

Spectroscopic Properties of Copper(II) Complexes with Quadridentate Derivatives of L-Proline Amide and L-Proline Methyl Amide

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Abstract

The copper(II) complexes with epaH₂, tpaH₂, epmaH₂, and tpmaH₂, potentially quadridentate derivatives of L-proline amide or methyl amide (see text), have been characterized by absorption, circular dichroism (CD), IR, and ESR spectroscopies. All of the spectral features of the complex with dianionic tpa indicated an ordinary planar geometry, whereas those of the tpma complex suggest an unusual ligand field containing a strong apical coordination. The epa and epma complexes appear to take a distorted geometry on the basis of the splitting of d-d bands and the rhombic ESR. The ultraviolet absorption and CD bands associated with the coordinating amide group are also discussed.

Introduction

The coordination chemistry of ligands with amide groups is of considerable interest due to its biological significance in that the amide group possesses a character essentially identical to peptide bonds in proteins [1]. In the absence of metal ions, most amide groups remain neutral even in basic solutions. For the interaction with a metal ion, there are two possible binding methods: through the carbonyl oxygen of the neutral amide group and through the ionized nitrogen after the dissociation of an amide proton. In addition to solution basicity, the structural restriction of the ligand, if any, would affect the method of coordination of the amide [2, 3].

This work is concerned with the copper(II) complexes of the ligands which have two primary or secondary (methyl) amide groups at terminals as shown in Fig. 1. Since these ligands also contain two (S)-pyrrolidinyl groups, they would act as potentially quadridentate ones. It is known that similar quadridentate ligands derived from L-proline display their

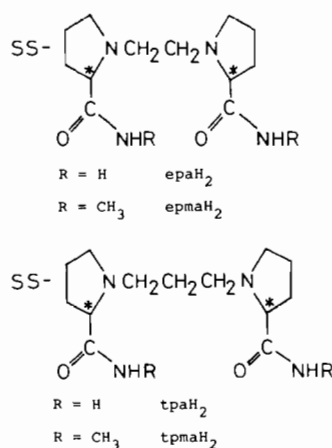


Fig. 1. Optically active quadridentate diamides and their abbreviations.

stereospecificities in complex formation of cobalt(III), nickel(II), and copper(II) [4–10].

As briefly reported in a previous letter [11], the terminal amide group alters its donor atom from the carbonyl oxygen into the deprotonated nitrogen upon the addition of base. From the drastic changes of the visible absorption and circular dichroism (CD) spectra, the donor alteration seems to cause a geometry conversion of the complexes.

In this article, we wish to report the ESR findings which coincide with the complex geometries expected from absorption and CD spectra. In addition, the absorption and CD bands in the ultraviolet region are also discussed. The ultraviolet bands are associated with the coordinating amide group and hence expected to provide a clue to the electronic correlation between the copper(II) and the amide group.

Experimental

The synthesis and nomenclature of the diamides in Fig. 1 have been described in previous papers [6,

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7], and only their abbreviations are given in Fig. 1. The samples for the spectral measurements were prepared by dissolving isolated complexes in methanol.

Electronic absorption and CD spectra were measured with a Jasco 520 spectrophotometer and a Jasco J-20A recording spectropolarimeter, respectively. All molar absorptivities, ϵ , and differential molar absorptivities, $\Delta\epsilon$, between left and right circularly polarized lights refer to 1 mol of copper(II), and their units are $\text{cm}^{-1} \text{M}^{-1}$. Solution ESR spectra were recorded on a Varian E-3 X-band spectrometer at room and liquid-nitrogen temperatures. IR spectra were measured with a Jasco IRA-2 spectrophotometer, by using KBr pellets for solid samples and small bags made of polyethylene films held between NaCl plates for solution samples.

Results and Discussion

Complexes with Neutral Ligands

Blue complexes were isolated from the solutions with copper(II) perchlorate and each of the four diamides. The elemental analyses clearly show that these complexes contain two molecules of perchlorate ion as a counter anion. The presence of perchlorate ion are also confirmed by solid IR spectra in that some strong bands appear around 1100 cm^{-1} . In addition, the so-called amide I band appears in the region of $1620\text{--}1650 \text{ cm}^{-1}$, but no band around 1600 cm^{-1} where the amide band for deprotonated amidates is generally observed [12, 13].

