The Conformations of Copper(II) Complexes with edda-Type Optically Active Polyamino Carboxylic Acids in Aqueous Solutions

Tasuku Murakami and Masahiro Hatano

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, 2-1-1 Katahira, Sendai 980

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A copper(II) complex with (*S*,*S*)-1,1′-ethylenedipyrrolidine-2,2′-dicarboxylic acid (H_2epro) was prepared, and its absorption and CD spectra were measured in an aqueous solution. A weak absorption band at 9500 cm^{-1} was indicative of the apical coordination of the carboxylate group. Furthermore, from the fact that the effect of unidentate bases, such as pyridine and ammonia, on the absorption and CD spectra of the epro complex was quite different from that of bidentate bases, the epro complex was expected to take a Λ-uns-*cis* conformation. In addition, the base-addition effect was measured for the complexes of (*S*,*S*)-α,α′-dimethyl-*N*,*N*′-ethylenediaminediacetic acid(H_2eddp), (*S*,*S*)-α,α′-diisopropyl-*N*,*N*′-ethylenediaminediacetic acid(H_2eddv), and (*S*,*S*)-α,α′-dibenzyl-*N*,*N*′-ethylenediaminediacetic acid(H_2eddc). The conformations of these complexes are also discussed on the basis of the information obtained for the epro complex.

In the previous paper,[1)] we have reported that the copper(II) complexes with ethylenediamine-*N*,*N*′-diacetic acid(H_2edda)-type optically active polyamino carboxylic acids, such as (*S*,*S*)-α,α′-dimethyl-*N*,*N*′-ethylenediaminediacetic acid(H_2eddp),[2,3)] (*S*,*S*)-α,α′-diisopropyl-*N*,*N*′-ethylenediaminediacetic acid(H_2eddv), and (*S*,*S*)-α,α′-dibenzyl-*N*,*N*′-ethylenediaminediacetic acid(H_2eddc), exhibited quite different circular dichroism (CD) spectra from each other and that, hence, these complexes might adopt different conformations in aqueous solutions.

In order to obtain further information on the conformations of the edda-type copper(II) complexes, we have now prepared a new edda-type complex of a copper(II) ion with (*S*,*S*)-1,1′-ethylenedipyrrolidine-2,2′-dicarboxylic acid (abbreviated to H_2epro). As may be seen in Fig. 1, this acid has two pyrrolidinyl groups in its inner parts and, hence, may be expected to coordinate to a metal ion with a large stereospecificity. In this paper, we wish to report the absorption and CD spectra of the epro complex of copper(II) and, in addition, the effects of unidentate and bidentate bases on the CD spectra of other edda-type complexes. The conformations of these complexes will be discussed on the basis of the behavior of the spectra.

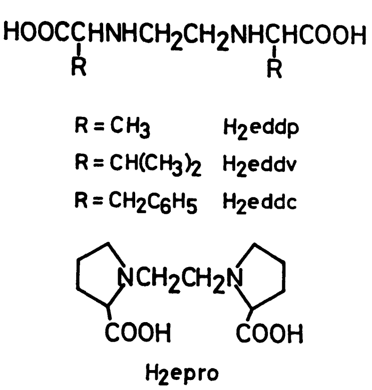

Fig. 1. Optically active edda-type polyamino carboxylic acids.

Results and Discussion

Conformation of [Cu(epro)] and Other edda-Type Complexes. Figure 2 shows the absorption and CD spectra of the epro complex in the region of 7000 to 22000 cm^{-1}, together with those of the eddp, eddv, and eddc complexes which have been reported previously.[1)] The epro complex exhibited a main absorption at 15400 cm^{-1} and a weak band at about 9500 cm^{-1}. Corresponding to these two bands, two CD bands were observed with the opposite sign. The existence of this weak absorption band plays an important role when discussing the conformation of the epro complex, as will be described below.

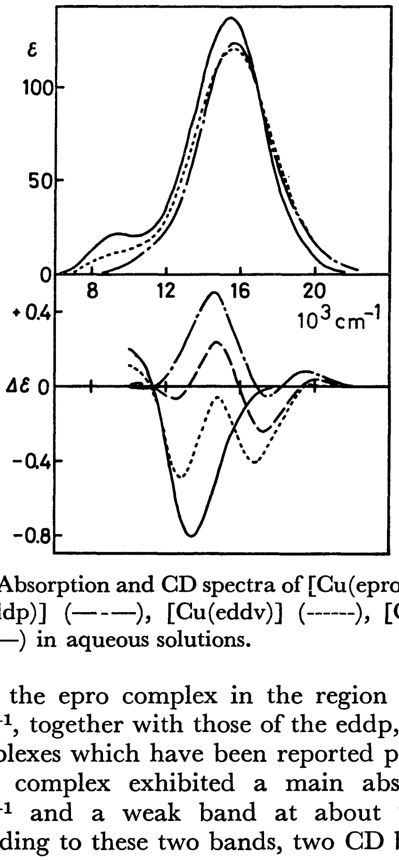

Fig. 2. Absorption and CD spectra of [Cu(epro)] (——), [Cu(eddp)] (— — —), [Cu(eddv)] (------), [Cu(eddc)] (— - — -) in aqueous solutions.

