INDUCED DISTANT COTTON EFFECTS IN MIXED Cu(II) COMPLEXES OF AMINO AND HYDROXY ACIDS AND HETEROCYCLIC LIGANDS

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Abstract—Mixed 1:1:1 complexes of proline or aspartic acid with Cu(II) and 9:10-phenanthroline (phen) or 2,2'-bipyridine (bipy) show induced Cotton effects in the aromatic region. The effect is ascribed to interactions between the charge transfer transitions from the amino acid and the longitudinal π–π^* transitions of the aromatic ligand. There is not such induced optical activity in the mixed glutamate or valinate complexes with Cu(II) and phen, and the behavior of the prolinates and aspartates is explainable in terms of the arrangement of the ligands around the metal ion. The mixed 1:1:1 complex of L-malic acid and phen with Cu(II) also shows induced Cotton effects in the aromatic region, but here in addition to the usual two positive aromatic bands there is a very weak negative band (at *ca.* 315 nm) associated with a short axis polarized π–π^* transition.

INTRODUCTION

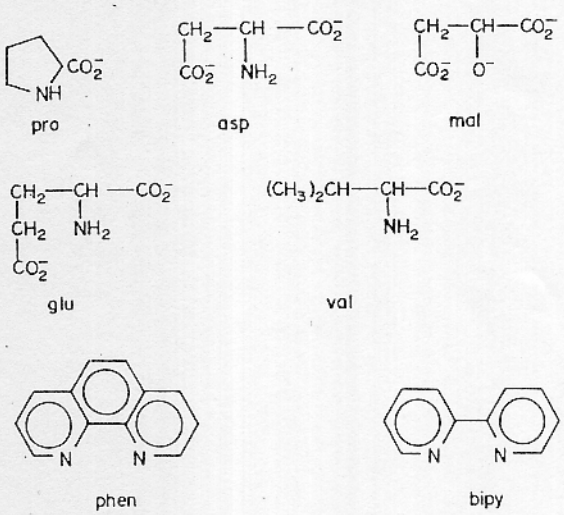
Induced Cotton effects in Cu(II) complexes have been observed by a number of workers [1a, b]. In most systems induction has corresponded to d-d transitions in the visible, and charge transfer (CT) transitions in the ultraviolet regions, mediated by chiral amino acid ligands. However in mixed complexes of Cu(II) with L- and D- proline (pro) and 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) there was distant induced optical activity in the aromatic region (260–320 nm) as well as activity in the *d-d* and CT regions. Preliminary accounts of this work have been given [2, 3]. Mixed complexes of other amino acids had no activity in the aromatic region [4].

Induction in the aromatic region appeared to involve a mechanism different from that of excitonic coupling [5]. Induction by excitonic coupling is however observed in 2:1:1 complexes of phen or bipy with zinc(II) and a chiral amino acid [6].

The strong absorbances of mixed Cu(II) complexes in the aromatic region make it difficult to observe weak circular dichroism (CD) here and one aim of this work was to confirm the earlier reported absence of induction with simple mixed aminoacidates [4]. In addition we hoped to find other examples of induction in the aromatic region, and to date we have observed them in mixed Cu(II) complexes of both pro and L- and D-aspartate (asp) with phen and bipy, and of L-malate (mal) with phen. These results suggest that induction requires not only a chiral ligand but also a grouping around copper other than strictly square planar, due e.g. either to a strained chelate ring, as with pro, or to the presence of a potentially tridentate chiral ligand (asp or mal). We therefore also examined the mixed complex of Cu(II) with phen and L-glutamate (glu), and our results illustrate at least some of the requirements for induction.

We also examined CD spectra in the *d–d* and CT regions and they will be described elsewhere.

The key to the ligands is shown in Scheme 1.



EXPERIMENTAL

Complexes were prepared from L- and D- pro and asp and from L-glu, mal and valine. The acids were at least 95% optically pure. There is evidence for the existence of 1:1:1 complexes in solution [7].

The complexes are usually hydrated and the numbers of waters of crystallization depend critically upon the conditions of

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crystallization and sometimes change from one preparation to another, and is some cases, they change on storage.