The visible–near infrared absorption and CD spectra have already been shown in the letter [11]. Their remarkable absorption shape, a main band in the region of $14000\text{--}16000 \text{ cm}^{-1}$ and a side band around 8000 cm^{-1} , is much different from that usually observed for ordinary square-planar copper(II) complexes.

The solution ESR spectra of the epaH₂ and tpaH₂ complexes are almost identical to those of the epmaH₂ and tpmaH₂ complexes, respectively, both at room temperature (RT) and liquid-nitrogen temperature (LNT). Such spectral similarities between

the present complexes containing primary amides and methyl amides have also been observed for their absorption and CD [11]. In Table I are summarized the values of ESR parameters.

All LNT ESR spectra observed are of axial symmetry and suggest that these complexes are essentially planar. The epaH₂ and epmaH₂ complexes, however, show considerably larger g_{\parallel} and smaller $|A_{\parallel}|$ values compared with those of the tpaH₂-type complexes and bis(amino acidate) complexes [14], which indicates some distortion of the coordination geometry around the copper [15, 16]. This distortion may come from a quite large tension due to the 5,5,5-trifused chelate system with rigid pyrrolidine rings. It also appears in the RT ESR that these complexes show poorly-resolved four-line hyperfine structures due to the nuclear spin of the copper, whereas the tpaH₂-type complexes exhibit clearly-resolved structures.

Complexes with Deprotonated Ligands

Figure 2 shows the base-varied stretching vibration band for the coordinating amide group in deuterio-methanol. For the tpaH₂ and tpmaH₂ complexes in which the amide groups remain neutral, the amide band is observed at 1620 cm^{-1} . As the amount of

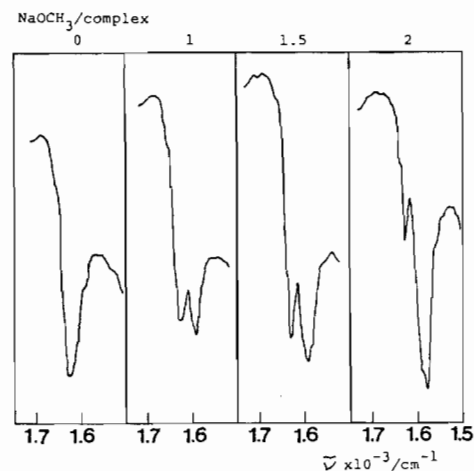


Fig. 2. Base-varied amide I band of the tpmaH₂ complex in CH₃OD.

TABLE I. ESR Parameters in Methanol at Liquid-nitrogen Temperature

Complex	g_0^a	g_{\parallel}	$ A_0 ^{a,b}$	$ A_{\parallel} ^b$	$ A_{\perp} ^b$
[Cu(epaH ₂)] ²⁺	2.14	2.336		153.6	
[Cu(epmaH ₂)] ²⁺	2.13	2.337		154.7	
[Cu(tpaH ₂)] ²⁺	2.124	2.256	75.5	188.2	12.0
[Cu(tpmaH ₂)] ²⁺	2.125	2.254	75.5	189.1	12.0
[Cu(tpa)] ^c	2.090	2.185	88.3	209.4	13.8
[Cu(tpma)] ^c	2.102	2.201	69.0	201.2	13.4

^aAt room temperature. ^b $\times 10^4 \text{ cm}^{-1}$. ^cComplexes formed with the addition of two equivalent amounts of sodium methoxide.

added base (sodium methoxide) increases, the 1620 cm^{-1} band becomes weak and a new band appears at 1580 cm^{-1} . After the addition of two equivalent amounts of base, the 1620 cm^{-1} band almost disappears while the 1580 cm^{-1} band becomes very strong. This IR behavior indicates the proton release to make both of the two amide groups ionized.

In general, the deprotonation of an amide group causes the transformation of its donor atom from the carbonyl oxygen into the ionized nitrogen owing to the difference of binding ability [17]. The d-d band of the complex with dianionic tpa* is observed at a quite high wavenumber (19 400 cm^{-1}), which results from the strengthened ligand field in the equatorial plane containing two amino and two amidate nitrogens [2, 10, 18, 19]. As can be seen in Fig. 3, the ESR spectrum of the same system is of axial symmetry at LNT and shows nine superhyperfine structures on the g_{\perp} signal, which may be due to four nitrogens surrounding the equatorial plane of the copper(II) ion [20, 21].

