BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2456—2459 (1973)

The pH-dependent Variation of the Absorption and Circular Dichroism Spectra in Some Ternary Mixed Complexes of Copper(II) Containing Diethylenetriamine and Optically Active Amino Acids

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(Received February 8, 1973)

The absorption and circular dichroism(CD) spectra of some ternary mixed complexes of copper(II) with diethylenetriamine(dien) and various optically active α-amino acids have been measured in an aqueous solution at various pH values. The amino acid may coordinate to one of the planar positions, with its carboxylate or amino group as a unidentate ligand, in a neutral or a very high pH region. On the other hand, from the red shift of the d–d absorption band and the augmentation of the visible CD magnitude, it seems reasonable to expect that a large portion of the amino acid will form a chelate ring with an axial ligation in the pertinent pH region.

In general, coordination compounds of copper(II) typically consist of four nearby donor atoms arranged approximately in a plane about the metal ion, with the possibility of one or two more distant axial donors. The effect of the axial ligation on the spectral feature of copper(II) complexes has been investigated by many workers,[1–4] and it has been clarified that the stronger ligation to the copper ion along the tetragonal axis causes the d–d absorption band to shift to a lower energy and the intensity of the band to increase appreciably. However, little attention has been paid to the formation of the chelate ring containing an axial ligation in an aqueous solution, probably because of the instability of the chelate. Wellman *et al.*[5] detected the axial chelation of potential tridentate α-amino acids by optical rotatory dispersion. Recently, such an axial chelation has been confirmed by Martin and his co-workers.[6]

In a previous communication,[7] we reported that the copper(II) complex of L-alaninamide with dien has its amide nitrogen coordinated to the copper(II) ion at the axial position. Recently, Aiba *et al.*[8] have reported that when diamine or amino acid is added to an aqueous solution of $[Cu(dien)(H_2O)]^{2+}$, the d–d absorption band shifts to a much longer wavelength; this phenomenon suggests the formation of a sort of five-coordinated complex. In this study, we wish to report the pH-dependent variations of the CD magnitude and of the d–d absorption observed in the ternary mixed complexes of copper(II) with dien and various optically active α-amino acids; such knowledge will help to clarify the axial interaction between donor

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[1] J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

[2] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[3] L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, **7**, 567 (1968).

[4] A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc.*, *A*, **1968**, 1685 (1968).

[5] K. M. Wellman, T. G. Mecca, W. Mungall, and C. R. Hare, *J. Amer. Chem. Soc.*, **90**, 905 (1968).

[6] E. W. Wilson, Jr., M. H. Kasperian, and R. B. Martin, *ibid.*, **92**, 5365 (1970).

[7] T. Murakami, T. Nozawa, and M. Hatano, *ibid.*, **92**, 5768 (1970).

[8] H. Aiba, A. Yokoyama, and H. Tanaka, presented at the 26th annual meetings of Chemical Society of Japan held in Hiratsuka, April, 1972.

groups and the copper ion in aqueous solutions.

Experimental

Complex Formations and Measurements. Each solution of the ternary mixed complexes for the spectral observation was prepared by mixing equimolar aliquots of stock solutions of copper(II) nitrate, dien, and amino acids, whose equivalent weights has been checked by titration. The concentrations used here varied over the range from 1.5×10^{-3} to 6.0×10^{-2} M. To follow the same solution with a change in pH, additional drops of 0.1 or 1.0 M NaOH were added. The measurements of the pH of the solutions were performed with a Toa-Dempa HM-8 or Hitachi-Horiba M-5 pH meter.

The following optically active α-amino acids were used: L-alanine(abbreviated to L-alaH), L-valine(L-valH), L-proline(L-proH), and D-phenylglycine(D-phglyH). The D-phenylglycine was supplied by the Ajinomoto Co., Ltd. The CD curves in the region from 400 to 1000 nm were obtained by means of a JASCO J-20A spectropolarimeter at room temperature. The absorption measurements were made on a Hitachi EPS-3T spectrophotometer at room temperature.

