

CHARGE TRANSFER CIRCULAR DICHROISM OF COMPLEXES OF COPPER (II)
WITH AMINOACIDS AND HETEROCYCLIC LIGANDS

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In the u.v. region the C.D. spectra of mixed complexes of Cu (II), aminoacids and heterocyclic ligands depend upon the nature of the heterocyclic ligand, and work on the Cotton effects of bis-L-aminoacidates of Cu (II) in the charge transfer region [1] has now been extended to mixed complexes of Cu (II) with an aminoacid anion and 2,2'-dipyridyl or 1,10-phenanthroline. We also examined the $n \rightarrow \pi^*$ transitions in zinc bis-L-serinate which has no charge transfer band.

Experimental

Mixed complexes of Cu (II) were prepared by the method of Dutta and Dé [2], and zinc bis-L-serinate was prepared from $Zn(OH)_2$ [3]. (Other zinc complexes were found to hydrolyze rapidly.) C.D. spectra were run on a Cary 60 spectropolarimeter, generally with 10^{-4} M solutions in 1 mm cells.

Results and Discussion

The mixed complexes of Cu (II) show three C.D. peaks in the range 350-200 nm, irrespective of the nature of the nonactive ligand (Table 1 and Figure 1). At $\lambda < 240$ nm the two bands of the mixed complexes have opposite signs, whereas

TABLE I

Circular Dichroism Bands of Complexes of Cu (II) with Mixed Ligands^a

Compounds	Band I		Band II		Band III	
	λ_{CD} nm	$\Delta\epsilon$	λ_{CD} nm	$\Delta\epsilon$	λ_{CD} nm	$\Delta\epsilon$
[Cu dip ala]Cl.H ₂ O	240	-0.9	220	+1.0	205	-0.7
[Cu dip ser]Cl.H ₂ O	265	-0.5	220	+1.5	<205	~ -2.2
[Cu dip val]Cl.3H ₂ O	265	-1.0	220	+2.4	<205	~ -2.3
[Cu dip threo]Cl.3H ₂ O	265	-2.0	220	+1.6	<210	~ -2.7
[Cu phen ala]Cl.3H ₂ O	252	-1.1	235	+2.6	220	-2.7
[Cu phen ser]Cl.H ₂ O	255	-1.0	235	+1.2	<220	~ -2.0
[Cu phen val]Cl.2H ₂ O	255	-1.5	235	+2.3	220	-2.1
[Cu phen threo]Cl.3H ₂ O	255	-1.5	235	+1.7	220	-1.9
[Cu threo ₂]H ₂ O ^b	257	-2.9	(217)	(+1.4)	205	+3.8
[Cu isoleu ₂]H ₂ O ^b	255	-2.1	(225)	(+2.0)	205	+5.7
Zn ser ₂					215	-1.3

(a) $\Delta\epsilon$ is the difference of the molar extinction coefficients of right and left handed circularly polarized light. dip \equiv 2,2' dipyridyl; phen \equiv 1, 10 phenanthroline; ala \equiv L-alanine; ser \equiv L-serine; val \equiv L-valine; threo \equiv L-threonine; isoleu \equiv L-isoleucine. (b) From ref 1; values in parentheses correspond to shoulders.

those of the bis-complexes have the same sign. Band I has similar λ and the same sign as the lower energy charge transfer band of Cu (II) bisaminoacidates [1]. At shorter wavelength the C.D. spectra differ in that the mixed complexes have bands II and III of opposite sign whereas in the bis-aminoacidates the bands are not resolved, but there is a shoulder at approximately the wavelength of Band II (Cu(II)bis-L-serinate has three C.D. bands [1], but unlike the other complexes it has cis-geometry [4]). Protonated [5] and coordinated [1] amino acids have low intensity $n \rightarrow \pi^*$ transitions at 210-215 nm, which could