Mixed aspartates. Two methods were used and gave the same products.

(a) Starting from Cu(II) asp. A solution (10 ml EtOH) of 0.01 moles of phen or bipy was added to a well stirred suspension of 0.01 mol of Cu(II) asp in H_2O (70 ml). When the solid was dissolved the pH was adjusted to 8 (NH_3), the solution was concentrated four fold by gentle heating and deep blue crystals were obtained.

Kinoshita and Yoshina had already prepared Cu(II) asp as a monohydrate[9]. We prepared it from CuO and L- or D- asp (H_2O, 80°C). On cooling we obtained an amorphous light blue solid as di-or trihydrate depending on the temperature of the crystallizing solution.

(b) Starting from CuO. Freshly prepared CuO (0.01 mol) was added slowly to a warm solution of L- or D- asp (H_2O)[10]. The heterocyclic base (0.01 mol in EtOH) was then added and the product obtained as in (a).

The mixed aspartates are very soluble in water. The calculated compositions in the following microanalytical data are in parentheses. CuL-asp bipy. $3H_2O$: C,40.8(41.5); H,4.5(4.7); N,10.7(10.4); Cu,15.3(15.7)%. Cu D-asp bipy. $2H_2O$: C,44.3(43.5); H.4.0(4.4); N,11.0(10.9); Cu,16.0(16.4)%. Cu L-asp phen. $3H_2O$: C,44.6(44.8); H,3.9(4.4); N,9.4(9.8); Cu, 14.5(14.8)%. Cu D-asp phen. $3H_2O$: C,45.0(44.8); H,4.0(4.4); N,10.0(9.8); Cu,15.0(14.8)%.

Mixed prolinates. The method of Dutta and Dé[8] was originally used, but we also used an alternative approach because of problems of separating the complexes from NH_4Cl. The acid (0.0025 moles) in minimum H_2O was added to 0.0025 mol of freshly prepared, electrolyte free $Cu(OH)_2$. The monohydrochloride of the aromatic base (0.0025 mol) was added in a minimum amount of EtOH with gentle warming. After reaction any residual solid was removed and the solution was concentrated under reduced pressure and crystals appeared. Cu L-pro bipy $Cl.2H_2O$: C,44.9(44.5); H,4.6(5.0); N,10.6(10.4); Cl, 8.9(8.8); Cu,15.7(15.7)%. CuL-pro phen Cl $3H_2O$: C,46.4(45.7); H,4.4(4.9); N,9.3(9.4); Cl,8.3(7.9); Cu,14.2(14.2)%.

Mixed malates. Sodium malate cuprate(II). H_2O was prepared from L-malic acid (0.008 mol) in minimum H_2O and an equivalent of CuO, followed by Na_2CO_3(0.004 mol). Light blue powdery crystals appeared when the solution was concentrated. A solution of phen (0.004 moles) in EtOH (10 ml) was added to a well stirred solution of the malate cuprate in H_2O (50 ml) with gentle warming and the light blue solution became a deeper blue. After concentration the greenish-blue complex was obtained by precipitation (Me_2CO). It is very soluble in H_2O and EtOH.
Cu L-mal phen Na.1.5 H_2O: C,45.2(45.2); H,3.3(3.2); N,6.8(6.6); Cu,14.5(15.0)%.

Mixed valinate or glutamate with phen. The mixed L-valinate was prepared by the method of Dutta and Dé[8], and the mixed glutamate from CuO as described for the aspartate.
Cu L-glut phen. $4H_2O$: C,43.8(44.3); H,4.2(4.9); N,9.1(9.1); Cu,13.3(13.8%).

Spectral measurements. The absorbance spectra were measured in water, generally using a Zeiss PMQ II spectrophotometer, and CD using a Cary 60 spectropolarimeter with a modified CD attachment. The CD measurements were in water at 27°C, in 0.5 or 1 mm cells and $10^{-4}-10^{-3}$ M complex. It is difficult to measure the CD spectra in the strongly absorbing aromatic region and we used the combination of concentration and pathlength which gave the best signal:noise ratio. Despite this the CD spectra were noisy especially at absorbance maxima. so that values of $\Delta\epsilon$ are much less reliable than the positions of the peaks. When we varied the concentrations of the complexes we saw no change in λ_{max} and $\Delta\epsilon$ agreed within the scatter due to the noise.

