

## The visible circular dichroism of mixed complexes of Cu(II) with chiral acids and amines

Aminoacidates of Cu(II) exhibit optical activity in the visible region of the  $d-d$  transitions and a theoretical analysis of these induced Cotton effects predicts that there should be three CD bands in this region. Hawkins and Wong have observed

three bands with some copper bis-aminoacidates, using either the solid in KBr discs or solutions in methanol or aqueous DMSO, but in some cases they had to use low temperatures in order to observe all three bands[1]. For the L-tyrosine and L-valine

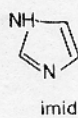
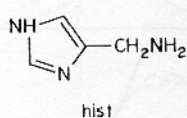
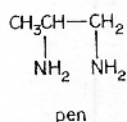
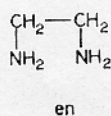
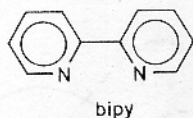
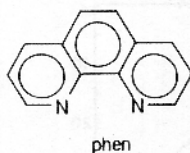
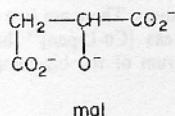
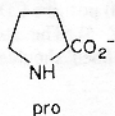
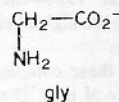
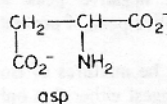
complexes in KBr discs the sequence of signs was  $+-+$ , but it was reversed for the bis-L-prolinate. However at room temperature in water, methanol or aqueous DMSO, copper bis-L-prolinate showed only two CD bands, whose positions and signs were similar to those exhibited by other bis L-amino acidates.

The difference in these induced Cotton effects has been explained in various ways. One suggestion was that the bis-L-prolinate had a *cis*-configuration, whereas most other L-amino acidates were *trans*[2], however the secondary amino group of proline becomes chiral on coordination, and this additional chiral center could perturb the CD spectra[3].

The possible role of *cis-trans* isomerism can be resolved by examining mixed copper complexes of an amino acid and such achiral bidentate ligands as 1,2-bipyridine (bipy) and 9,10-phenanthroline (phen). A number of such mixed complexes have been prepared and their CD spectra have been examined in the visible and ultraviolet regions, and in this work we show that three CD bands can be observed in the visible region in solution at room temperature, although in general the third CD band at the lowest wavelength is weak, as in generally found[1]. However we found two and sometimes only one band in several complexes which we examined, probably because of overlapping of the bands, but in general we could relate the pattern of the visible CD spectra to the absorption spectra.

The amino acids were L- and D-proline (pro) and L- and D-aspartic acid (asp), and L-malic acid (mal) was also used. As the second ligand in the mixed complexes we used phen, bipy, 1,2-diaminoethane (en), 1,2-diaminopropane (pen), histamine (hist), imidazole (imid) and glycine (gly). Some of the results have been reported in preliminary form[4].

The key to the ligands is shown below.



#### EXPERIMENTAL

The syntheses of the complexes have been reported[5]. The absorption spectra in water were measured on a Zeiss recording spectrophotometer with concentrations ranging from  $10^{-2}$ M to  $10^{-3}$ M and with 1 cm cells. The mono-aspartates have very low solubility in water, and the absorption spectra of  $[\text{Cu-L-asp}] \cdot 3\text{H}_2\text{O}$  was determined by reflectance and the absorbance is in arbitrary units.

The CD spectra in water were measured on a Cary 60 spectropolarimeter with a modified CD attachment at 27°C. Concentrations ranged from  $10^{-2}$  to  $10^{-4}$ M and 1, 2 and 5 cm cells were used. The mono-aspartates,  $4 \times 10^{-4}$ M, were dissolved with the aid of an ultrasonic bath, and a 10 cm cell was used.

The CD signals are weak in the visible region, and the signal-noise ratio is low, especially at high wavelengths. However, we obtained reasonable agreement for enantiomers, especially as regards the frequencies,  $\bar{\nu}$ ,  $\text{cm}^{-1}$ , of the CD maxima (Table I).

