ORIGIN OF CHIRALITY IN CHARGE TRANSFER BANDS OF Cu(II) ACIDATES

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Abstract—Complexes of Cu(II) with L-aminoacids have positive charge transfer bands in their CD spectra at *ca.* 230 nm and negative at *ca.* 270 nm. Examination of complexes with L-malic acid or L-1,2-diamino propane shows that the positive band is due to charge transfer from nitrogen and the negative from oxygen to copper. This sign difference is consistent with a theoretical model. The effects of added nonchiral ligands on the CD spectra in the charge transfer region are analyzed.

INTRODUCTION

Mono-and bis-aminoacidates of Cu(II) typically have three bands in their circular dichroism (CD) spectra in the UV region. The lowest wavelength band, in the region of 190 nm, is negative for L-aminoacidates and is ascribed to $n \rightarrow \pi^*$ transitions of the carboxylate group [1–6]. It is present also in Zn(II) aminoacidates and in the aminoacids, where it has the opposite sign to that of the complexes. The other two bands, which for Cu(II) L-aminoacidates are at *ca.* 230 nm (positive) and *ca.* 270 nm (negative) are ascribed to charge transfer (CT) transitions and are absent in the zinc complexes [4]. Because of the role of metal protein interactions in enzymology it would be useful to distinguish between charge transfers to Cu(II) from nitrogen and oxygen.

The pattern is more complicated for mixed complexes of Cu(II) with aminoacids and mono- or bidendate ligands. For example, mixed complexes involving 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) and L-aspartate (asp) or prolinate (pro) have strong positive CD bands in the region of the aromatic chromophore which may partially obscure any negative CT band (7–9]. We have examined a number of amino acidates and mixed complexes of Cu(II) in order to rationalize these observations and permit assignment of the CT bands. We also examined Cu(II) L-malates [10].

The types of complexes studied are Cu-L-asp X; where X = asp, glycinate (gly), oxalate (ox), phen, bipy, 1,2-diaminoethane (en), 1,2-diamino propane (pen), histamine (hist), imidazole (imid). Cu L-pro X; where X = phen, bipy. Cu L-mal phen (where mal denotes the formally trinegative ion). Cu $(L\text{-pen})_n$, $n = 1,2$.

In some cases we used both L- and D- aminoacids.

The key to the ligands is shown in Scheme 1.

EXPERIMENTAL

Materials. Preparations of the aspartates and prolinates and their mixed complexes with phen and bipy have been described, as have those of Cu-L-mal and Cu L-mal phen [3,4,7–9,11].

Mixed aspartates with en or pen. A solution of the organic base (1 mmole in 20 ml EtOH) was added to a well stirred suspension of Cu asp in 50 ml EtOH. The monoaspartate dissolved, the solution became deep blue, and after partial evaporation of the solvent crystals were isolated by centrifugation and dried *in vacuo.*

Mixed aspartates with imid or hist. The procedure was that described above except that Cu asp was suspended in H_2O and an excess of imidazole was used.

Mixed aspartate-glycinate. Solid Cu L-asp was added to an equivalent amount of aqueous sodium glycinate. The solution was concentrated and the mixed complex was crystallized by addition of EtOH.

Microanalyses of the new complexes are in Table 1.

In a few cases we did not attempt to isolate the complexes but added an equivalent amount of the ligand to Cu^{2+} or its monacidate in solution. This method was used with: Cu en^{2+}, Cu en_2^{2+}, Cu L-asp en, Cu L-asp ox^{2-}, Cu L-mal en^-.

Spectrophotometry. The methods and conditions have been described [9]. Sonication was used to dissolve Cu asp for spectrophotometry and in the preparation of mixed complexes *in situ.*

We performed several experiments in order to determine the position of the CT band ($\sigma_o \rightarrow Cu$) from an alkoxide group. Methanolic solutions of 1,2—ethanediol and $Cu(NO_3)_2$ or $CuSO_4$ or $CuCl_2$ were mixed and dil. NaOH was added until a slight ppte formed. The filtered solutions had peaks or shoulders in their absorption spectra at 250–270 nm. In another experiment the solvent was iPrOH + iPrONa and a peak was observed at *ca.* 250 nm.

With some of the complexes, especially those containing aromatic ligands, the absorbance was too high for us to determine λ max for the CD band of the $n \rightarrow \pi^*$ transition of the carboxylate group, but where this transition was observed λ max was *ca.* 200 nm and the sign was negative for the L-acidates.

