

## Stereoselective Isomerism in Amino-acid Complexes of Copper(II)

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IN agreement with the conformational theory of Corey and Bailar,<sup>1</sup> Gillard and his co-workers<sup>2</sup> have shown stereoselectivity to be absent in solutions of bis(amino-acidato)copper(II) complexes. However, when the amino-acid chelate also possesses a third possible co-ordinating site, *e.g.*, as in histidine and asparagine, stereoselective effects do apparently

arise.<sup>3,4</sup> In the solid state, *cis-trans*-isomerism has been observed in the complexes of glycine<sup>5</sup> and D- and L-alanine<sup>6</sup> but, since no comparable results were reported for the DL-alanine complex it is not known whether the isomerism is stereoselective or not.

In the absence of the latter information we

report the first examples of stereoselective isomerism, in the solid state, of bis(amino-acidato)-copper(II) complexes. Bis-(DL-phenylalaninato)-copper(II) has been obtained in three forms: (i) semi-stable blue scales ( $\lambda_{\max}$  620 m $\mu$ ), obtained by precipitation from an aqueous solution at 0°; (ii) a blue-violet stable form ( $\lambda_{\max}$  570, 530), from precipitation at room temperature, or from suspension of (i) in a small volume of hot water; (iii) an unstable blue form ( $\lambda_{\max}$  620 when moist), obtained by neutralizing an acidic solution of the complex; on drying this changed into (ii). [ $\lambda_{\max}$  refers to their diffuse reflectance spectra, all forms in solution gave identical visible spectra ( $\lambda_{\max}$  ca. 620)]. Under all conditions L-phenylalanine formed only one complex ( $\lambda_{\max}$  625). Since *trans*-bis(amino-acidato)copper(II) complexes generally<sup>7</sup> absorb around 620 m $\mu$ , we tentatively assign to (i) a *trans*-configuration, (ii) being the corresponding *cis*-isomer, and (iii) a weakly hydrated *trans*-form.

Isomeric copper complexes of tyrosine (*p*-hydroxyphenylalanine), were obtained in a similar manner to the phenylalanine complexes and are summarized in the Table.

spectral changes, of the DL-phenylalanine and DL-tyrosine complexes in hot water means that in the "mauve" form the phenolic group of tyrosine is in some way influencing the environment of the copper ion. Direct co-ordination to the copper ion of an adjacent molecule can be overruled since complexes of the type  $M_2^I[Cu(tyr)_2]$ , in which the phenolic groups are fully ionized, are green ( $\lambda_{\max}$  ca. 640). Moreover, there is now overwhelming evidence<sup>8</sup> that reduction in the number of axial-co-ordinating groups to  $Cu^{II}$  results in  $\lambda_{\max}$  shifting to lower wavelengths, so a more likely structure is one in which the axial co-ordination positions are blocked by the aromatic rings, possibly due to the oxygen of the phenolic group begin involved in hydrogen-bonding. Such a structure would also be consistent with the lower solubility of the "mauve" form. Whether the configuration around the copper ion is *cis* or *trans* is not known at present.

Rather surprisingly perhaps, no isomerism was found to occur in the complexes of L- and DL-tryptophan where there is potentially a third co-ordinating site (*indole-N*). In conclusion, it would

TABLE

Complex <sup>a,b</sup>	Appearance	$\lambda_{\max}^c$	Solubility (10 <sup>-3</sup> M) <sup>d</sup>	Decomp. temp. <sup>e</sup>
Cu(DL-tyr) <sub>2</sub> .. ..	blue, needles	590	2.3	230°
Cu(DL-tyr) <sub>2</sub> .. ..	mauve, needles	495†	1.0	238°
Cu(L-tyr) <sub>2</sub> .. ..	blue, needles	590	1.0	235°
Cu(L-tyr) <sub>2</sub> .. ..	blue, scales	620	—	244°

<sup>a</sup> tyr = tyrosine. <sup>b</sup> Satisfactory C, H, N, and Cu analyses. <sup>c</sup> Diffuse reflectance spectra in m $\mu$ . <sup>d</sup> In water at 20°. <sup>e</sup> Lowest temperature at which decomposition began, all complexes decompose before melting. † Shoulders at 560 and 530 (weak).

The mauve DL-tyrosine complex was obtained by suspending the blue form in a small volume of water at 60° for 30 min.; both forms gave identical solution spectra. Precipitation at room temperature gave the needle-like form of Cu(L-tyr)<sub>2</sub>; at 60° the scaly form was precipitated.

The difference in behaviour, as indicated by the

appear that in complexes of the type {Cu[RCH(NH<sub>2</sub>)·CO<sub>2</sub>]<sub>2</sub>} stereoselective interactions arise when R is of such a nature that the packing of this group within the crystal controls the immediate environment of the  $Cu^{II}$  ion; the absence of similar effects in solution would not be unexpected.

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