#### RESULTS

*Aspartates.* We see the expected  $+-+$  pattern in the CD spectra of copper bis-L-asp and of the mixed L-asp-bipy complex (Fig. 1). There may be a very weak high energy CD band in the mixed L-asp-phen complex (Fig. 1) but its intensity is hardly more than the noise, although it has the predicted sign. Two other mixed L-amino acidates also show three CD bands with the expected  $+-+$  pattern; they are  $[\text{Na}[\text{Cu L-asp-gly}]]$  and  $[\text{Cu L-asp-pen}]$  (Fig. 2), but here there are structural ambiguities because both complexes could be mixtures of isomers, and in the

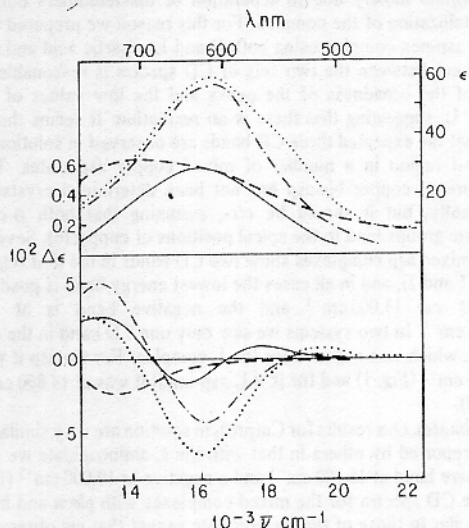


Fig. 1. Absorption and CD spectra of:  $[\text{Na}_2[\text{Cu}(\text{L-asp})_2] \cdot 2\text{H}_2\text{O}]$ —;  $[\text{Cu L-asp-bipy}] \cdot 3\text{H}_2\text{O}$ ····;  $[\text{Cu L-asp-phen}] \cdot 3\text{H}_2\text{O}$ ---;  $[\text{Cu L-asp}] \cdot 3\text{H}_2\text{O}$ - - - . The absorption spectra for  $\text{Cu-L-asp}$  was obtained by reflectance and the absorbance scale is in arbitrary units.

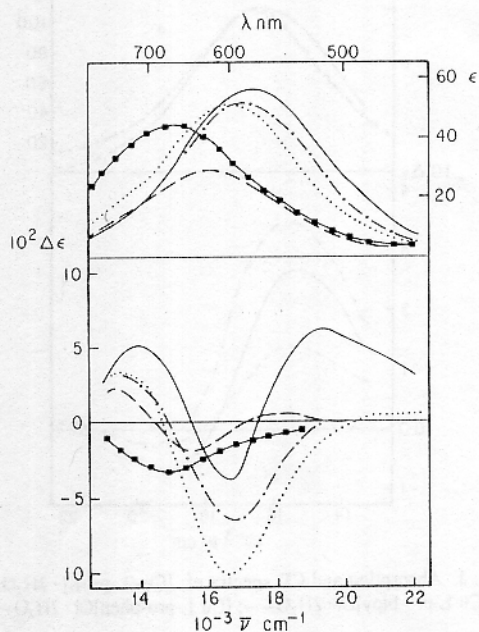


Fig. 2. Absorption and CD spectra of:  $[\text{Cu L-asp-phen}] \cdot \text{H}_2\text{O}$ —;  $[\text{Cu L-asp-en}] \cdot 2\text{H}_2\text{O}$ ····;  $[\text{Cu-L-asp-imid}] \text{H}_2\text{O}$ — — —;  $[\text{Cu L-asp-hist}] \cdot \text{H}_2\text{O}$ — · — · —;  $[\text{Na}[\text{Cu L-asp-gly}]2\text{H}_2\text{O}]$ — · — · —.