A number of the mixed aspartates were prepared from both L- and D- acid and whenever this was done the absorbance and CD bands were at very similar wavelengths and were of opposite sign. The values of $\Delta\varepsilon$ generally agreed, except where the signal to noise ratio was low because of the high absorbance of the complex. Generally, experiments with L- and D- complexes were run sequentially and any base line shift then amplifies the error.

RESULTS

The values of ε and $\Delta\varepsilon$ and positions of the maxima in the absorption and CD spectra (cm^{-1}) are given in Table

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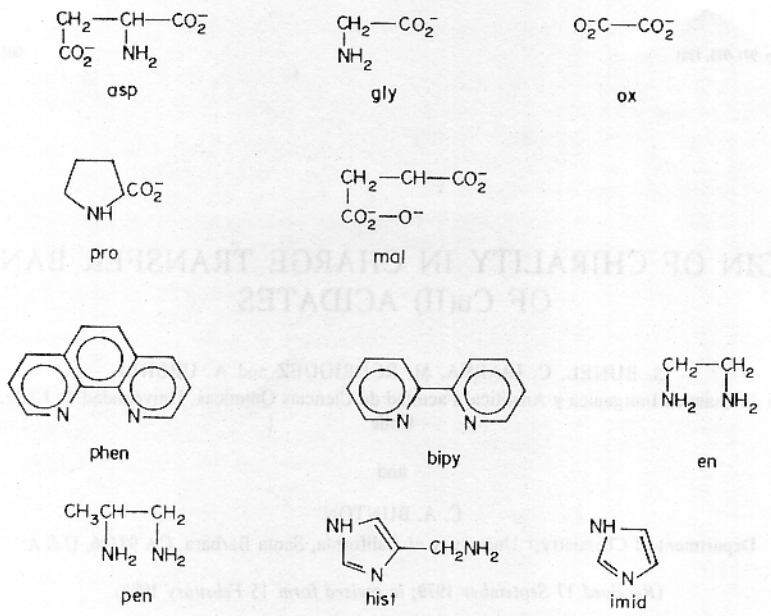

Scheme 1.

Table 1. Analyses of copper compounds

Complex	C Found	C Calc	H Found	H Calc	N Found	N Calc	Cu Found	Cu Calc
Cu(L-asp)$_2$Na$_2$.2H$_2$O	23.7	23.6	3.7	3.5	6.8	6.9	15.4	15.6
Cu(D-asp)$_2$Na$_2$.2H$_2$O	23.3		3.5		6.7		15.2	
Cu L-asp.en.2H$_2$O	24.9	24.8	5.8	5.9	14.5	14.5	22.0	21.9
Cu D-asp en.2H$_2$O	25.0		5.9		14.7		22.2	
Cu L-asp pen.H$_2$O	29.05	29.3	6.0	5.9	14.6	14.7	22.2	22.2
Cu D-asp pen.H$_2$O	29.6		5.7		14.5		22.4	
Cu L-asp hist. 0.5 H$_2$O	34.8	34.4	4.7	4.7	17.8	17.8	19.6	20.2
Cu L-asp imid.H$_2$O	29.8	30.0	3.6	3.9	15.5	15.0	22.1	22.6
Cu L-asp gly Na.2H$_2$O	21.6	22.0	3.6	4.0	8.5	8.6	19.8	19.4

2 for those complexes for which we examined both enantiomers or where the spectra are not shown in the figures.

Aminoacidates and effects of achiral acids

The CD spectra of Cu asp, Cu asp$_2^{2-}$ and Cu pro$_2$ (Fig. 1 and Table 2) are similar to those of other aminoacidates which have CT and $n \rightarrow \pi^*$ transitions [3–5,7]. Mixed complexes of the aspartate with gly or ox anions behave similarly (Table 2). Replacement of second aspartate in Cu asp$_2^{2-}$ by a nonchiral aminoacidate, such as glycinate, decreases $\Delta\varepsilon$ only slightly, whereas replacement by the bidentate oxalate ion approximately halves $\Delta\varepsilon$ for both the positive and negative CT bands (Table 2). (The positive and negative CD bands are close enough to overlap and this overlap complicates discussion of the magnitude of $\Delta\varepsilon$).

Mixed complexes of aspartate and basic amines

The expected negative CT band of the L-aspartates at *ca.* 38,000 cm^{-1} (260 nm) is small or absent in the CD spectra of mixed complexes with such basic amines as en, pen, hist or imid (Fig. 2, Table 2).

