

Composition, stability, and lability of copper(II) dipeptide complexes

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Abstract

Complex formation of copper(II) with glycylglycine (HL) has been studied spectrophotometrically over a wide range of ligand concentration ($0.005\text{--}1.0\text{ mol dm}^{-3}$) and pH (0.5–13) in aqueous potassium nitrate ($1.0\text{ mol dm}^{-3}\text{ KNO}_3$). The complexes $[\text{CuL}]^+$, $[\text{Cu(HL)}]^{2+}$, $[\text{Cu(LH-1)}]$, $[\text{Cu(LH-1)(OH)}]^-$, $[\text{Cu(LH-1)L}]^-$, $[\text{Cu(LH-1)}_2]^{2-}$, and $[\text{Cu}_2(\text{LH-1})_2(\text{OH})]^-$ were found and their formation constants determined. The ligand in $[\text{Cu(HL)}]^{2+}$ is co-ordinated through the carboxylate group, and the terminal amino group remains protonated. Such a co-ordination mode is more favourable for depeptides as compared to amino acids. Both of the ligands in $[\text{Cu(LH-1)}_2]^{2-}$ are bound to the metal ion in a bidentate mode through the terminal amino nitrogen and the deprotonated peptide nitrogen. The species $[\text{Cu}_2(\text{LH-1})_2(\text{OH})]^-$ has an intense absorption band in the near-u.v. region which indicates that the OH^- group is bridging. The lability of complexes $[\text{Cu(LH-1)L}]^-$ with five aliphatic dipeptides has been investigated by n.m.r. relaxation of water protons. The ligand-exchange rates (R_{ex}) in solutions of these complexes follow the kinetic equation $R_{\text{ex}} = (k_1 + k_2[\text{L}^-])[\text{Cu(LH-1)L}]^-$. Increasing the size of the side chain of the dipeptides leads to a lower R_{ex} , and a good correlation between $\log k_2$ and the steric constants E_s^0 of the side-chain substituents is observed. The high values for k_1 obtained indicate a considerable trans effect of the deprotonated peptide group.

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