by Gaussian analysis.[9] A set of Gaussian analyses is presented in Fig. 4. The analyses led to only the three bands at the higher wavenumber side, for we failed to observe the whole of the CD band at the lowest wave number. The slight discrepancies between the summed curves and the measured curves are within the limits of experimental error. Thus, it is almost certain that the curves in the visible region are composed of four components, which are related to the four possible d-d transitions.[10] The corresponding resolved components in the three spectra are situated at almost the same wave numbers, but with different magnitudes. Since the relative magnitudes of the respective components change with the variation in the equilibrium distribution between the two conformers, different CD spectra might be observed for the present three complexes. On the basis of the curve resolutions for the obtained CD curves, the assignments of the four components in the visible region of these complexes will be reported in the next paper.

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[9] The analyses of the band envelopes were accomplished by trial and error, assuming a symmetrical and purely Gaussian shape for every component band, and assuming that the corresponding resolved components in the respective curves may be the same d-d origin and hence have the same band widths.

[10] Wilson and Martin reported that four ligand field bands are identified in the solution circular dichroism of the bis type complex of *N*-methyl-L-alanine with copper(II). E. W. Wilson, Jr., and R. B. Martin, *Inorg. Chem.*, **10**, 1197 (1971).