Results and Discussion

Some typical absorption spectra observed here for the ternary mixed complexes of dien and α-amino acid are shown in Fig. 1. At pH 6.3, the absorption exhibits a maximum at about 16400 cm^{-1} with ε(molar absorptivity)∼78, a value which almost coincides with that of $[\text{Cu(dien)}(\text{H}_2\text{O})]^{2+}$. Titration experiments predict that the amino group of the amino acid may be protonated in the neutral pH region in these systems.[9] Consequently, the predominant species in the neutral pH region seem to be those involving dien and an amino acid, which may coordinate to the copper(II) ion only with its carboxylate end as a unidentate ligand. As the pH of the solution is raised, the absorptivity on the lower wavenumber side of the visible absorption band becomes appreciably high and the band, as a whole, shifts to the lower wavenumber side. This spectral feature is nearly identical with those observed in the formation of the five-coordinated complexes, such as $[\text{Cu(NH}_3)_5]^{2+}$[10] and $[\text{Cu(dien)(diamine)}]^{2+}$.[8]

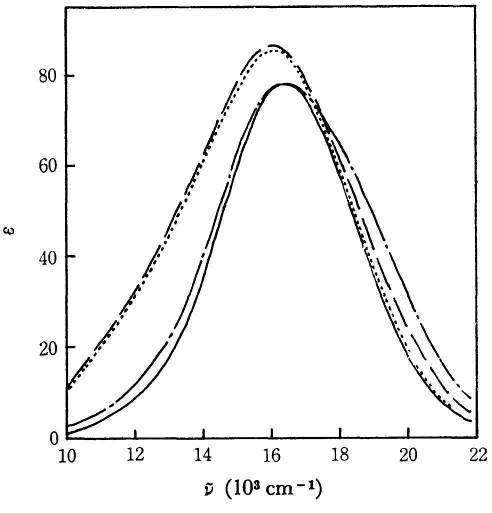

Fig. 1. Typical absorption spectra of amino acid-copper(II) complex with dien in aqueous solution (L-valine); concentration of complex is *ca.* 6×10^{-2} M.
—— pH 6.3, ----- pH 8.4
— — pH 10.5, —·— pH 11.9

Figures 2—5 show the variation in the CD spectra of the mixed complexes with the pH values in solution. Each of the mixed complexes except for the L-proline complex exhibits two extrema, at about 13000 and 17000 cm^{-1} in the neutral pH region. As the pH is increased, both of the two CD components become

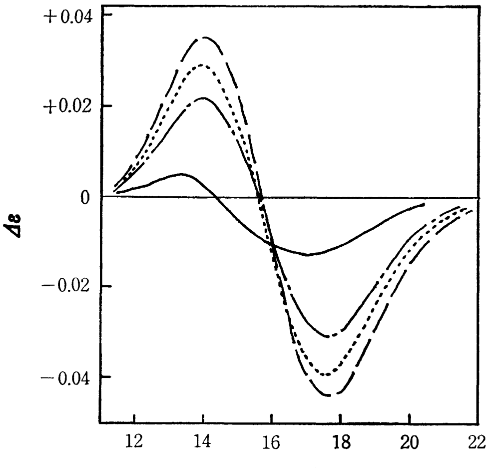

Fig. 2. CD spectra of L-alanine-copper(II) complex with dien in aqueous solution; concentration of complex is *ca.* 6×10^{-2} M.
—— pH 6.7, ----- pH 8.4
— — pH 10.1, —·— pH 11.3

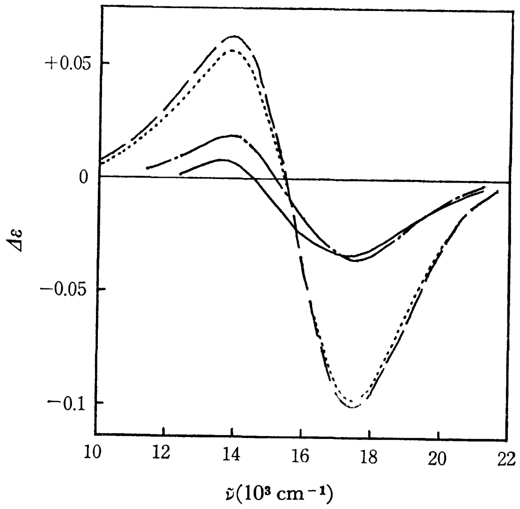

Fig. 3. CD spectra of L-valine-copper(II) complex with dien in aqueous solution; concentration of complex is *ca.* 6×10^{-2} M.
—— pH 6.3, ----- pH 8.4
— — pH 10.5, —·— pH 11.9

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9) Unpublished experiments performed in this laboratory.

10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd Ed., Interscience Publishers, New York (1966) p. 906.