In general, copper(II) complexes typically consist of four nearby donor atoms arranged approximately in a plane around the central metal ion, with the possibility of one or two more distant apical donors. A stronger ligation to the copper(II) ion along the tetragonal axis would cause the d-d absorption band to shift to a lower energy.[4—7)] In many cases, a shoulder band appears at about 10000 cm^{-1} as a result of such a ligation.[7—9)] Therefore, the weak band observed for the epro complex leads us to expect the apical ligation of one or two carboxylate group(s) of epro, that is, a *cis*-type coordination of epro to the copper(II) ion.[10)] The chelated

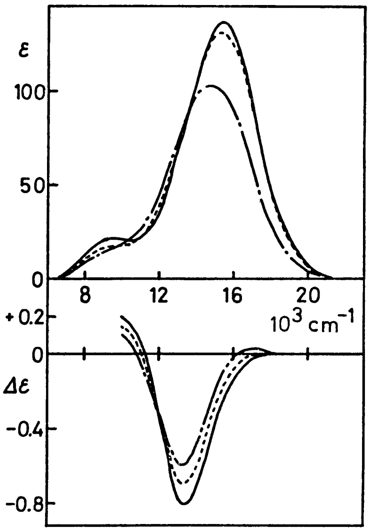

Fig. 3. The pH-dependent absorption and CD spectra of [Cu(epro)].
——: pH 5.3—9.0, ------: pH 10.5, —·—: pH 11.8.

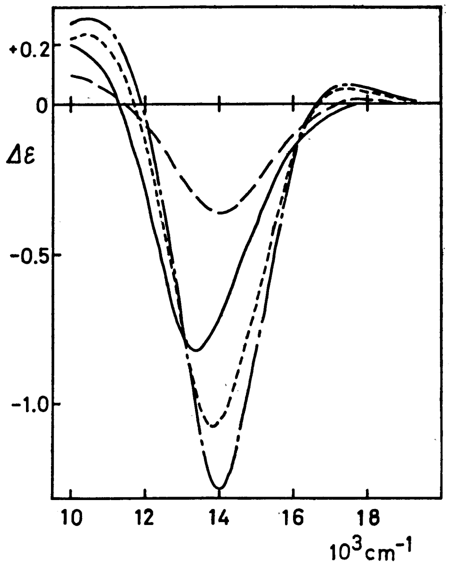

Fig. 4. Base-induced variation of the CD spectrum of [Cu(epro)] (mole ratio; in base/complex).
——: (0), ------: py (15), —·—: py (700), — —: bipy (5).

carboxylate group will possess a stronger ligand field than water, in spite of having the same coordination atom. Thus, the weak band is thought to become visible.

It has been observed that the optical activity of the ternary mixed complexes of copper(II) with diethylenetriamine and L-α-amino acids decreases in a high pH region.[7] This extreme decrease in the optical activity was concluded to result from the displacement of the carboxylate group coordinated at an apical position by a hydroxide ion. Therefore, if the epro complex contains an apical ligation, the intensity of the CD band is expected to decrease significantly in a high pH region. Figure 3 shows the variable-pH absorption and CD spectra of the epro complex. These spectra varied little in the pH 5 to 9 region. However, as the pH was further increased, the intensities of the absorption and CD bands appreciably decreased. Therefore, this is some evidence for the apical ligation of the carboxylate group in the epro complex. On the other hand, the absorption and CD spectra of the epro complex did not vary with the temperature (0—70 °C) and the concentration (2×10^{-3}—5×10^{-2} M) in a neutral pH region, indicating that the epro complex exists not as an equilibrium mixture, but as a single species in a neutral solution.

