

INDUCED DISTANT COTTON EFFECTS IN AN AROMATIC CHROMOPHORE
IN MIXED AMINOACIDATES OF COPPER (II)

S. Bunel, C. Ibarra and A. Urbana
Departamento de Química Inorgánica y Analítica
Facultad de Ciencias Químicas
Universidad de Chile, Santiago, Chile

and

C. A. Bunton
Department of Chemistry
University of California
Santa Barbara, California, 93106, U.S.A.

Chiral amino acids bonded to copper (II) induce Cotton effects in the visible and UV regions corresponding to d-d and charge transfer transitions [1, 2] but an induced Cotton effect on a distant ligand has not been observed to date. We have now observed such an effect with mixed complexes of copper (II) with L- and D-proline (pro) and 2,2'-dipyridyl (dip) or 1,10-phenanthroline (phen), 1 and 2, respectively, in the UV region (Fig. 1).

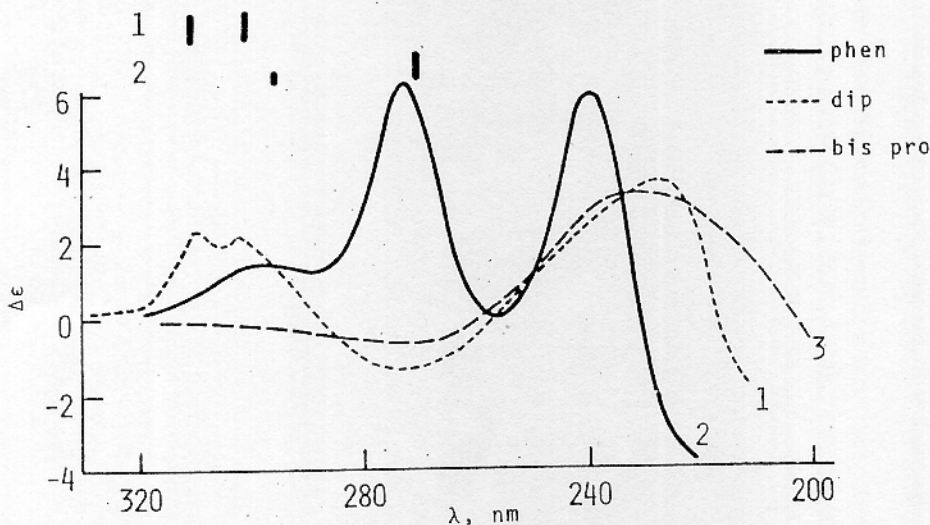


Fig. 1. C.D. spectra of $[\text{Cu dip-L-pro}]^+$ (1), $[\text{Cu phen-L-pro}]^+$ (2) and $[\text{Cu-L-pro}_2]$ (3). The vertical bars indicate absorbance maxima or shoulders of the mixed complexes in the aromatic region.

The circular dichroism (C.D.) spectra are compared with those of copper bis-L-prolinate (3)* which are very similar to those of other bis-L-aminoacidates [4] having a positive band at 235 nm, and negative bands at 275 nm and <205 nm. The bis-prolinates show a small red shift compared to the other bis-aminoacidates.

Both $[\text{Cu dip-L-pro}]^+$ (1) and $[\text{Cu phen-L-pro}]^+$ (2) show strong positive C.D. bands at 310 and 275 nm respectively, in the region of the ${}^1A_1 \rightarrow {}^1B_1$ transitions of the heterocyclic diamines and $[\text{Cu dip-L-pro}]^+$ also shows the C.D. bands due to charge transfer and $n \rightarrow \pi^*$ transitions which are characteristic of aminoacidates [5, 6]. However with $[\text{Cu phen-L-pro}]^+$ the negative C.D. band at ca. 275 nm is obscured by the strong positive band due to the ${}^1A_1 \rightarrow {}^1B_1$ transition of 1,10-phenanthroline.

The C.D. spectra of these three complexes in the visible region (Fig. 2) are very similar and agree with those reported earlier for $[\text{Cu-L-pro}_2]$ and $[\text{Cu phen-L-pro}]^+$ [7]. These C.D. spectra correspond to the broad absorbance maxima at ca. 600 nm due to d-d transitions [2].