Table I. Absorption and spectra in the visible region

COMPLEX	ABSORPTION		CIRCULAR DICHROISM					
	$10^{-3}\bar{\nu}$	$\epsilon$	$10^{-3}\bar{\nu}_{CD_1}$	$10^2 \Delta\epsilon_1$	$10^{-3}\bar{\nu}_{CD_2}$	$10^2 \Delta\epsilon_2$	$10^{-3}\bar{\nu}_{CD_3}$	$10^2 \Delta\epsilon_3$
$\text{Na}_2[\text{Cu}(\text{L-asp})] \cdot 2\text{H}_2\text{O}$	16,0	29	13,2	+ 2,8	15,6	-1,7	17,9	+0,8
$\text{Na}_2[\text{Cu}(\text{D-asp})] \cdot 2\text{H}_2\text{O}$	15,9	26	13,2	- 1,9	15,6	+1,8	18,2	-0,2
$[\text{Cu L-asp-pen}] \cdot \text{H}_2\text{O}$	17,4	56	14	+ 5	16,4	-3,9	19,4	+ 6,1
$[\text{Cu D-asp-pen}] \cdot \text{H}_2\text{O}$	17,4	64	13,8	- 4,1	16,4	+3,8	19,4	- 4
$[\text{Cu}(\text{L-pro})_2] \cdot 2\text{H}_2\text{O}$	16,4	108	15,3	+26,5	19	-7		
$[\text{Cu}(\text{D-pro})_2] \cdot 2\text{H}_2\text{O}$	16,4	119	15,3	-28	19	+7,7		

mixed complex with DL-pen there could be partial resolution of the diamino moiety due to separation of diastereomers during recrystallization of the complex. For this reason we prepared the mixed asp-pen complex using both D and L-aspartic acid and the agreement between the two sets of CD spectra is reasonable in view of the broadness of the peaks and the low values of  $\Delta\epsilon$  (Table I), suggesting that there is no resolution. It seems therefore that the expected three CD bands are observed in solution in the *d-d* region in a number of mixed copper aspartates. The structure of copper bis-asp has not been determined crystallographically, but it should be *cis*-, assuming that both  $\beta$ -carboxylate groups bind to the apical positions of copper [6]. Several other mixed asp complexes show two CD bands in the *d-d* region (Figs. 1 and 2), and in all cases the lowest energy band is positive and at *ca.*  $13,000\text{ cm}^{-1}$  and the negative band is at *ca.*  $16,000\text{ cm}^{-1}$ . In two systems we saw only one CD band in the *d-d* region, which was negative for the L-complex. For Cu-asp it was  $13,500\text{ cm}^{-1}$  (Fig. 1) and for [Cu L-asp-imid] it was at  $14,800\text{ cm}^{-1}$  (Fig. 2).

**Prolinates.** Our results for  $\text{Cu}(\text{pro})_2$  in solution are very similar to those reported by others in that with the L-aminoacidate we see a positive band at  $15,300\text{ cm}^{-1}$  and a negative at  $19,000\text{ cm}^{-1}$  (Fig. 3). The CD spectra for the mixed complexes with phen and bipy are similar to those of the bis-prolinate except that we observe a shoulder at *ca.*  $25,000\text{ cm}^{-1}$  which is positive for complexes of L-proline. This signal is probably due to the tail of a band due to

$\pi \rightarrow \pi^*$  transitions of the aromatic ligands. These ligands absorb very strongly below 300 nm, but they have weak absorbances at higher wavelengths [7]. It has been suggested that the unusual sequence of the CD bands of  $\text{Cu}(\text{pro})_2$  at low temperature in the *d-d* region arose from a *cis*-relation of the two prolines [2]. This suggestion has been discounted, and it is clearly inconsistent with our observation with other mixed complexes.

**Malates.** Malic acid is potentially tridentate ligand. The CD spectra of [Cu L-mal-phen], and [Cu L-mal-en] are very similar to those of the corresponding aspartates in that the lower energy band is positive and the higher negative (Fig. 4). However there is a difference in that we observe very similar CD spectra for Cu-L-mal and the mixed malate complexes.

**Relation between CD and absorption spectra.** For many of these complexes there are simple relations between spectra and chemical composition. For example  $[\text{Cu}(\text{L-asp})_2]^{2-}$  and all the mixed L-aspartates, except that with imidazole, have a positive peak at  $13,000\text{ cm}^{-1}$  and a negative peak at *ca.*  $16,000\text{ cm}^{-1}$ , and the highest energy positive peak, if present, is at  $18,000\text{--}19,500\text{ cm}^{-1}$ .

