

Stereoselective Interactions between Aminoacids and Optically Active β -Diketones in Copper(II) Complexes of Their Schiff Bases

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In the course of our studies¹⁻⁴ on metal complexes with optically active ligands we have synthesized copper(II) complexes of the addition products of α -aminoacids with (+)hydroxymethylenecamphor⁵ (hmc) or (+)hydroxymethylenementhone⁵ (hmm). The general formula of these complexes is N-(+)hydroxymethylidenecamphor- α -aminoacidatocopper(II), (I), and N-(+)hydroxymethylidenementhone- α -aminoacidatocopper(II), (II), where the aminoacidato anions are derived from glycine (gly) and *L* and *D*-phenylalanine (phe).⁶

The molecular nature of these complexes is still under investigation; in particular it is not yet clear whether the organic ligand has an enamine (a), a Schiff base (b) or an intermediate structure (see also ref. 1). Moreover preliminary results seem to suggest a trimeric structure, at least in chloroform, in order to fill the coordination valences of the metal ion.

In this note we wish to report a rather interesting stereoselective interaction between the chiral β -diketones and α -aminoacids in these complexes as it appears from the circular dichroism (c.d.) spectra.

In Figs. 1 and 2 the electronic and c.d. spectra of the complexes in chloroform and pyridine are reported. The main feature of the c.d. spectra is the

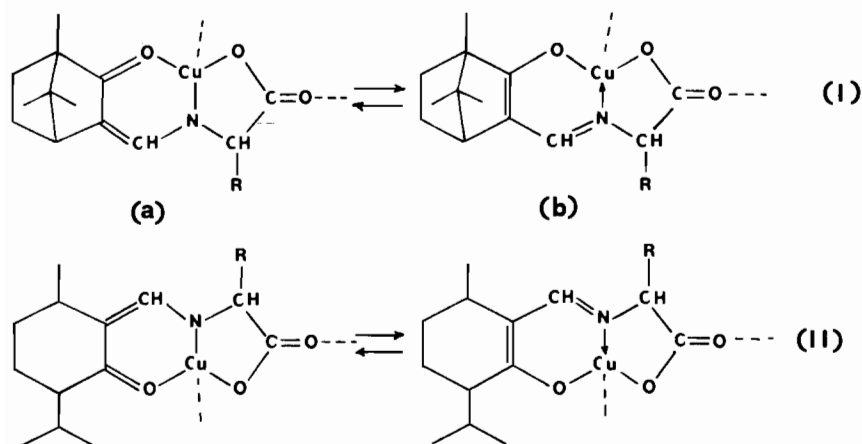
inversion of the Cotton effects passing from *L* to *D*-phe complexes, throughout all the spectral range studied; in other words the pattern of the spectra depends mainly on the absolute configuration of the aminoacid and not on that of the terpenic part of the ligand. Moreover this effect seems to be a general one, since preliminary results show a similar behaviour in the case of *L* and *D*-leucine complexes.

The spectra are not enantiomeric, the diastereoisomerism being shown by the different intensity of the Cotton effects of the *L* and *D*-phe derivatives and not by a difference in shape; this is more evident in the case of the complexes with (+)hmm. The spectra of the glycine derivatives show only a very small optical activity in contrast with the high optical activity usually displayed by the compounds of the type $M[(+)\text{hmc}]_n$,^{3,7} they also often approach the average of the spectra of the *D* and *L*-phe containing compounds.

In the (+)hmc derivatives there is also a solvent effect, causing a change in the shape of the c.d. spectrum of $\text{Cu}[(+)\text{hmc}\cdot L\text{-phe}]$ in pyridine with respect to chloroform in the 400–500 nm region. However this is the only case because the c.d. spectra of $\text{Cu}[(+)\text{hmc}\cdot D\text{-phe}]$ are practically identical in shape and intensity in the two solvents, as in the derivatives of (+)hmm.

Clearly the conformations of the two fused chelate rings are essentially dictated by the chirality of the aminoacid, since the Cotton effects are opposite for the diastereoisomeric ligands derived from the same terpenic part and the enantiomeric aminoacids.