The agreement between $\Delta\epsilon$ for L- and D- complexes is reasonable in view of the high absorbance of the solutions in the aromatic region (Table 1).

The values of $\Delta\epsilon$, which denotes the difference between the extinction coefficients for left and right circularly polarized light, are given by:

$$\Delta\epsilon = 3300\,[\theta]$$

where $[\theta]$ is the molar ellipticity[11].

Whenever possible CD measurements on L- and D- complexes were made in sequence, so that baseline shifts in the instrument between measurements exaggerate errors in $\Delta\epsilon$ of the enantiomers.

RESULTS

Phenanthroline complexes

The mixed complexes with L-asp, L-pro or L-mal show strong positive CD signals under the absorbance band of the aromatic chromophore (Figs. 1 and 2). They were not found in the mixed complexes with either l-glu or L-valinate (val). The results with the val complex confirm earlier work[4]. The L-glu complex had a positive CD peak at 235 nm, and negative at 260 and below 220 nm. These signals are typical of L-aminoacidates of Cu(II) [1b, 4, 12, 13].

All the induced CD spectra in the aromatic region show a shoulder at *ca.* 295 nm and a peak at *ca.* 242 nm., corresponding to the p and β' absorbance bands of the aromatic ligand. Both transitions are polarized along the

Table 1. Absorption and CD spectra in the aromatic region[a]

Ligands	Absorption				CD			
	$10^{-3}\bar{\nu}_1$	$10^{-3}\epsilon_1$	$10^{-3}\bar{\nu}_2$	$10^{-3}\epsilon_2$	$10^{-3}\bar{\nu}_1$	$\Delta\epsilon_1$	$10^{-3}\bar{\nu}_2$	$\Delta\epsilon_2$
L-asp phen	(34)	(10.4)	37	35	(34)	(+2)	36	+ 9
D-asp phen	(34)	(9.8)	37	34	(34)	(-4)	36	-12
L-pro phen	(34)	(9.3)	37	30	(34)	(+2)	37	+ 7
D-pro phen	(34)	(8.7)	37	27	(34)	(-2)	36	- 7
L-asp bipy	32.6	13.6			32.3	+1.4		
	33.7	14.2			33.1	+1.5		
D-asp bipy	32.6	14.7			32.3	-1.7		
	33.7	15.3			33.1	-1.7		

a The values in parentheses denote shoulders and $\bar{\nu}$ is in cm^{-1}.

major axis of this ligand[14]. However in the mal complex we also see a very weak negative CD signal at higher wavelength.

Bipyridine complexes

The mixed complexes with L-asp or L-pro have similar CD spectra (Figs. 1 and 2). Bipy has an $^1A_1 \rightarrow {}^1B_1$ transition at 305 nm which is polarized along the major axis of the ligand and the corresponding positive CD bands of the mixed complexes are split due to vibrational interactions[14].

Aspartate, prolinate and malate complexes

Neither the mono-nor bis-acidates show Cotton effects above 280 nm[15]. The negative and positive bands at *ca.* 270 and 230 nm respectively in the L-aminoacidates are ascribed to CT transitions [1b, 13], and in all the L-acidates there is also a negative CD band, generally below 200 nm due to the $n-\pi^*$ transition of the carboxylate moiety[16].

DISCUSSION

Earlier we noted that the mixed pro complexes differed from most other aminoacidates in that the rigidity of the chelate ring of pro to copper could influence the conformation of the complexes[2]. Inspection of models suggests that there are strong non-bonding interactions between the 5-position of pro and the aromatic ligands (Fig. 3).