An examination of molecular models showed that epro hardly coordinates in a plane because of the rigid pyrrolidinyl groups. This is supported by the fact that some tetraamines, which have two pyrrolidinyl groups in their inner parts as well as epro, did not form planar species of the nickel(II) ion, but formed only octahedral ones.[11-13] Not only epro, but also other edda-type polyamino carboxylic acids seem to have primarily a certain characteristic that they hardly coordinate to a metal ion in a plane.[14] For example, as of now, no cobalt(III) complex with an edda-type acid in the planar configuration has been reported. Only s-*cis* and uns-*cis* isomers have actually been obtained.[10,15-17] Also, in the case of the edda-type complexes of the nickel(II) ion, the configuration in solution has been assigned to an s-*cis* form on the basis of NMR measurements.[18,19] Thus, the apical ligation of the one or two carboxylate group(s) which is derived from the absorption spectrum is also supported from the stereochemical point of view for epro.

In order to discriminate whether only one or both of the two carboxylate groups of epro coordinate(s) at the apical position, the effects of unidentate bases, such as pyridine and ammonia, added to the complex solution on the absorption and CD spectra were compared with those of bidentate bases, such as 2,2′-bipyridyl and ethylenediamine.

When a great excess of pyridine or ammonia was added to a solution of the epro complex, the absorption and CD bands became appreciably intense, but, in particular, the CD shape varied only to a lesser extent, as is shown in Fig. 4. However, when excess 2,2′-bipyridyl or ethylenediamine was added, the absorption spectral shape changed entirely and the intensity of the CD band decreased considerably. These findings indicate that the conformation of the epro complex remains essentially unaltered by the coordination of the unidentate bases, but the coordination of the bidentate bases alters the conformation.

The spectral behavior observed can be reasonably explained by supposing that the epro complex takes a conformation in which only one of the two carboxylate groups coordinates at an apical position, that is, a uns-*cis* form. It is expected that the bidentate base occupies two positions in the square plane about the copper(II) ion and displaces the carboxylate group coordinated in the plane, and that, consequently, the original conformation of epro is destroyed. On the other hand, the unidentate base probably coordinates to one position in the square plane and to one apical position, neither of which is occupied by epro; hence, the unidentate base may not alter the conformation

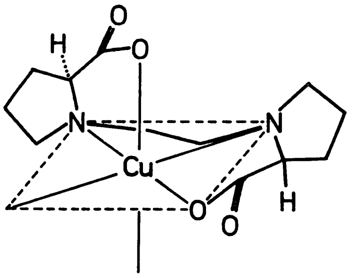

Fig. 5. Schematic drawing of a uns-*cis* structure proposed for [Cu(epro)].

of the epro complex. 2,2′-Bipyridyl or 1,10-phenanthroline act little as a unidentate base; the effect of α-methyl substituted pyridines such as α-picoline and 2,6-lutidine has been much smaller than that of pyridine.[20]

There are only two structures with apical ligation possible for the epro complex: *Λ*-uns-*cis* and Δ-s-*cis*,[21] because of the large strain originating from the pyrrolidine rings in epro. Therefore, the epro complex may be on the basis of the spectral behavior described above expected to take a *Λ*-uns-*cis* form. This structure is illustrated in Fig. 5. Each of the two tertiary nitrogen atoms in the epro complex has an *R* configuration, and the central ethylenediamine-like chelate ring seems to become an envelope.

As may be seen from Fig. 2, the eddv complex also exhibited a shoulder band at about 10000 cm^{-1} as a tailing of the main band. This implies that the apical ligation of the carboxylate group takes place to some extent in the eddv complex as well as in the epro complex. In addition, a high temperature dependence has been observed for the CD spectrum of the eddv complex.[1] This is apparently based on a binary equilibrium, as derived from the presence of isosbestic points. In the previous paper,[1] the temperature dependence observed for the eddv complex was expected to result from an equlibrium between two types of planar forms, in which the ring substituent groups are equatorial or axial. However, the contribution of the form in which the substituents are axial is probably small. The apical ligation of the carboxylate group appears to be a more plausible explanation of the weak band observed for the epro and eddv complexes.

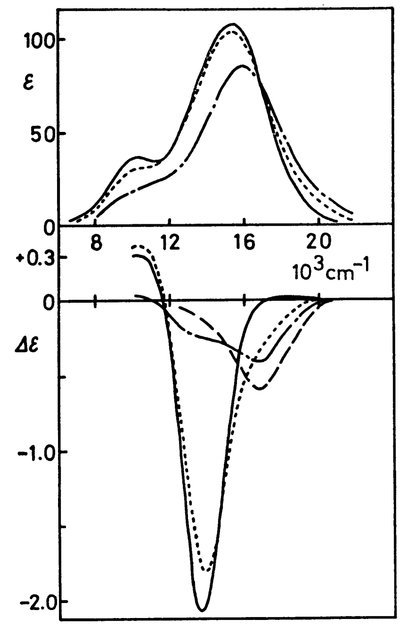

Fig. 6. Base-induced variation of the absorption and CD spectra of [Cu(eddv)] (mole ratio; in base/complex).
——: py (60), ----: NH$_3$ (5), —-—: en (1), – – –: bipy (5).