It is known that the five membered chelate ring of an aminoacid is quite rigid⁸ and consequently it is likely that the conformation of the chelate ring of the β -diketone, although fused with the terpenic



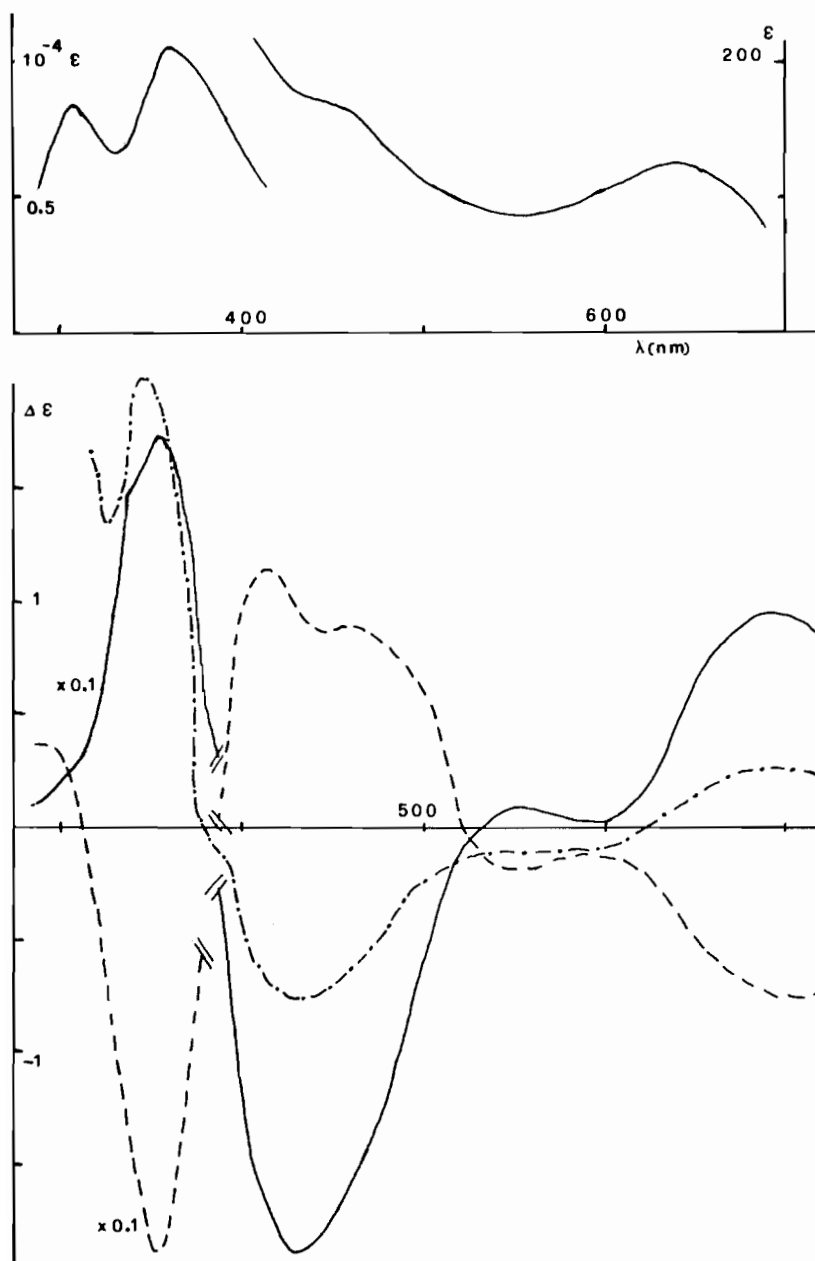


Fig. 1. Electronic and circular dichroism spectra of (+)hydroxymethylidene- α -amino acidato-copper(II) (a) and of (+)hydroxymethylidene-menthone- α -amino acidato-copper(II) (b) in CHCl_3 . The amino acids are: -.-.- gly; --- L-phe and ----D-phe.

ring, is stereoselectively dictated by the chirality of the amino acid. In agreement with this point when the amino acid is not chiral (glycine derivatives) the two fused rings are probably very near planarity,

as the low optical activity of these compounds suggests. The conformational behaviour of the six membered chelate ring of the β -diketone can be related to the enamine-Schiff base equilibrium