Both asp and mal are tridentate ligands so that their Cu(II) complexes are akin to square pyramids (Fig. 4). We assume that the planar ligands are carboxylate and alkoxide or amino for mal and asp respectively, so that the β-carboxylate group should be coordinated in the apical position, in a six membered ring[17]. Similar coordination of the γ-carboxylate group of glu would-

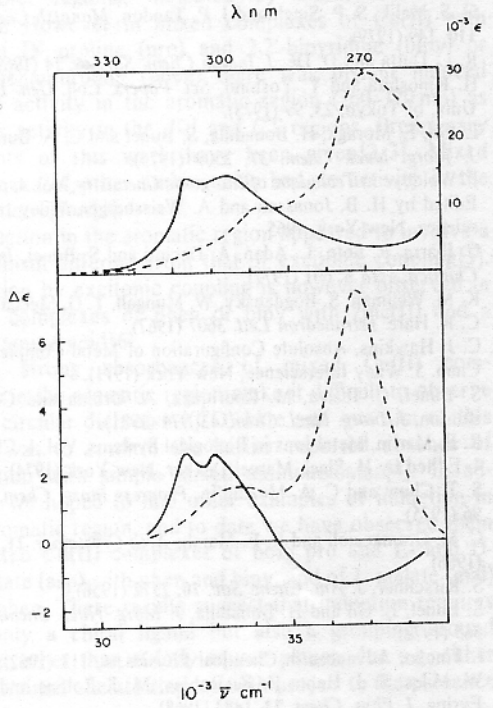

Fig. 1. Absorption and CD spectra of mixed prolinates; ——— Cu-L-pro-bipy$^+$; ----- Cu L-pro-phen.$^+$

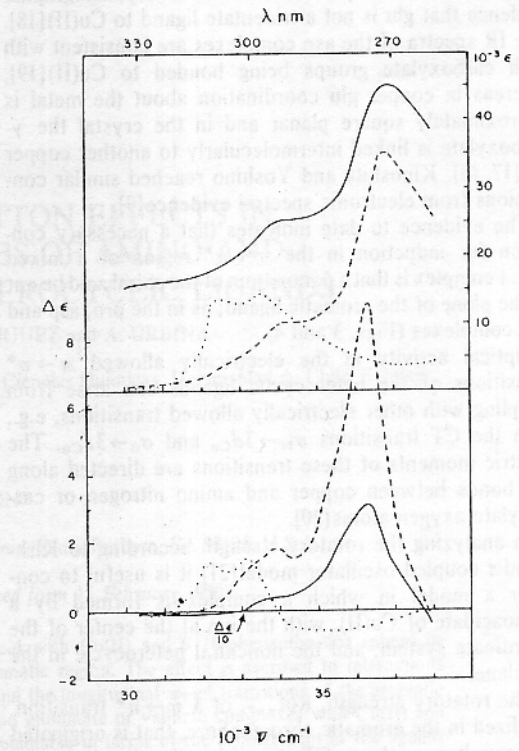

Fig. 2. Absorption and CD spectra of mixed tridentate acidates; ····· Cu-L-asp-bipy; ----- Cu-L-asp phen; ——Cu-L-mal-phen.$^-$

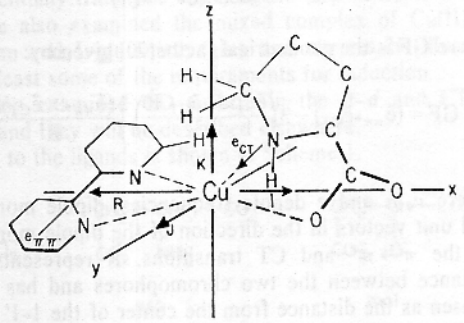

Fig. 3. Idealized model of Cu-L-pro phen.$^+$ or Cu-L-pro bipy.$^+$ Arrows represent either the electric dipole moments, e, of the π, π^* and CT transitions or the unit vectors along the coordinate axes, and R is the distance between the chromophoric groups.

