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A NEW TYPE OF COPPER(II) COMPLEXES SHOWING CURIOUS CD BEHAVIOR; COPPER(II) COMPLEXES WITH QUADRIDENTATE LIGANDS CONTAINING TWO (S)-PYRROLIDINYL GROUPS AND TWO AMIDE GROUPS

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The copper(II) complexes described in the title exhibited absorption spectra quite different from ordinary planar copper(II) complexes. Addition of base transformed the donor atom of the amide group and hence the absorption and CD spectra intensively changed. On the basis of these findings, the stereochemistry was discussed.

There have been a number of studies on the stereospecific coordination of the ligands containing pyrrolidinyl group(s). Recently, it has been reported that a series of optically active tetraamines containing (S)-pyrrolidinyl groups coordinated to cobalt(III) and nickel(II) ions to give stereospecific isomers.[1-3] An edda-type optically active quadridentate ligand derived from L-proline also seemed to form stereospecific nickel(II) and copper(II) complexes.[4,5]

In this letter, we wish to report the optical characterization of the copper(II) complexes with optically active quadridentate ligands shown in Fig. 1. These ligands possess two (S)-pyrrolidinyl groups and two primary or secondary(methyl) amide groups. The synthesis and the nomenclature of these diamides have been descrived in the previous papers,[2,3] and only their abbreviations are given in the figure. The upper two ligands in Fig. 1 form 5,5,5-membered trifused chelate rings, while the lower ones 5,6,5-type chelate rings. The amide group would coordinate to a metal ion with its carbonyl oxygen. However, when base is added, then the amide group may deprotonate to transform the donor atom into the ionized nitrogen.[6)]

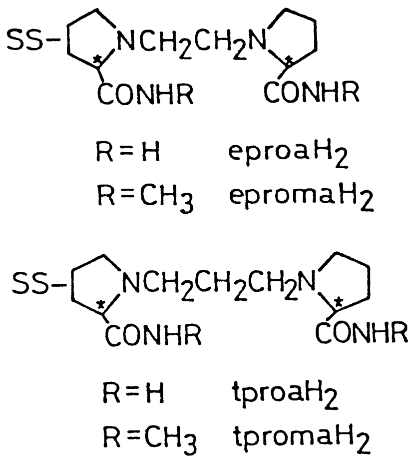


Fig. 1 Optically active quadridentate diamides

Equimolar amounts of each diamide and copper(II) perchlorate were mixed in water, and the solution was evaporated to dryness. The solid was recrystallized from hot water. The elemental analyses for the obtained complexes indicated that they contained two molecules of perchlorate ion as couter ions. Therefore, both of the two amide groups are neutral and they coordinate to the copper(II) ion through the carbonyl oxygen. Such a carbonyl coordination was also clear from the IR spectra; the amide band appeared in the region of 1620-1640 cm^{-1}, but no band around 1600 cm^{-1}.7)