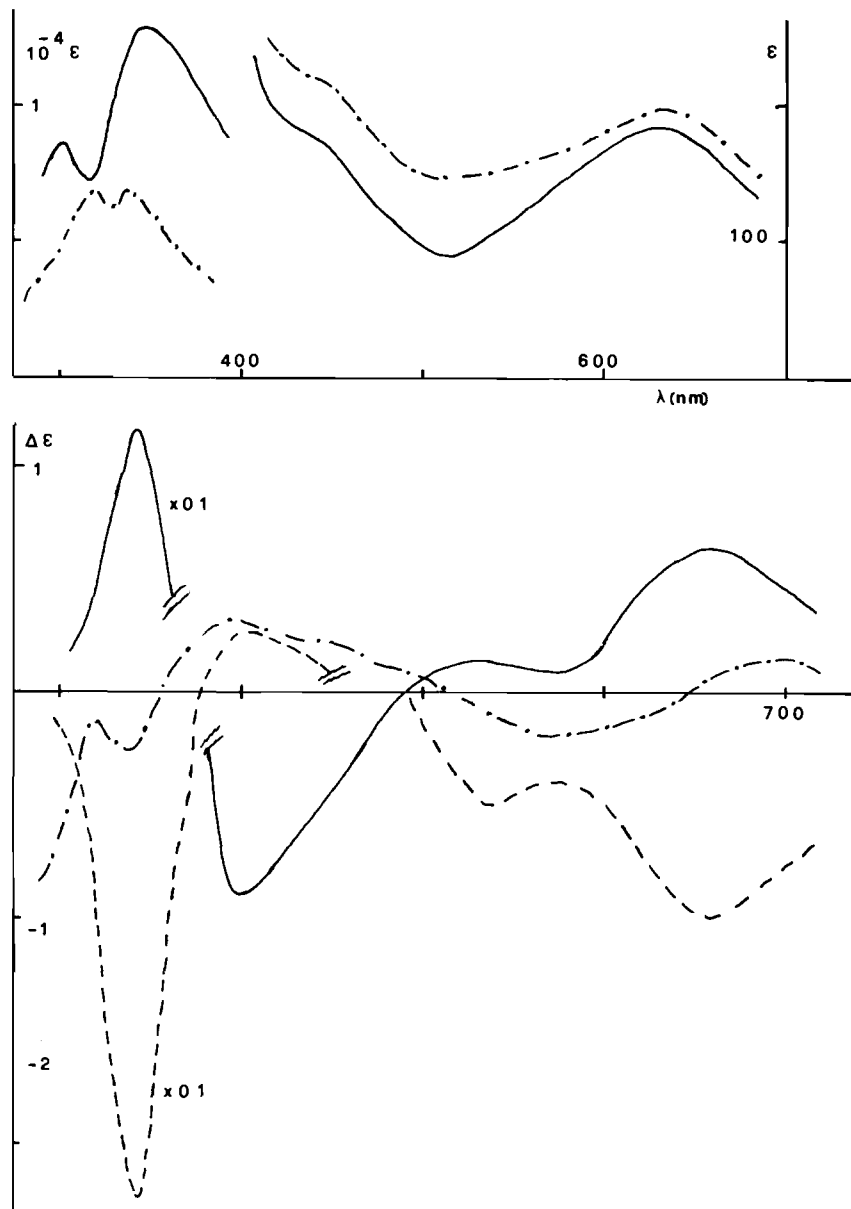


Fig. 1(b). (For caption see page L10)

(a \rightleftharpoons b) which is likely on the basis of previous studies of (+)hmc Schiff bases.¹

We think that the peculiar behaviour described above may be of general interest either in relation to the conformation of fused chelate rings or to the stereoselectivity of the interactions between natural compounds of different chirality.

Acknowledgment

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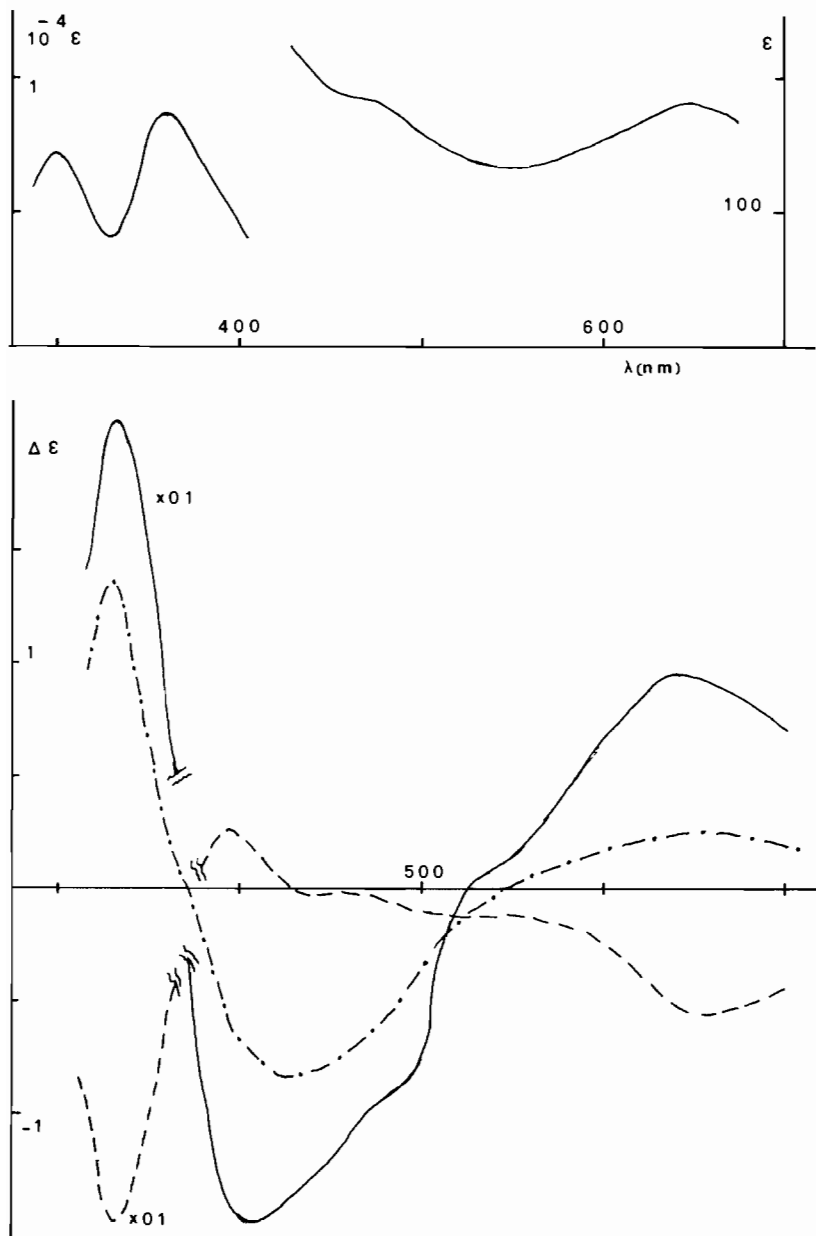