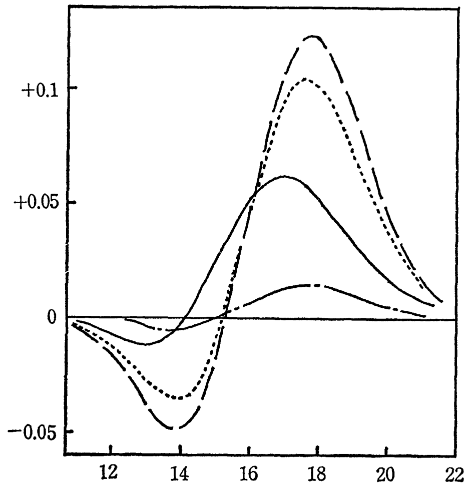

Fig. 4. CD spectra of D-phenylglycine-copper(II) complex with dien in aqueous solution; concentration of complex is *ca.* 6×10^{-2} M.
—— pH 6.7, ----- pH 8.4
—— pH 10.5, —— pH 12.0

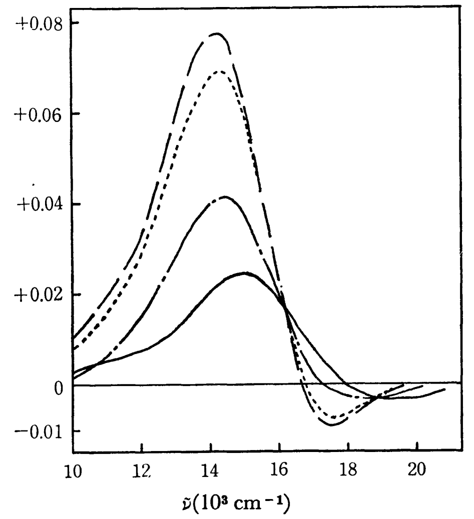

Fig. 5. CD spectra of L-proline-copper(II) complex with dien in aqueous solution; concentration of complex is *ca.* 6×10^{-2} M.
—— pH 7.1, ----- pH 8.8
—— pH 10.2, —— pH 12.0

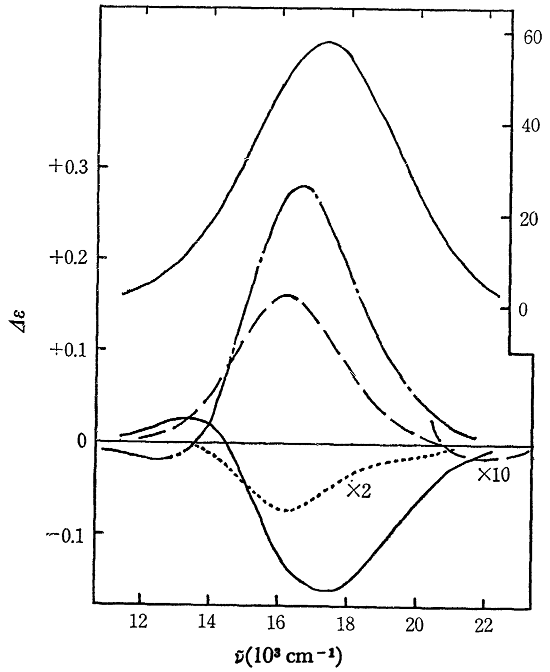

Fig. 6. Absorption and CD spectra of [Cu(en)(am)]-type complexes in aqueous solution.
—— L-valine, ----- L-alanine
—— L-proline, —— D-phenylglycine

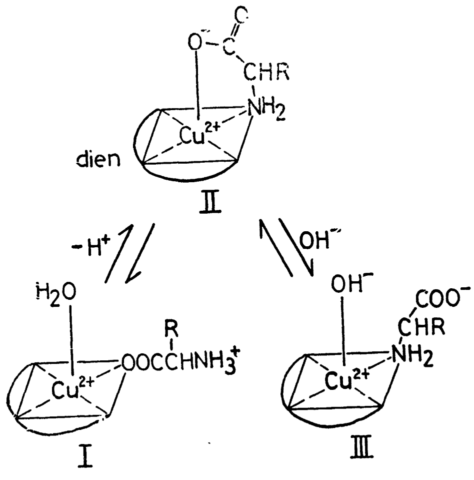

Fig. 7. Proposed equilibrium scheme for the ternary mixed complexes of copper(II) with dien and amino acids in aqueous solution.

very intense.[11] Therefore, the Δε values of the two components are comparable to those of complexes with optically active amino acids chelated in the square plane about the copper(II) ion, such as [Cu(L-am)$_2$] and [Cu(en)(L-am)]$^+$ (see Refs. 12 and 13, and Fig. 6). However, as the pH is increased further, the intensities of the CD bands revert to those in the low pH region.