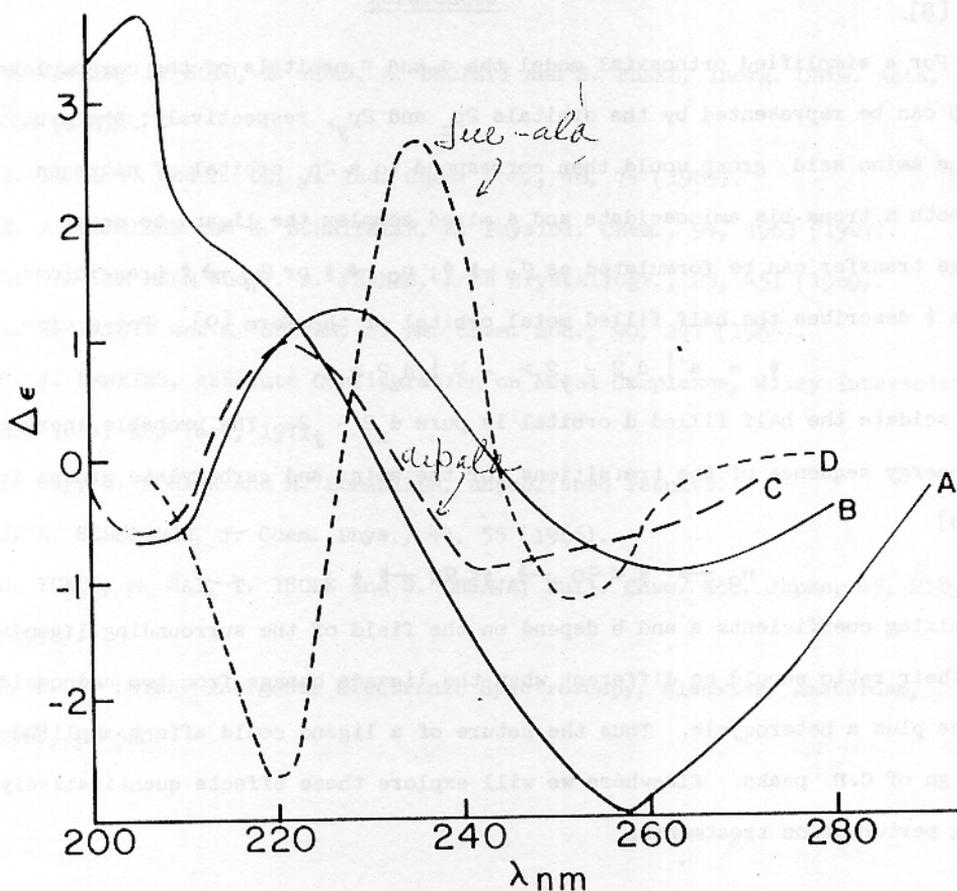


Figure 1. C.D. spectra of: A, $[\text{Cu}(\text{L-threo})_2]\text{H}_2\text{O}$; B, $\text{Cu}(\text{L-ser})_2$; C, $[\text{Cu dip L-ala}]\text{Cl}\cdot\text{H}_2\text{O}$; D, $[\text{Cu phen L-ala}]\text{Cl}\cdot 3\text{H}_2\text{O}$.

contribute with charge transfer transitions to the observed C.D. spectra.

There are no Cotton effects under the first absorption bands of dipyriddy and phenanthroline at 300 and 275 nm respectively. (The mixed complexes show strong absorptions at the wavelengths of the heterocyclic ligands, with a minimum at approximately 270 nm for the dipyriddy and 260 nm for the phenanthroline complex, and a broad band at lower wavelengths.) The heterocyclic ligands probably do not markedly perturb the distorted octahedral structure of the mixed complexes [6] because the visible absorption bands of both types of complex are very similar [7]. The C.D. bands for both the bis- and the mixed

complexes span similar wavelengths so the different Cotton effects probably depend on differences in symmetry rather than in energy levels. In the bis-aminoacidates the charge transfer transitions are electrically allowed and magnetically forbidden, and the rotatory strength derives from the mixing of the states with the d-d states perturbed by the asymmetric carbon of the amino acid [8].

For a simplified orthoaxial model the σ and π orbitals of the carboxylate group can be represented by the orbitals $2p_z$ and $2p_y$, respectively; the orbital of the amino acid group would then correspond to a $2p_z$ orbital of nitrogen. For both a trans-bis aminoacidate and a mixed complex the ligand to metal charge transfer can be formulated as $\sigma_O \rightarrow \psi$; $\pi_O \rightarrow \psi$ or $\sigma_N \rightarrow \psi$ transitions, where ψ describes the half filled metal orbital of the form [9]. For a cis-

$$\psi = a \left| d_x^2 - y^2 \right\rangle - b \left| d_z^2 \right\rangle$$

aminoacidate the half filled d orbital is pure $d_x^2 - y^2$. The probable increasing energy sequence of the transitions for the amino and carboxylate groups is: [1,10]



The mixing coefficients a and b depend on the field of the surrounding ligands, and their ratio should be different when the ligands change from two aminoacids to one plus a heterocycle. Thus the nature of a ligand could affect amplitude or sign of C.D. peaks. Elsewhere we will explore these effects quantitatively using perturbation treatments.

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