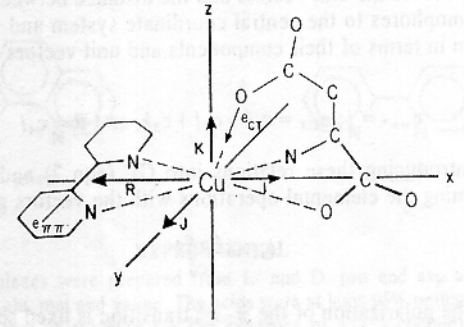

Fig. 4. Idealized model of Cu-L-asp-phen or Cu-L-asp-bipy. Symbols are as in Fig. 3. Replacement of the amino group of aspartate by oxygen would give the malate model.

require formation of a seven membered ring. The absence of CD bands in the aromatic region in the mixed glu complex (Results) is consistent with crystallographic evidence that glu is not a tridentate ligand to Cu(II)[18]. The IR spectra of the asp complexes are consistent with both carboxylate groups being bonded to Cu(II)[19], whereas in copper glu coordination about the metal is approximately square planar and in the crystal the γ-carboxylate is linked intermolecularly to another copper ion[17, 18]. Kinoshita and Yoshino reached similar conclusions from electronic spectral evidence[9].

The evidence to date indicates that a necessary condition for induction in the $\pi \rightarrow \pi^*$ region of a mixed 1:1:1 complex is that a donor atom of the chiral acid be out of the plane of the aromatic ligand; as in the pro, asp and mal complexes (Figs. 3 and 4).

Optical activity in the electrically allowed $\pi \rightarrow \pi^*$ transitions of the heterocyclic ligands can arise from coupling with other electrically allowed transitions, e.g., with the CT transitions $\sigma_N \rightarrow 3d_{Cu}$ and $\sigma_O \rightarrow 3d_{Cu}$. The electric moments of these transitions are directed along the bonds between copper and amino nitrogen or carboxylate oxygen atoms[20].

In analyzing the rotatory strength according to Kirkwood's coupled oscillator model[21] it is useful to consider a model in which a complex is formed by a monoacidate of Cu(II), with the ion at the center of the coordinate system, and the nonchiral heterocycle in the xy plane.

The rotatory strength, $Rot_{\pi\pi^*}$, of a $\pi \rightarrow \pi^*$ transition, localized in the aromatic chromophore, that is originated by coupling with a CT transition localized in the monoacidate moiety is given by:

$$Rot_{\pi\pi^*} = \frac{2\pi\nu_{pp^*}\nu_{CT}\mu^2_{\pi\pi^*}\mu^2_{CT}}{hc(\nu^2_{\pi\pi^*} - \nu^2_{CT})} \cdot gF \qquad (1)$$

where GF is the geometrical factor[20] given by:

$$\left[GF = (\vec{e}_{\pi\pi}\cdot\vec{e}_{CT}) - 3\left(\frac{\vec{e}_{\pi\pi}\cdot\vec{R}\ \vec{e}_{CT}\ \vec{R}}{R^2}\right)\right]\frac{(\vec{e}_{\pi\pi^*}\times\vec{e}_{CT})R}{R^3} \qquad (2)$$

where ν, μ and e denote frequencies, dipole moments and unit vectors in the direction of the dipole moments of the $\pi \rightarrow \pi^*$ and CT transitions. $\vec{R}$ represents the distance between the two chromophores and has been chosen as the distance from the center of the 1–1′ bond of the aromatic ligand and the copper ion (Figs. 3 and 4).

A $\pi - \pi^*$ transition of either phen or bipy that is polarized along the major axis of these ligands ($^1A_1 \rightarrow {}^1B_1$) can couple with, for example, a CT transition originating in the amino group or in the apical β-carboxylate group of asp or mal.

We refer the unit vectors and the distance between the chomophores to the central coordinate system and write them in terms of their components and unit vectors i, j, k as:

$$e_{\pi\pi^*} = j;\ e_{CT} = c_1 i + c_2 j + c_3 k, \text{ and } R = c_4 i$$

Introducing these relations into GF (eqn 2) and performing the elemental operations with the vectors gives:

$$GF = \frac{c_2\, c_3}{c_4^2} \qquad (3)$$

The polarization of the π–π^* transition is fixed so that its rotatory strength depends on the components of the CT transition, and will be zero for either a planar structure ($c_3 = 0$) or in an orthoaxial complex with a tridentate ligand ($c_2 = 0$).

