The Stabilities of the Metal Complexes of Optically Active Amino-Acids

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STEREOSPECIFIC effects are well known when several optically active ligands complex with a metal ion, notably[1] for diamine ligands. In general, the most stable complexes are those in which the ligands co-ordinated to the metal are all of the same optical hand. The possibility that optically active hydroxy- or amino-acid ligands may form metal complexes in solution which differ in stability from those of the racemic ligands has been demonstrated by Fronaeus[2] and by Bennett.[3] However, in both these cases the ligands (tartaric acid and asparagine, respectively) contain more than two co-ordinating centres, making it difficult to ascertain the exact nature of

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[1] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.
[2] S. Fronaeus, *Dissertation*, Lund, 1948.
[3] W. E. Bennett, *J. Amer. Chem. Soc.*, 1959, **81**, 246.

the chelation; it seems possible that polynuclear complexes form in solution.

The currently accepted theory[1] of the origin of stereospecific effects in metal complexes rests on the puckering of the chelate rings formed by optically active ligands such as diamines. For complexes containing almost planar chelate rings, such as those formed by α-amino-acids, no stereospecificity is expected. We have initiated an investigation of the properties of complexes of simple optically active amino-acids, both in solution and in the solid state. The results for the copper(II)–α-alanine system reported here show that there is indeed no stereospecificity whatsoever in complexes containing two bidentate amino-acid ligands in the *trans*-configuration about the metal.

We have prepared analytically pure complexes of racemic, *dextro*-, and *laevo*-α-alanine with copper(II). The complexes containing the resolved ligands crystallised from water as anhydrous [Cu{D (or L)-α-alanine}$_2$] [Found: D-: C, 30·0; H, 5·2; N, 11·7. L-: C, 30·1; H, 5·0; N, 11·9. Calc. for $C_6H_{14}O_4N_2$:Cu, C, 30·0; H, 5·1; N, 11·7%]. The complex prepared from the racemic ligand crystallized as the monohydrate [Cu(DL-α-alanine)$_2$]H_2O [Found: C,27·6; H, 5·5; N, 11·1. Calc. for $C_6H_{14}O_4N_2Cu,H_2O$: C, 28·0; H, 5·5; N, 10·9%]. Dehydration of the latter was difficult, requiring heating *in vacuo* at 160°. Infrared spectra of the solids show the expected differences for the two forms. The spectrum of the dehydrated [Cu(DL-α-alanine)$_2$] bears only a superficial resemblance to those of the D- and L-ligands. In all cases, the complexes formed from the pure D- and L- isomers gave identical spectra. Powder photographs further confirm the difference in structure between [Cu(DL-α-alanine)$_2$]H_2O and [Cu{D(or L)-α-alanine}$_2$]. The complex with DL-α-alanine is less soluble ($2{\cdot}5 \times 10^{-2}$M at 21°) than those of the resolved isomers ($7{\cdot}5 \times 10^{-2}$M).

Dijkgraaf[4] has recently reported differences in the electronic spectra of the complexes of copper(II) with DL-α-alanine and L-α-alanine. We find that the three forms (D, L, and DL) have superposable absorption spectra in aqueous solution, with $\epsilon_{620} = 54{\cdot}0$, whether the isolated complex was dissolved in water, or the complexes were formed *in situ* by mixing solutions of copper sulphate and the amino-acids in a borax buffer of pH 8·86. (Curchod[5] has shown that, above pH 8, the complexes are entirely of the form CuL_2.) The spectra of the three complexes in solutions at pH < 8 are also identical, indicating that they have the same stabilities. This was confirmed by calculating the $\bar{n}$–pL plots, which are superposable. The differences found[4] for the dipole strengths of the band at 620 mμ. between the racemic and active isomers of bis-α-alaninatocopper(II) disappear when allowance is made for the difference in hydration of the solid complexes.

It is relevant that the absorption spectra are also superposable when [Cu(D-α-alanine)$_2$] and [Cu(L-α-alanine)$_2$] are mixed as solutions in any ratio, the copper concentration being kept constant. This is not true for the tartrato–copper(II) system,[6] indicating that stereospecific effects may occur for tartaric acid as a ligand, just as they do[7] for the tridentate histidine when it forms complexes with cobalt(II).

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[5] J. Curchod, *J. Chim. phys.*, 1956, **53**, 126.

[6] A. Cotton, *Trans. Faraday Soc.*, 1930, **26**, 304.

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