The hist, pen and imid mixed complexes with asp may be mixtures of isomers, but nonetheless the main spectral features are similar for all these mixed complexes which contain basic amines, and the behavior is very different from that of the simple aminoacidates, or of the mixed complex with bipy (Figs. 1 and 3.) Inspection of Figs. 1–3 shows that a broad, positive CD band above 37,000 cm^{-1} could overlap and obscure a negative CD band in the mixed complex containing en, pen, hist or imid.

Mixed complexes with weakly basic amines

Both the L-asp and L-pro complexes of Cu(II) with bipy and the L-asp phen complex show a negative CD band at 36,000–39,000 cm^{-1} (280–255 nm) and a positive band at 42,000–44,000 cm^{-1} (238–227 nm) and in this respect they are similar to the bis-aminoacidates (Figs. 1 and 3). However in the pro phen complex this negative

Table 2. Absorption and CD spectra in the charge transfer and $n \rightarrow \pi^*$ regions

Ligands	Absorption		CD					
	$10^{-3}\nu$	$10^{-3}\varepsilon$	$10^{-3}\nu_1$	$\Delta\varepsilon$	$10^{-3}\nu_2$	$\Delta\varepsilon$	$10^{-3}\nu_3$	$\Delta\varepsilon$
L-asp	44	4.1	38	−0.2	44	+0.5	> 49	−ve
D-asp	44	3.4	38	+0.2	45	−0.6		
$(L\text{-asp})_2$	45	3.2	38	−0.6	45	+0.7	> 50	−ve
$(D\text{-asp})_2$	43	2.8	38	+0.6	46	−0.7		
L-asp bipy	43	13.4	35	−0.6	43	+1.7		
D-asp bipy	43	14.4	35	+1.0	43	−2.1		
L-asp en	43	5.5			43	+1.1	49	−2.8
D-asp en	43	5.2			44	−0.7	49	+2.4
L-asp pen	43	5.5			43	+1.8	49	−3.1
D-asp pen	43	5.5			43	−1.6		
L-asp ox	42	2.9	38	−0.23	44	+0.2		
L-asp gly	44	3.9	37	−0.42	44	+0.5	> 49	−ve

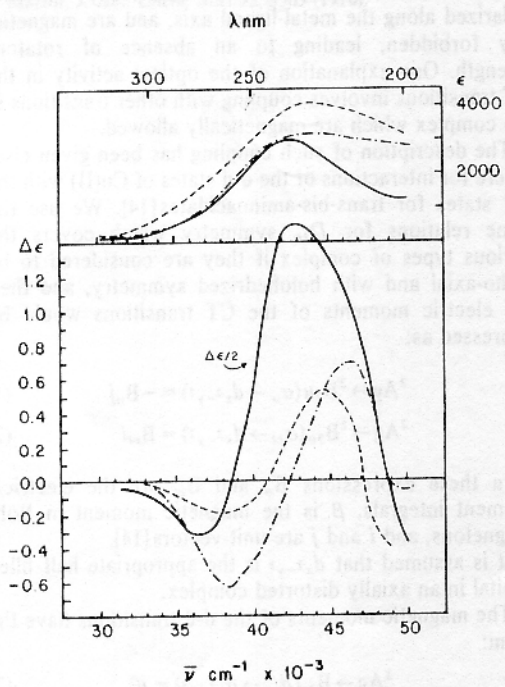

Fig. 1. Absorption and CD spectra of Cu–L–asp, ---; Cu–$(L\text{–asp})_2^{2-}$ –·–·–; and $Cu(L\text{–pro}_2)$ ——.

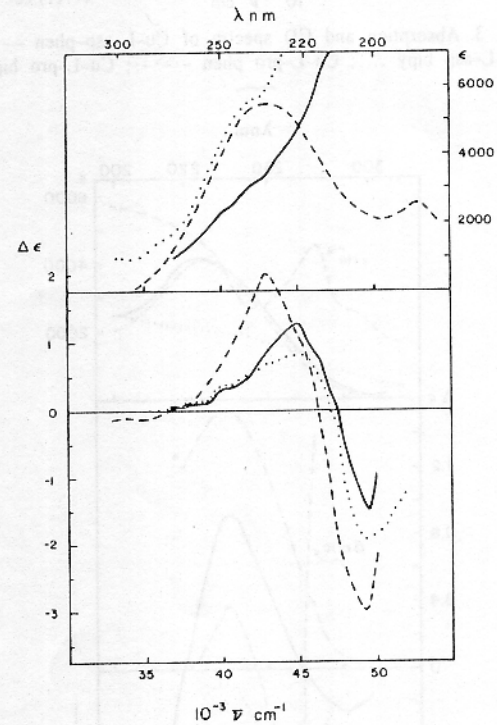

Fig. 2. Absorption and CD spectra of Cu–L–asp–pen ---; Cu L–asp–hist ....; Cu–L–asp imid ——.

band is obscured by the strong positive CD band associated with the aromatic chromophore [7,9].