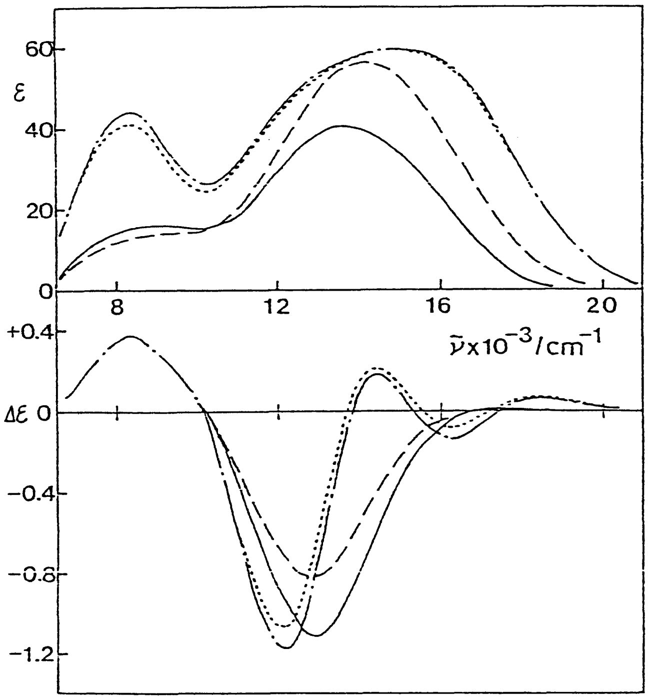


Fig. 2 Absorption and CD spectra in MeOH

———————— $[Cu(eproaH_2)]^{+2}$

—— —— —— $[Cu(epromaH_2)]^{+2}$

———— - ———— $[Cu(tproaH_2)]^{+2}$

- - - - - - - - - - - $[Cu(tpromaH_2)]^{+2}$

Figure 2 shows the absorption and CD spectra of these complexes in the visible-near infrared region. Their absorption shapes, a main band in the region of 14000-16000 cm^{-1} and a side band around 8000 cm^{-1}, were fairly similar to each other. However, these absorption shapes were much different from those usually observed for ordinary square-planar copper(II) complexes, and the magnitudes of their CD bands were much more intense than that of bis(L-proline amide) complex.6) In addition, the complexes of $eproaH_2$ and $epromaH_2$ exhibited very similar CD curves to that of the copper(II) complex of epro, which is an edda-type ligand derived from L-proline.5) Therefore, the complexes containing these two diamides are also expected to take an uns-cis form, in which one carbonyl group coordinates at an apical position as in the case of the epro complex. Similarly, the configuration around the central copper ion is thought to be Λ.5) Also for the complexes of $tproaH_2$ and $tpromaH_2$, the similar geometry is reasonably expected, although their absorption and CD spectra are somewhat different from those of the $eproaH_2$-type complexes with reflecting the difference in the central chelate ring. On the basis of the findings that the $epromaH_2$ complex exhibited almost identical spectra with the $eproaH_2$ complex and the $tpromaH_2$ complex with the $tproaH_2$ complex, the amide N-methyl groups in the $epromaH_2$ and $tpromaH_2$ complexes seem to affect little the complex structure when the amide groups coordinate through the carbonyl oxygen.

When two equivalent molar amounts of sodium methoxide were added to the methanol solutions of these complexes, their absorption and CD spectra entirely changed as shown in Fig. 3. The fact that these spectral changes were completed by the addition of two molar amounts of the base corresponds to the deprotonation from the two amide groups which leads to the transformation of the donor atom from the carbonyl oxygen into the deprotonated nitrogen. This transformation must affect the complex geometries and the electronic states of the copper(II) ion. The absorption band of the tproa8) complex was observed at a fairly high wave number with somewhat increased intensity compared with that of the $tproaH_2$ complex, while the CD magnitude decreased reversely. This spectral change may correspond to the rearrangement of the ligand distribution to a square-planar geometry.

For the tproma complex having two N-methyl groups, on the other hand, the absorption band became very intense and accompanied a shoulder band at 13000 cm^{-1}. This absorption feature is obviously a manifestation typical for the ligand field with a strong apical coordination.[5,9] The most remarkable profile of the CD spectrum of this complex is the extremely intense magnitude of the bands. Probably this CD magnitude is the largest observed for the d-d transitions of discrete copper(II) complexes so far.[10] In the case of the tproma complex, both of the two deprotonated amidate nitrogens can not coordinate simultaneously in the main plane containing two pyrrolidinyl nitrogens because of the steric repulsion between the methyl groups, and then the uns-cis structure in which one of the amidate nitrogens binds at an apical position would be held even after the transformation of the donor atom. Since the coordination through the deprotonated amidate nitrogen is thought to be much stronger than that through the carbonyl oxygen, the two terminal chelate rings asymmetrically-distributed around the copper(II)ion(probably in Λ) may contribute much greatly to the optical activity compared with those containing the carbonyl coordination.