The tpma complex exhibits an intense d-d absorption band ($\epsilon_{\text{max}} = 200$) at 17 600 cm^{-1} with a shoulder around 12 500 cm^{-1} [11]. This spectral feature is typical for the tetragonal ligand-field with a strong apical coordination [22]. The terminal two chelate rings are nearly planar due to the amidate group and the bonding direction of the ionized nitrogen is trigonal-planar. Therefore, if in the tpma complex the ligand takes a planar geometry, the two *N*-methyl groups would face each other and consequently the steric repulsion between them would be very large. Then, an *uns-cis*** structure in which one of the amidate groups binds at an apical position should be taken into account.

Concerning the amide coordination, it has been claimed that there was no evidence for the apical coordination of an amidate nitrogen, on the basis of quantitative potentiometries and previously reported data [24]. There is another viewpoint that the main plane converts and consequently one of the pyrrolidinyl nitrogens leads to occupy an apical position, since the coordination potency of the ionized amidate nitrogen is thought to be stronger than that of the pyrrolidinyl nitrogen. Even with such a viewpoint, however, the situation would be the same in that the ligand field contains the strong apical coordination.

This geometry is also supported by the ESR finding at LNT that only seven superhyperfine structures are observed on the g_{\perp} signal (Fig. 3(b)). Since the nitrogen at an apical position is usually insensitive for ESR [25], the fine structures are

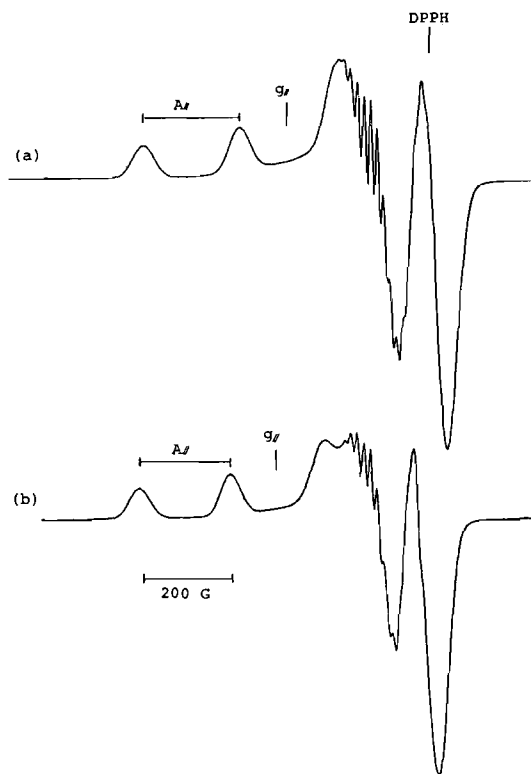


Fig. 3. ESR spectra of [Cu(tpa)] (a) and [Cu(tpma)] (b) in methanol at liquid-nitrogen temperature.

probably due to three nitrogen donors in the equatorial plane.

The most remarkable profile in the visible CD spectrum of the tpma complex is the extremely intense magnitude of the bands. By a Gaussian curve-fitting, both absorption and CD spectra are analyzed into three components: 12 600 (−1.6), 16 400 (+4.9), and 18 300 (−3.4) cm^{-1} (numbers in parentheses are values of $\Delta\epsilon$ for each Gaussian CD component). This CD magnitude is probably one of the largest observed for the d-d transitions of discrete copper(II) complexes. The two terminal chelate rings with the amidate group asymmetrically distributed around the copper ion undoubtedly contribute to the large optical activity. An inspection using molecular models provides the possibility of the stable Λ -*uns-cis* conformation owing to the large strain originating from the (*S*)-pyrrolidinyl groups, as well as the other complexes with similar L-proline derivatives [9, 10].

The interrelationships of ESR g values and electronic parameters for the $3d^9$ configuration in D_{4h} symmetry are given by the well-known approximate expressions

$$g_{\parallel} = 2.0023 - 8\lambda\alpha^2\beta^2/\Delta E_{xy \rightarrow x^2-y^2}$$

$$g_{\perp} = 2.0023 - 2\lambda\alpha^2\gamma^2/\Delta E_{xz, yz \rightarrow x^2-y^2}$$

*The charges of anionic ligands are omitted for clarity.