A number of these complexes could be mixtures of isomers, but the similarity of the CD spectra suggest either that only one isomer is present, or that different geometrical isomers have similar CD spectra. With only one complex  $[\text{Cu}(\text{L-pen})_2]^{2-}$  we see CD spectra which could be indicative of the presence of diastereomers. There are two (partially resolved) positive CD signals, whereas  $[\text{Cu-L-pen}]^{2+}$  has only one (Fig. 5). The absorption spectrum of the bis-complex has an ill-defined shoulder at *ca.*

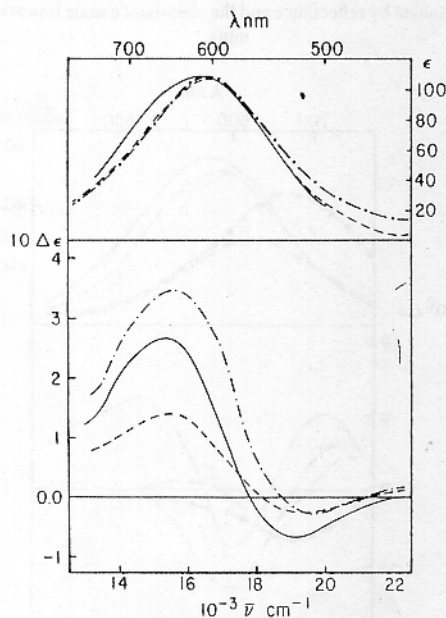


Fig. 3. Absorption and CD spectra of:  $[\text{Cu}(\text{L-pro})_2] \cdot 2\text{H}_2\text{O}$ —;  $[\text{Cu L-pro-bipy}]\text{Cl} \cdot 2\text{H}_2\text{O}$ —;  $[\text{Cu L-pro-phen}]\text{Cl} \cdot 2\text{H}_2\text{O}$ —.

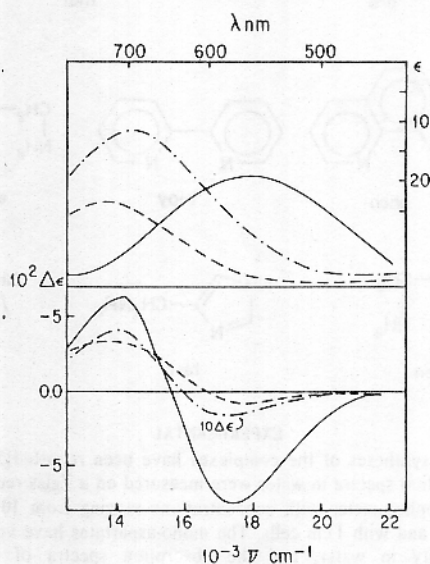


Fig. 4. Absorption and CD spectra of:  $\text{Na}[\text{Cu L-mal}] \cdot \text{H}_2\text{O}$ —;  $\text{Na}[\text{Cu L-mal-en}]$ —;  $\text{Na}[\text{Cu L-mal-phen}] \cdot 2\text{H}_2\text{O}$ —.

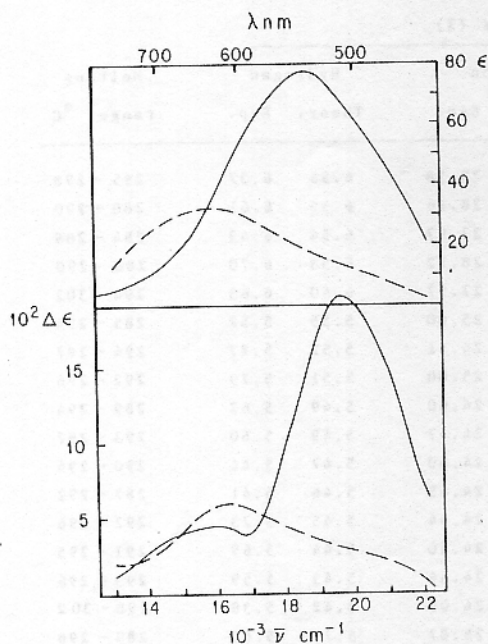


Fig. 5. Absorption and CD spectra of:  $[\text{Cu(L-pen)}_2]2\text{Cl}^-$  ---;  $[\text{Cu(L-pen)}_2]2\text{Cl}^-$  —.