Malate and mixed malate complexes

The CD spectra of these complexes show some distinctive features, e.g. Cu–L–mal^- has no positive CD band at 41,000 cm^{-1} (244 nm), but this band appears whenever a nitrogen containing ligand is present (Fig. 4), and it is especially strong for Cu–L–pen^{2+}. However the negative CT band at 35,000–39,000 cm^{-1} is present in all the malate complexes, and in other complexes it appears only when an oxygen containing ligand is present.

These observations suggest that the negative CD band in the L-acidates can be ascribed to charge transfer from oxygen, (alkoxide or carboxylate), and the positive CD band to charge transfer from nitrogen. This hypothesis is supported by observation of a positive CD band at 43,000 cm^{-1} (233 nm) in Cu–L–pen^{2+} (Fig. 4). This band is also present in the CD spectrum of Cu $(L\text{-pen})_2^{2+}$, but here geometrical isomers may be present.

DISCUSSION

The experimental evidence allows assignment of the CD bands in the CT region. In some complexes, e.g.

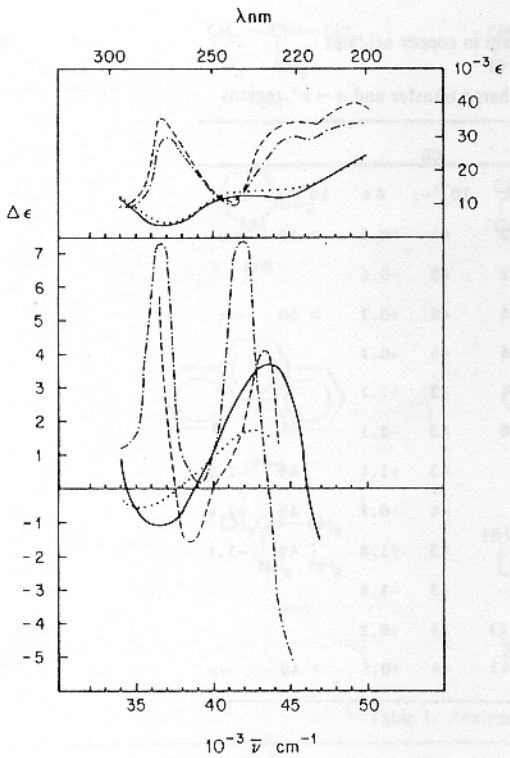

Fig. 3. Absorption and CD spectra of Cu–L–asp–phen ---; Cu–L–asp bipy ....; Cu–L–pro phen -·-·-·; Cu–L–pro bipy ——.

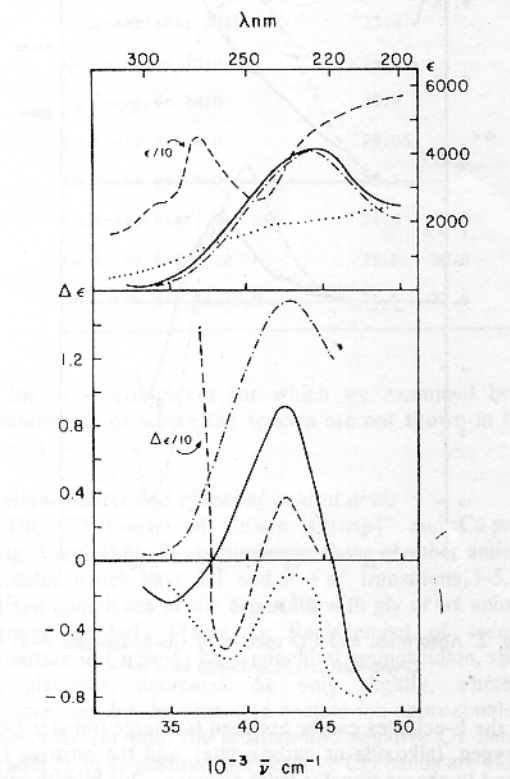

Fig. 4. Absorption and CD spectra of Cu-L-malate$^{=}$ ....; Cu–L–mal phen$^{=}$ ---; Cu–L–mal en$^{=}$ ——; Cu–L–pen^{2+} -·-·-·.

†Here ψ_{3d} describes the partially filled metal orbital and corresponds to $3d_{z^2}$ or $3d_{x^2-y^2}$, depending upon the extent of distortion of the complex[14].