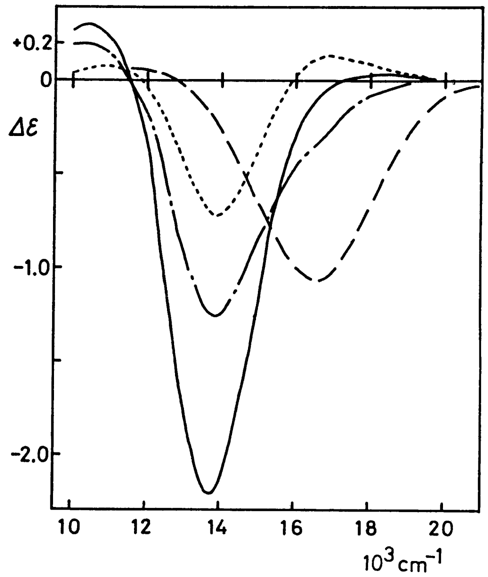

Fig. 7. Base-induced variation of the CD spectra of [Cu(eddp)] and [Cu(eddc)] (mole ratio; in base/complex).
——: [Cu(eddc)], py(100); —-—: [Cu(eddc)], NH$_3$ (5); – – –: [Cu(eddc)], bipy(6); ------: [Cu(eddp)], py (13300).

The CD spectra of the four copper(II) complexes with optically active edda-type polyamino carboxylic acids are quite different from each other, as is shown in Fig. 2. The negative components of the CD spectra increase in this order; [Cu(eddp)]<[Cu(eddc)]<[Cu(eddv)]<[Cu(epro)]. This order is the same as that of the intensity of the shoulder band at about 10000 cm^{-1}. When excess unidentate bases, such as pyridine and ammonia, were added to the aqueous solutions of the copper(II) complexes with eddp, eddv and eddc, the intensities of these CD spectra increased extremely and their CD shapes became almost the same. In addition, the shoulder band at about 10000 cm^{-1} became very intense (see Figs. 6 and 7).[22] Furthermore, this CD shape is identical with the CD curve of the epro complex, which is affected to a lesser extent by the addition of the unidentate bases.

This spectral behavior, especially the conformity in the CD spectra, is very significant when discussing the conformations of these complexes. From these findings, the mixed complexes of eddp, eddv, and eddc with pyridine or ammonia may be expected to take the same conformation as the epro complex, that is, the *Λ*-uns-*cis* form. The remarkable augmentation of the intensity of the CD band is evidence in support of the occurrence of the dissymmetry about the metal ion. If the mixed complexes take the *Λ*-uns-*cis* form, each of the two secondary nitrogen atoms has an *R* configuration as well as those of the epro complex. Thus, the unidentate base may be expected to convert the *trans*-type configuration of the edda-type acids into a uns-*cis*-type one. This conversion of the planar form into the uns-*cis* form may result from the stereospecific characteristic of the edda-type acids that they form a planar configuration only with difficulty.

The amount of unidentate bases necessary for the conversion of the eddp complex was much more than those needed for the addc and eddv complexes, as can be seen from Fig. 7. This may be a reflection on the higher stability of the planar configuration of eddp. This stability is probably related to the bulkiness of the substituent groups. Thus, the planar configuration of the edda-type acids is thought to become unstable with an increase in the bulkiness of the substituent groups. On the other hand, the effect of the bidentate bases on the spectra was entirely different from that of the unidentate bases, as is shown in Figs. 6 and 7. This finding is similar to the case of the epro complex.

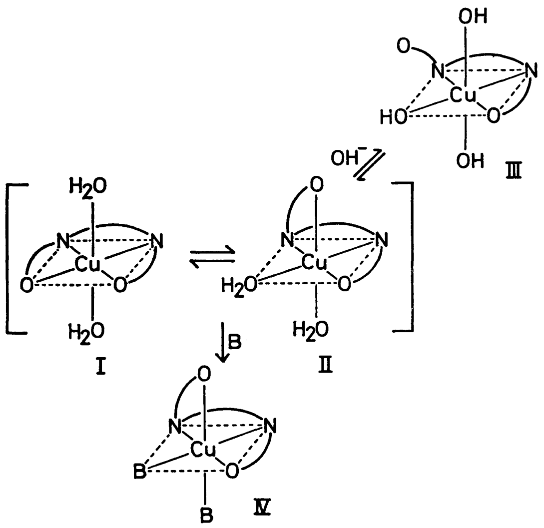

Fig. 8. Proposed equilibrium scheme for the edda-type copper(II) complexes in aqueous solutions. O–N–N–O represents edda-type ligands and B is a unidentate base. The charges on the central metal ion and coordinating groups are omitted for the simplicity.