These profiles of the absorption and CD spectra in the mixed complexes can be reasonably explained by assuming the equilibrium scheme shown in Fig. 7. In the present mixed complexes, dien should occupy three coordination positions in the square plane about the copper(II) ion; then the amino acid cannot form a chelate ring in the plane. Therefore, the amino acid would coordinate to the copper(II) ion, with its carboxylate end as a unidentate ligand, in the neutral pH region(species I). In the higher pH region suitable for the deprotonation of the protonated amino group, it is anticipated that a large portion of the amino acid will form a chelate ring with an axial coordination, that is, an axial chelation(five-coordinated species II). Such a chelate formation appears to be a more plausible elucidation for the red shift of the absorption band and

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[11] When L-lactic acid, which coordinates to copper(II) ion with its carboxylate group as a unidentate ligand, was used instead of the amino acid, the similar spectral behaviors could not be observed. The absorptivity at only higher wavenumber side increases with increase of pH, and the observed CD magnitude remains much small (Δε∼+0.005).

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

the augmentation of the CD magnitudes. For the following two reasons, the amino group of amino acid instead of the carboxylate group seems to coordinate in the plane, as is illustrated in the five-coordinated species II. The first reason is the tendency of the copper(II) ion to coordinate to strong donor groups in the square plane. The second reason is the labile character of the copper(II) ion, which makes an exchange of ligand groups in the coordination plane possible. As the pH in solution is increased so as to make the concentration of the hydroxide ion comparable to that of the complex ion, a large portion of the carboxylate group at the axial position may be displaced by the hydroxide ion (species III).

The CD curves for the mixed complexes increase in magnitude with an increase in the concentration of complexes. For example, the $\Delta\varepsilon$ values of the higher wave number component in the L-alanine complex are −0.030, −0.045, and −0.055 at about pH 10, corresponding to the concentrations of 1.5×10^{-3}, 1.5×10^{-2}, and 6×10^{-2} M respectively. The concentration dependence seems to be evidence for the preceding scheme that the hydroxide ion would displace the carboxylate group in an axial position, that is, for the (II) $\rightleftharpoons$(III) equilibrium shown in Fig. 7. There seem to be fewer species with other five-coordinated structures in the solution. We say this because, if the amino acids in the ternary mixed complexes, [Cu(dien)(L-am)]$^+$, would chelate in the square plane, we could expect that the CD spectral features would be very similar to those for [Cu(en)(L-am)]$^+$-type complexes. However, this does not seem to be the case.

So far as the donor atoms in the square plane about the copper(II) ion are concerned, when [Cu(N_3O)] is converted to [Cu(N_4)], such as in (I)→(II) in Fig. 7, the absorption spectrum should shift to a higher wavenumber. However, the difference in the absorption maxima, $\tilde{\nu}_{\max}$, for [Cu(N_3O)]- and [Cu(N_4)]-type complexes is not very much— *e.g.*, 16400 cm^{-1} for [Cu(dien)(H_2O)]$^{2+}$ and 16700 cm^{-1} for [Cu(dien)-(RNH_2)]$^{2+}$ (R=CH_3– or CH_3CH_2–).[8] In addition, the axial ligation may play a role in shifting the absorption band to a lower wavenumber. Therefore, the more the five-coordinated species(II) are formed in solution, the lower the observed absorption shifts.

Most L-amino acid copper(II) complexes of the [Cu-(L-am)$_2$]- and [Cu(en)(L-am)]$^+$-type, except for the L-proline complexes, exhibit a negative main CD band in the higher wavenumber region, with a much smaller positive component at lower wavenumbers.[12,13] The present mixed complexes also exhibit similar CD curves in the neutral or very high pH regions. In both pH regions, L-amino acid coordinates with its carboxylate or amino group as a unidentate ligand. Thus, the unidentate L-amino acids impose a dominant negative CD curve in the d–d band of the copper(II) ion as well as in the case of the chelated L-amino acids. This seems also to be the case with the observed CD cuvres for amino acid complexes of cobalt(III) in aqueous solutions.[14] In the pH region where the five-coordinated species(II) may be formed, the CD magnitude of the lower wavenumber component becomes comparable to that of the higher wavenumber component. Therefore, the chelation containing an axial position seems responsible for the increase in the $\Delta\varepsilon$ of the lower wave number component in particular.

We wish to thank Professor Kazuo Saito and Dr. Junnosuke Fujita for their valuable comments. We wish also to acknowledge the help of the Ajinomoto Co., Ltd., in supplying many amino acids. This research was supported in part by a grant from the Ministry of Education.

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

14) T. Yasui, J. Hidaka, and Y. Shimura, This Bulletin, **39**, 2417 (1966).