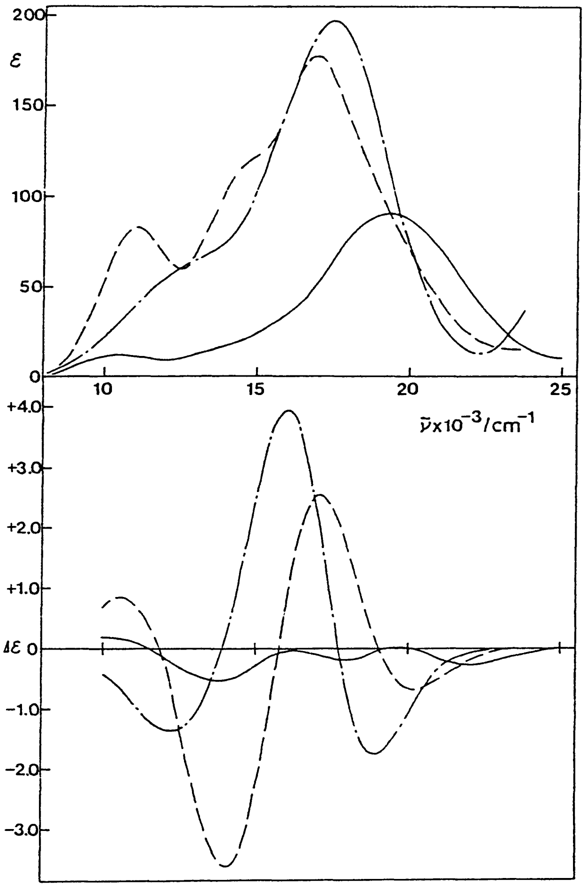


Fig. 3 Absorption and CD spectra in MeOH

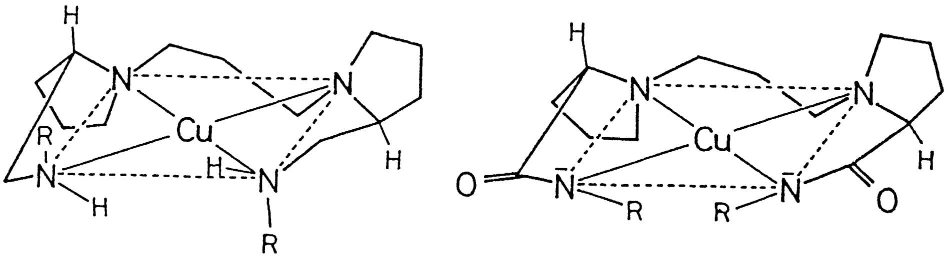
— — — [Cu(eproma)]

——— [Cu(tproa)]

—— - —— [Cu(tproma)]

However, in the copper(II) complexes of the (S)-pyrrolidine-containing tetraamines which form similar 5,6,5-type chelate rings, it has been found that the steric repulsion between terminal N-methyl groups was quite small even for nearly square-planar geometry.[11] This was expected from the fact that the MMPP complex having N-methyl groups exhibited almost identical absorption and ESR spectra with the AMPP complex having no methyl group. As can be seen in Fig. 4a, the two methyl groups in the MMPP complex can be away from each other by orientating to axial, since the terminal two chelate rings are of gauche. On the other hand, the two chelate rings in the tproma complex are nearly planar due to the amidate group and the bonding direction of the deprotonated amidate nitrogen is trigonal-planar. Therefore, the two N-methyl groups would face to each other and the repulsion be very large, if taking a planar geometry shown in Fig. 4b. This may be the reason why tproma still takes an uns-cis form.

Contrary to the case of the tproa and tproma complexes, the absorption and CD spectra(Fig. 3) of the eproma complex were very similar to those of the eproa complex even after the addition of base, which indicates that the base addition causes the same structural conversion despite possessing terminal N-methyl groups or not. Thus,



(a) (b)

Fig. 4 Schematic drawing of planar structures for the MMPP complex(a) and the tproma complex(b).

the ligand skeleton itself, especially the ethylene-linked two (S)-pyrrolidinyl groups, seems to control the specificity on complex formation, as well as in the cases of other similarly-skeletonized quadridentate ligands such as epro and AMPE.5,11) The huge CD magnitude suggests the large asymmetry around the central copper(II) ion just as the tproma complex. However, since the ESR spectra of these complexes with eproa and eproma diamidates were not of axial symmetry, the coordination structure is not confirmed yet.

Thus, the copper(II) complexes containing the ligands in Fig. 1 and their dianions showed very curious spectral behavior, suggesting unusual ligand fields different from ordinary square plane. The details including the findings from ESR and the discussion on the electronic states will be presented soon.

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