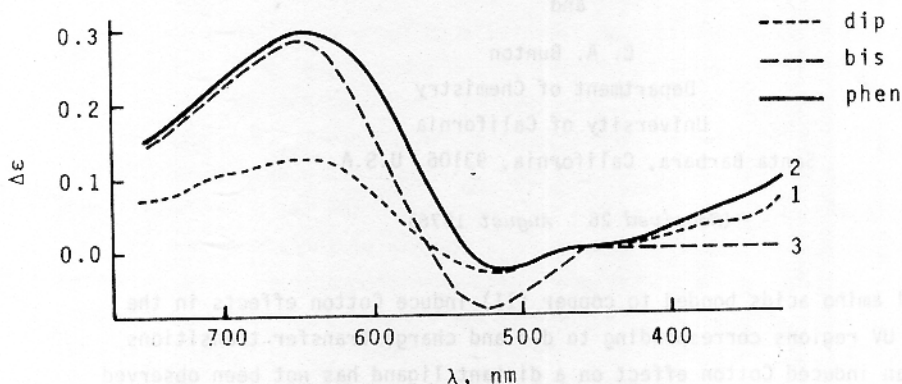


Fig. 2. C.D. spectra of $[\text{Cu dip-L-pro}]^+$ (1), $[\text{Cu phen-L-pro}]^+$ (2) and $[\text{Cu-L-pro}_2]$ (3) in the visible region.

DISCUSSION

The proline complexes differ from those of the other aminoacids in several respects. The rigidity of proline influences their conformations, and chelation introduces chirality into the proline amino group, and in addition there are strong nonbonded interactions between the hydrogen atoms at the 5 position of proline and the 6,6' and 2,9 positions of dipyriddy and phenanthroline respectively. Inspection of molecular models suggests that these interactions may force the chiral amino group of proline out of coplanarity about the central copper atom.

*The copper bis-DL-prolinate has trans-geometry [3].

The ${}^1A_1 \rightarrow {}^1B_1$ transition of dipyriddyI at ca. 305 nm is polarized along the principal axis of the organic chromophore. We see a splitting in this positive C.D. band of 1, which is probably due to vibrational interactions [8]. This splitting is also evident in the absorbance spectra of 1, and appears to be typical of bipyridyl complexes [9, 10]. In the phenanthroline complex (2) the ${}^1A_1 \rightarrow {}^1B_1$ transitions which generate the p and p' bands are also polarized along the principal axis and we see a positive C.D. maximum at 272 nm and a shoulder at 295 nm corresponding to these bands in the absorbance spectra (Fig. 1).

Induction of rotatory strength to the $\pi \rightarrow \pi^*$ transitions of the heterocyclic ligands can be explained qualitatively in terms of Kirkwood's coupled oscillator model [11]. For the electrically allowed $\pi \rightarrow \pi^*$ transitions to become optically active they must couple with other electrically allowed transitions. The most probable contributors are the electrically allowed charge transfer transitions, $\sigma_N \rightarrow 3d_{Cu}$ and $\sigma_O \rightarrow 3d_{Cu}$ which have their electric moments directed along the bands but can couple with the ${}^1A_1 \rightarrow {}^1B_1$ transitions of the heterocyclic ligands if the electric moments of the $\pi \rightarrow \pi^*$ and charge transfer transitions are not coplanar. This condition appears to be satisfied in the mixed proline complexes, but not in the complexes of other aminoacids examined to date [5].

EXPERIMENTAL

The complexes were prepared by standard methods [12]. The C.D. spectra were run in water at 27° on a Cary 60 spectropolarimeter with a C.D. attachment using $3 \times 10^{-3} - 10^{-2}$ M solutions in a 1 cm cell in the visible region and $10^{-4} - 10^{-3}$ M in a 0.1 cm cell in the UV. Good agreement was observed using different concentrations, and although we only show the C.D. spectra of the L-complexes in Figs. 1 and 2, the spectra of the D-complexes were their mirror images within experimental error.

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