Fig. 2. Electronic and circular dichroism spectra of (+)hydroxymethylenecamphor- α -aminoacidatocopper(II) (a) and of (+)hydroxymethylenementhone- α -aminoacidatocopper(II) (b) in pyridine. The amino acids are: -.-.- gly; --- *L*-phe and ----- *D*-phe.

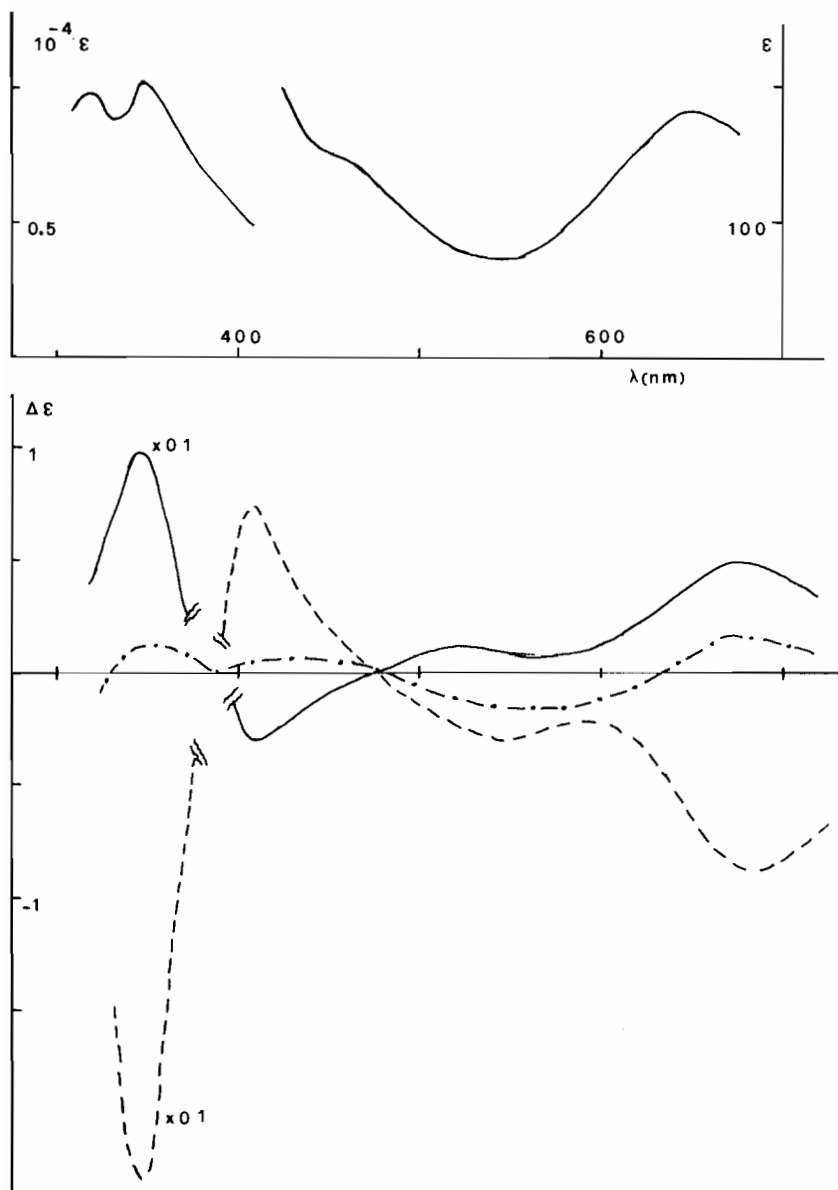


Fig. 2(b). (For caption see page L12)

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