Equilibrium Scheme. In conclusion, the equilibrium scheme for the edda-type copper(II) complexes in aqueous solutions is represented by Fig. 8, which is derived from the spectral results described above. Species (I) and (II) are predominant in a neutral pH region, which constitute an equilibrium state. In particular, however, the epro complex which exhibits the weak absorption band at 9500 cm^{-1} takes the uns-*cis* form (II) completely, and the eddp complex, almost the planar form (I). The eddv and eddc complexes may be equilibrium mixtures of these two forms. In a high pH region, the carboxylate group coordinated at the apical position is displaced by a hydroxide ion, and then Species (III) may be formed.

When an excess of the unidentate bases is added to the complex solutions, these complexes are converted from Form (I) or (II) into Form (IV). This is verified by the finding that, on the addition of unidentate bases, the CD spectra of these complexes become the same shape as that of the epro complex. Furthermore, the fact that the CD shape of the epro complex changes little on the addition of the unidentate bases is very important when introducing the above conclusion.

However, no data suitable for determining the structure of these edda-type complexes in the solid state has yet been obtained. In the near future, the structure in the solid state will be clarified in more detail.

Assignment of the CD Bands. In general, the absorption spectra observed for copper(II) complexes should consist of three d-d transitions, $d_{z^2}\rightarrow d_{x^2-y^2}$, $d_{xy}\rightarrow d_{x^2-y^2}$, and d_{xz}, $d_{yz}\rightarrow d_{x^2-y^2}$, if the molecular symmetry is taken as D_{4h}. In the case of the complexes with the stronger ligation along the tetragonal axis, the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition is the lowest energy, as is well-known.[23,24] The weak band at about 10000 cm^{-1} observed for the epro complex and the mixed complexes with pyridine or ammonia apparently corresponds to the $d_{z^2}\rightarrow d_{x^2-y^2}$ transition. These complexes imposed the positive CD band for this transition, as can be seen from the figures.

On the other hand, within the main absorption band were observed a large negative CD band a very small positive band at the lower- and higher-wavenumber sides respectively. These CD bands should correspond to the other two transitions, $d_{xy}\rightarrow d_{x^2-y^2}$, and d_{xz}, $d_{yz}\rightarrow d_{x^2-y^2}$. The former transition seems to have a lower energy than the latter;[23] hence, the large negative band may be the $d_{xy}\rightarrow d_{x^2-y^2}$ transition. However, since these complexes apparently possess a molecular symmetry much lower than D_{4h}, the degenerate transition may split into two bands in practice. In this case, the main band consists of three transitions; consequently, the assignment of the two CD bands becomes more difficult. The following two descriptions may be convincing arguments: the split of the degenerate transition is probably small, or one of the three transitions may contribute little to the optical activity.

Experimental

Materials. The copper(II) complexes of eddp, eddv, and eddc were prepared as has been described in the previous paper.[1] The epro complex was isolated in the following manner. Basic copper(II) carbonate was mixed with an equimolar amount of the dimethyl ester of (*S*, *S*)-1,1′-ethylenedipyrrolidine-2 2′-dicarboxylic acid (H_2epro), which had been previously prepared,[11] in an aqueous solution. The solution was then allowed to stand at room temperature. Within a few days, a blue product was precipitated. The product was washed with ethanol and then reprecipitated from water. Found: C, 43.69; H, 5.89; N, 8.52%. Calcd for $[Cu(C_{12}H_{18}N_2O_4)]\cdot 1/2(H_2O)$: C, 44.10; H, 5.86; N, 8.57%.

The pyridine, ethylenediamine, 2,2′-bipyridyl, and 1,10-phenanthroline which were added to the complex solution were of commercial grades and were purified, if necessary, by the usual procedures. In the case of ammonia, equimolar amounts of ammonium chloride and sodium hydroxide were added to the complex solution.

Measurements. The absorption spectra were obtained by means of a Hitachi EPS-3T spectrophotometer, while the CD measurements in the region of 400 to 1000 nm were made on a Jasco J-20A spectropolarimeter. To follow the solution of the epro complex with a change in the pH, additional drops of 0.1 or 1.0 M sodium hydroxide were added. The pH of the solution was measured with a Toa HM-20B digital pH meter.

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