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670 nm ( $14,900\text{ cm}^{-1}$ ) which could be related to the lower energy positive band in the CD spectra which itself is similar and at the same frequency to that of the single band of the mono complex.

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## Adducts of lanthanide trifluoromethanesulfonates and hexamethylphosphoramide (HMPA)

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Lanthanide complexes containing HMPA as ligand have been extensively studied by several authors. Emphasis has been given to perchlorates, due to the different compositions obtained. The first complex prepared was that of composition  $[\text{Ln}(\text{NO}_3)_2(\text{HMPA})_2] \text{BPh}_4$ , by Pneumaticakis[1]. Adducts of lanthanide chlorides with general formula  $\text{LnCl}_3 \cdot 3\text{HMPA}$  have been described by Donoghue and Peters[2] and the structure of the praseodymium chloride complex determined by Radonovich and Glick[3]. Using different methods of preparation Donoghue *et al.*[4] and Giesbrecht and Zinner[5] independently obtained compounds with formula  $\text{Ln}(\text{ClO}_4)_3 \cdot 6\text{HMPA}$ . Durney and Marianelli[6] reported the preparation and characterization of complexes with composition  $[\text{Ln}(\text{ClO}_4)_2(\text{HMPA})_4] \text{ClO}_4$ . Scholer and Merbach[7] were able to synthesize both types of perchlorate adducts. The preparation of some lanthanide trifluoromethanesulfonate complexes, with composition  $\text{Ln}(\text{F}_3\text{C-SO}_3)_3 \cdot 4\text{HMPA}$  by Thom[8]; of nitrate complexes with several compositions, by Sylvanovich and Madan[9] and by Sinha[10]; of some tetraphenylborate complexes by Melo and Serra[11] and Kuya *et al.*[12] and of bromide adducts, with general formula  $\text{LnBr}_3 \cdot 4\text{HMPA}$ , by Mikleev *et al.*[13] have been described. Analysis of the fluorescence spectra of several europium complexes were also studied[14, 15].

In this article the preparation of adducts with formulas  $\text{Ln}(\text{F}_3\text{C-SO}_3)_3 \cdot 6\text{HMPA}$  ( $\text{Ln} = \text{La-Nd, Eu}$ ) and  $\text{Ln}(\text{F}_3\text{C-SO}_3)_3 \cdot 4\text{HMPA}$  ( $\text{Ln} = \text{Nd-Lu, Y}$ ) is described. The compounds

were characterized by elemental analysis, X-ray powder patterns, electrolytic conductance data in acetonitrile and nitromethane, IR spectra, absorption spectra of neodymium and emission spectra of europium compounds.

#### EXPERIMENTAL

The hydrated trifluoromethanesulfonates were prepared as recently described[16]. For the preparation of the adducts with six HMPA molecules, the hydrated salts were first heated at  $200^\circ\text{C}$  to eliminate the most part of hydration water, cooled and then reacted with an excess of HMPA; the mixture was gently warmed and treated with triethyl-orthoformate. The crystals were filtered, washed with small portions of triethyl-orthoformate and dried *in vacuo*, over anhydrous calcium chloride. Attempts to prepare compounds with six HMPA ligands of the heavy lanthanides were unsuccessful.

To obtain the compounds with four ligands, the hydrated salts were dissolved in an excess of HMPA at room temperature, after addition of triethyl-orthoformate, the crystals formed were filtered, washed with this solvent and dried as above.

**Analysis and measurements.** These were performed as described in[16].

#### RESULTS AND DISCUSSION

Table I contains a summary of the analytical data and melting ranges. The complexes are soluble in acetonitrile, nitromethane,