Cu–L–mal en and Cu–L–mal phen the chiral acidate induces activity into the positive CT band due to $\sigma_N \rightarrow$ Cu (Induction of chirality into π–π^* transition of aromatic ligands is discussed elsewhere[9]).

For the aspartates the relative intensities of the positive CD bands in the CT region generally follows the extinction coefficients, (Table 2 and Figs. 1–3), but the intensity of the corresponding CD bands of the bis-prolinate is stronger than expected on this basis. The negative band is correspondingly weaker, because of overlapping of the two opposing bands. These differences almost certainly reflect the presence of the additional asymmetric center formed by coordination of the secondary amino group of proline.

The geometries of some of the bis-acidates are not known, but Cu(II) bis DL-prolinate has trans-geometry[12] as has the bis-hydrogen malate which has the β-carboxylate moiety in the apical position[10], suggesting that malates and aspartates of Cu(II) have similar geometries, and there is no reason to believe that geometrical isomerism is playing a major role in these charge transfer regions.

Models for charge transfer CD[13]

Our experimental evidence assigns the higher energy band, which is positive for L-aminoacidates, to $\sigma_N \rightarrow \psi_{3d}$.†

If we regard the orbitals σ_N and σ_o as having pure p character the transitions are electrically allowed, polarized along the metal-ligand axis, and are magnetically forbidden, leading to an absence of rotatory strength. One explanation of the optical activity in the CT transitions involves coupling with other transitions in the complex which are magnetically allowed.

The description of such coupling has been given elsewhere for interactions of the d-d states of Cu(II) with the CT states for trans-bis-aminoacidates[14]. We use the same relations for D_{2h} symmetry which covers the various types of complex if they are considered to be ortho-axial and with holohedrized symmetry, and then the electric moments of the CT transitions would be expressed as:

$$^2\mathrm{Ag} \rightarrow {}^2\mathrm{B}_{2u}(\sigma_o \rightarrow d_{x^2-y^2}) = -\mathrm{B}_o j \qquad (1)$$

$$^2\mathrm{Ag} \rightarrow {}^2\mathrm{B}_{3u}(\sigma_N \rightarrow d_{x^2-y^2}) = \mathrm{B}_N i \qquad (2)$$

In these expressions B_o and B_N are the electrical moment integrals, β is the magnetic moment in Bohr magnetons, and i and j are unit-vectors[14].

It is assumed that $d_{x^2-y^2}$ is the appropriate half filled orbital in an axially distorted complex.

The magnetic moments of the d-d transitions have the form:

$$^2\mathrm{Ag} \rightarrow \mathrm{B}_{2g}(d_{xz} \rightarrow d_{x^2-y^2}) = j\beta \qquad (3)$$

$$^2\mathrm{Ag} \rightarrow \mathrm{B}_{3g}(d_{yz} \rightarrow d_{x^2-y^2}) = i\beta \qquad (4)$$

For the coupling of the d–d and CT states via the disymmetric potential from the chiral ligand the rotational force has the form:

$$R_{^2\mathrm{Ag}} \rightarrow {}^2\mathrm{B}_{2u} = \mathrm{Im}\left\{\frac{\langle {}^2\mathrm{B}_{2g}|\mathrm{V}|{}^2\mathrm{B}_{2u}\rangle}{\Delta E}\langle {}^2\mathrm{Ag}|u|{}^2\mathrm{B}_{2u}\rangle \times \langle {}^2\mathrm{B}_{2g}|m|{}^2\mathrm{Ag}\rangle\right\} \qquad (5)$$

$$R_{^2\mathrm{Ag}} \rightarrow {}^2\mathrm{B}_{3u} = \mathrm{Im}\left\{\frac{\langle {}^2\mathrm{B}_{3g}|\mathrm{V}|{}^2\mathrm{B}_{3u}\rangle}{\Delta E}\langle {}^2\mathrm{Ag}|u|{}^2\mathrm{B}_{3u}\rangle\langle {}^2\mathrm{B}_{3g}|m|{}^2\mathrm{Ag}\rangle\right\} \qquad (6)$$

(In eqn. (5) and (6) V is the potential, E is the energy difference between the d–d and CT states and u and m are respectively electric and magnetic moment operators.)

The products of the electric and magnetic components give:

$$-B_o\beta \text{ for the transition } \sigma_o \rightarrow d_{x^2-y^2} \text{ and}$$
$$B_N\beta \text{ for the transition } \sigma_N \rightarrow d_{x^2-y^2}$$

showing that the optical activities of the two transitions are of opposite sign.

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