Detection of Cross-plane Steric Interactions in Dissymmetric Copper(II) Complexes by Circular Dichroism Spectra[1]

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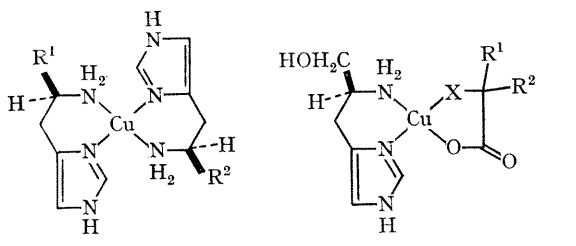
Summary Cross-plane steric interactions have been detected in copper(II)–L-histidinol complexes using circular dichroism spectroscopy.

CROSS-PLANE steric and electronic interactions between ligands and ligand-field changes have small or negligible effects on the rotational strength of a *d–d* transition in bis(amino-acid)–copper(II) complexes. This interesting observation holds for the cases when the amino-acid side-chain is methyl, ethyl, n-propyl, isopropyl, and phenyl. The ligand-field changes were effected by varying the cross-plane mixing ligand of the 1 : 1 : 1 copper–mixing ligand–amino-acid complexes to include glycine, oxalate, and ethylenediamine.[2] Because of the intimate relationship between molecular geometry, chromophoric symmetry, and observed rotational strengths,[3] the observed additive contribution of each chiral chelate ring indicates minor steric interactions between the rings. On the other hand, when cross-plane steric and electronic effects are not small or negligible, the resulting interactions can expect to manifest themselves in the *d–d* band circular dichroism (c.d.) spectrum, although such effects have not yet been reported. We present results here which indicate that serious cross-plane interactions do exist in the bis-(L-histidinol) copper(II) complex, and these interactions (or their absence) have dramatic effects on the c.d. spectra of the mixed copper(II) complexes of L-histidinol.

We have measured[4] the position of the mixing equilibrium

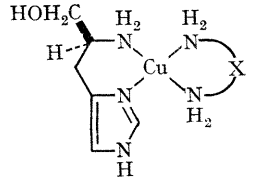
$$Cu(glycine)_2 + Cu(L)_2 \overset{K}{\leftrightharpoons} 2\,Cu(glycine)\,(L)$$

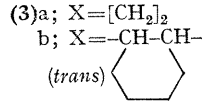
for a variety of ligands (L) including simple amino-acids and ethylenediamines and have found the concentration equilibrium constant to be 4—6. In striking contrast, when L is L-histidinol, $K > 1000$. It is likely that the driving force favouring the mixed complex in this latter case is a serious $NH_2 \longleftrightarrow$ imidazolyl interaction in (1a) which is replaced by a less severe O $\longleftrightarrow$ imidazolyl interaction in the mixed complex (2a).



(**1**)a; R^1, R^2=CH_2OH
b; R^1=CH_2OH, R^2=H

(**2**)a; X=NH_2, R^1=R^2=H
b; X=O, R^1R^2=O





(**3**)a; X=$[CH_2]_2$
b; X=–CH–CH– (*trans*)

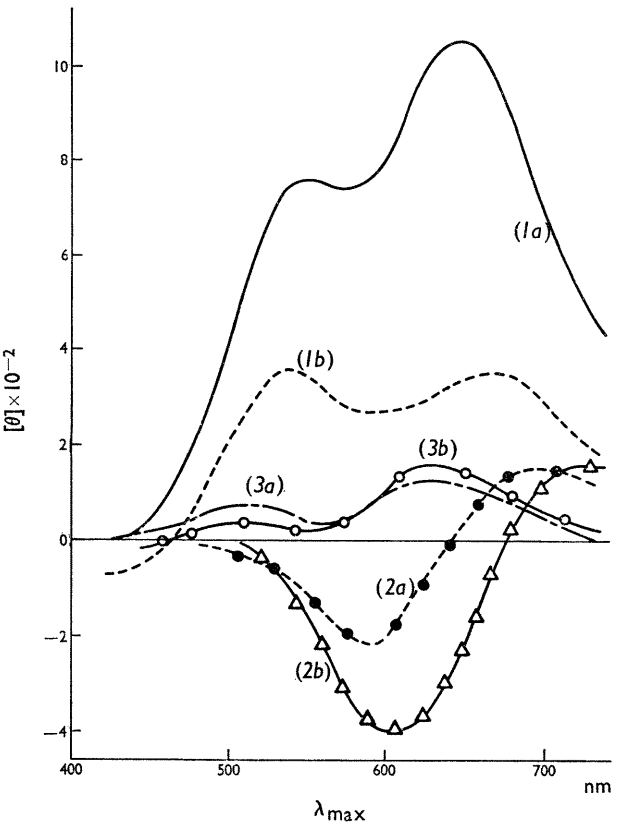


FIGURE. *Circular dichroism spectra of several copper(II) complexes of* L-*histidinol* (*see text*). *Concentrations are* ca. 2 × 10^{-3} M *in complex*, pH 8·3

The c.d. spectra for a number of L-histidinol–copper(II) complexes are shown in the Figure.† In the case of the parent 2 : 1 bis-histidinol complex (1a), positive maxima appear at 540 and 640 nm. The 1 : 1 : 1 mixed complex (1b) derived from *in situ* mixing of the bis-complexes of histamine and L-histidinol would be expected to have cross-plane steric and electronic interactions similar to that of the parent 2 : 1 complex. Accordingly, the structural similarities between (1a) and (1b) are reflected in similar c.d. spectra [see (1a) and (1b) in Figure]. The reduced

† Spectra were determined using a JASCO ORD/CD/UV-15 instrument with a spectral scan 190—815 nm.; the slit width was maintained at 0·6 mm. or less in the regions of interest. Cell lengths were varied to keep the photomultiplier voltage below 0·5 kv. Solutions of the complexes were prepared according to ref. 2 above.

rotational strength for (1b) is expected[2] as a result of replacing one of the chiral L-histidinol ligands of the parent complex by the achiral, but structurally similar, histamine ligand. The mixed complexes (3a) and (3b), involving the mixing ligands ethylenediamine and (±)-*trans*-1,2-diaminocyclohexane, have a single in-plane $NH_2 \longleftrightarrow$ imidazolyl interaction formally similar to that in the parent **2:1** complex, but the flexible geometric requirements of the ethylenediamine groupings will place reduced restraints on the L-histidinol chelate as compared to either (1a) or (1b). This reduced strain is illustrated by a greatly reduced rotational strength of (3a,b) as compared with (1a,b). The most striking c.d. changes occur when the mixing ligand is glycine (see 2a) or oxalate (see 2b). In these cases the steric interaction between the co-ordinating oxygen and the imidazolyl group will be greatly reduced compared with the complexes (1) and (3), and this difference reflects itself most strikingly in the short-wavelength band which actually inverts in sign [see (2a,b) in Figure]. The positions of the opposite-sign, overlapping bands are a function of the parent band widths, amplitudes, and wavelength positions.[5]

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