**The term, *uns-cis*, has been employed in order to express one of the three geometrical isomers for the edda-type complexes [23].

TABLE II. Bonding Parameters of the Complexes with Dianionic tpa and tpma^a

Complex	α^2	β^2	γ^2
[Cu(tpa)]	0.79	0.67	0.65
[Cu(tpma)]	0.85	0.58	0.66

^aValues used for the calculations; spin-orbit coupling $\lambda = -828 \text{ cm}^{-1}$, electron-nuclear dipole interaction $P = 0.036 \text{ cm}^{-1}$, ligand field transitions $\Delta E_{xy} \rightarrow x^2 - y^2$ and $\Delta E_{xy, yx} \rightarrow x^2 - y^2$ are 19 000 and 20 500 cm^{-1} for the tpa complex, 16 400 and 18 300 cm^{-1} for the tpma complex.

where α , β , and γ are the coefficients of d-orbitals in the molecular orbitals. The parameter α^2 gives a measure of the covalency of the in-plane σ -bonding, and β^2 and γ^2 of the in-plane and out-of-plane π -mixing, respectively. In Table II are presented the bonding parameters calculated for the tpa and tpma complexes. The large α^2 and small β^2 for the tpma complex indicate a weak σ -covalency and a strong π -interaction in the equatorial plane, which can be correlated to the complex geometry expected from the absorption and CD spectra.

The visible absorption and CD spectra of the epa and epma complexes are apparently composed of four bands [11] which may correspond to the d-d transitions between perfectly-splitting five d-orbitals. By a Gaussian curve analysis the peak positions are determined at 10 900, 14 100, 17 000, and 20 000 cm^{-1} . The ESR spectrum at LNT is rhombic rather than axial as shown in Fig. 4, and the RT ESR spectrum is poorly resolved. Thus, these spectral findings of absorption, CD, and ESR provide the conclusion that the epa and epma complexes are not tetragonal but greatly distorted. The intense CD magnitude, -4 and $+3$ in $\Delta\epsilon$ for the Gaussian components, suggests the configurational asymmetry around the copper ion just as for the tpma complex.

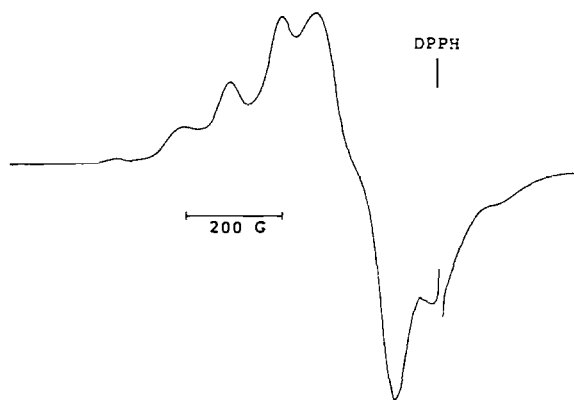


Fig. 4. ESR spectrum of [Cu(epa)] in methanol at liquid-nitrogen temperature.

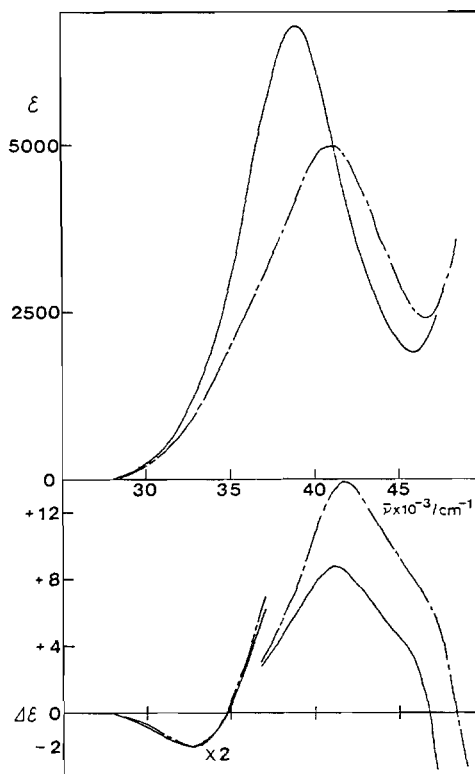


Fig. 5. Absorption and CD spectra in the ultraviolet region of [Cu(tpaH₂)]²⁺ (—) and [Cu(epaH₂)] (---) in methanol.