These general conclusions accord not only with the presence of induced optical activity in the aromatic region, but also with the intensities of the CD signals. The magnitudes of $\Delta\epsilon$ for the main band of phen at *ca.* 275 nm increase in going from pro to asp to mal (Figs. 1 and 2), suggesting that the strength of the coupling follows this sequence. We observed only positive CD signals in the aromatic region with pro and asp complexes, but with the mal-phen complex we saw an additional weak band at 31,700 cm^{-1} (315 nm) (Fig. 2) which almost certainly corresponds to the short axis polarized band, α, of phen, and is too weak to be seen in the corresponding asp and pro complexes. This observation suggests distortion is greatest in the mixed malphen complex.

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REFERENCES

1. (a) C. J. Hawkins and C. L. Wong, *Austral. J. Chem.* **23**, 2237 (1970); (b) J. M. Tsangaris, J. W. Chiang and R. B. Martin, *J. Am. Chem. Soc.* **91**, 726 (1969); E. W. Wilson, M. H. Kasperian and R. B. Martin, *J. Am. Chem. Soc.* **92**, 5365 (1970).
2. S. Bunel, C. Ibarra, A. Urbina and C. A. Bunton, *Inorg. Nucl. Chem. Lett.* **13**, 259 (1977).
3. S. Bunel, C. Ibarra and C. A. Bunton, *Proc. XVIII Int. Conf. on Coordination Chem.*, Sao Paulo, Brazil, July, 1977, III. b. 25.
4. S. Bunel, C. Ibarra and C. A. Bunton, *Inorg. Nucl. Chem. Lett.* **11**, 213 (1975).
5. B. Bosnich, *Accounts Chem. Res.* 2, 266 (1969); A. J. McCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.* A, 1428 (1969).
6. Unpublished results. A. Decinti and G. Larrazabal.
7. G. S. Malik, S. P. Singh and J. P. Tandon, *Monatsh Chemie*, **110**, 149 (1979).
8. R. L. Dutta and D. Dé, *J. Indian Chem. Soc.* **46**, 74 (1969).
9. H. Kinoshita and Y. Yoshino, *Sci. Papers. Coll. Gen. Edn.*, Univ. of Tokyo, **23**, 99 (1973).
10. L. Gil, E. Moraga, H. Bobadilla, S. Bunel and C. A. Bunton, *J. Inorg. Nucl. Chem.* **37**, 2509 (1975).
11. F. Woldbye in *Technique of Inorganic Chemistry*, Vol. 4, p.249 Edited by H. B. Jonassen and A. Weissberger, Wiley Interscience, New York, 1965.
12. C. Ibarra, R. Soto, L. Adań, A. Decinti and S. Bunel, *Inorg. Chimica Acta* **6**, 601 (1972).
13. K. M. Wellman, S. Bogdansky, W. Mungall, T. G. Mecca and C. R. Hare *Tetrahedron Lett.* 3607 (1967).
14. C. J. Hawkins, Absolute Configuration of Metal Complexes, Chap. 5. Wiley Interscience, New York (1971).
15. S. Bunel, C. Ibarra, M. Rodriquez, A. Urbina and C. A. Bunton, *J. Inorg. Nucl. Chem.* **43**, 971 (1981).
16. R. B. Martin, Metal Ions in Biological Systems, Vol. 1, Chap. 4, Edited by H. Sigel, Marcel Dekker, New York (1974).
17. S. T. Chow and C. A. McAuliffe, *Progress Inorg. Chem.* **19**, 96 (1975).
18. C. M. Gramaccioli and R. E. Marsh, *Acta Crystalogr.* **21**, 594 (1966).
19. S. Kirschner, *J. Am. Chem. Soc.* **70**, 2372 (1956).
20. S. Bunel, L. Gil and H. Bobadilla, *J. Inorg. Nucl. Chem.* **39**, 365 (1977).
21. I. Tinoco, Advances in Chemical Physics, **4**, 113 (1962); D. W. Miles, S. J. Hahn, R. K. Robins, M. J. Robins and H. Eyring, *J. Phys. Chem.* **72**, 1483 (1968).