Absorption and CD Spectra in The Ultraviolet Region

An intense absorption band with ϵ value of about 5000 is observed at 41 000 cm^{-1} for the epaH₂ and epmaH₂ complexes and at 39 000 cm^{-1} with ϵ of about 7000 for the tpaH₂ and tpmaH₂ complexes as shown in Fig. 5. Under this absorption envelope, all present complexes exhibit similar CD spectra, a main positive band at 41 000 cm^{-1} and a small negative one around 33 000 cm^{-1} . Although no evident absorption peak or shoulder corresponding to the small CD component is detected, its ϵ_{max} value probably lies between 500 and 1000 from the curve resolutions based on a Gaussian fitting. Since the $\Delta\epsilon_{\text{max}}$ values of the two CD bands are about -2 and $+10$, the dissymmetry factors ($\Delta\epsilon/\epsilon$) are estimated at less than 0.005 for both bands, which suggests the magnetic dipole-forbidden nature [26].

The ligands themselves exhibit no absorption or CD band in this region, but upon the complex formation these bands appear. The lowest energy absorption band of the non-coordinating amide group usually occurs near 45 000 cm^{-1} and its origin is an $n-\pi^*$ transition [27]. The other bands due to other intra-ligand transitions, such as $\pi-\pi^*$, should appear at higher wavenumbers. Therefore, the two bands observed can be assigned to the charge-transfer (CT)

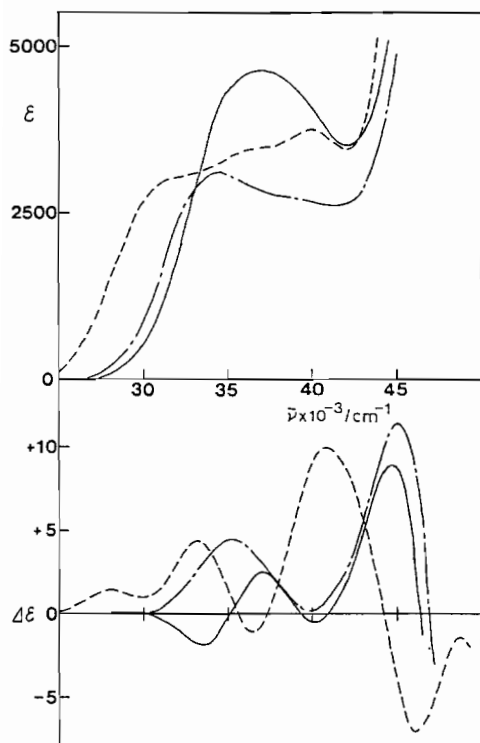


Fig. 6. Ultraviolet absorption and CD spectra of [Cu(tpa)] (—), [Cu(tpma)] (---), and [Cu(epa)] (- - -).

transitions between copper d-orbitals and π and/or π^* orbitals on the coordinating carbonyl group, although there has been no report on the CT band associated with the neutral amide group.

Similarly to the d-d spectra, the ultraviolet absorption and CD spectra also change entirely upon the amide deprotonation, as shown in Fig. 6. The tpa complex shows a new broad absorption band at $37\,000\text{ cm}^{-1}$ instead of the $41\,000\text{ cm}^{-1}$ band for the tpaH_2 complex and, under this absorption envelope, two CD bands are observed at $33\,600$ and $37\,000\text{ cm}^{-1}$ with opposite signs. The two bands are associated with the CT transitions between d-orbitals and amidate orbitals [28].

When zinc(II) ion is used as a metal ion, no absorption longer than 220 nm appears with or without base addition. The amide deprotonation is confirmed in advance by the IR measurements. This suggests the possibility that the bands observed for the copper complexes are due to the CT transitions from the ligand orbitals, not from the metal.

The tpma complex shows a very broad absorption spectrum spreading to much lower wavenumbers (Fig. 6). The CD curve has a somewhat complicated shape implying more than two components. However, the whole CD spectrum is rather similar to that of the tpa complex, with the shift of each CD band

to lower wavenumbers by $3000\text{--}4000\text{ cm}^{-1}$. This red-shift of the CT bands probably relates to the strong in-plane π -interaction expected from the small β^2 .

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