

N-terminal tyrosine interacts with cupric ion only through the amino and carbonyl groups. In earlier studies a Tyr residue plays a critical role in the formation of a dimeric cupric complex of Gly-Pro-Tyr-Gly [6], while a similar dimeric complex is only a minor species in the Tyr-Pro-Gly-Gly system and it is undetectable in the Gly-Pro-Gly-Tyr case [6].

REFERENCES

- [1] H.D. NIAL, in M. GOODMAN, J. MEIENHOFER (eds.), «Peptides: Proc. of the 5th Am. Peptide Symposium», Halsted Press, N.Y., 1977, p. 96.
- [2] T. TONOU, S. MINAGAWA, N. KATO, K. OHKI, *Pharmacol. Biochem. Behav.*, **10**, 201 (1979).
- [3] G. FORMICKA-KOZŁOWSKA, H. KOZŁOWSKI, G. KUPRYSZEWSKI, *Inorg. Chim. Acta*, **46**, 29 (1980).
- [4] G. FORMICKA-KOZŁOWSKA, H. KOZŁOWSKI, M. BEZER, L.D. PETTIT, G. KUPRYSZEWSKI, J. PRZYBYLSKI, *Inorg. Chim. Acta*, **56**, 79 (1981).
- [5] G. FORMICKA-KOZŁOWSKA, M. BEZER, L.D. PETTIT, *J. Inorg. Biochem.*, **18**, 335 (1983).
- [6] H. KOZŁOWSKI, M. BEZER, L.D. PETTIT, M. BATAILLE, B. HECQUET, *J. Inorg. Biochem.*, **18**, 231 (1983).
- [7] M. BATAILLE, G. FORMICKA-KOZŁOWSKA, H. KOZŁOWSKI, L.D. PETTIT, I. STEEL, *J. Chem. Soc., Chem. Commun.*, **231** (1984).



PS5.6 — TH

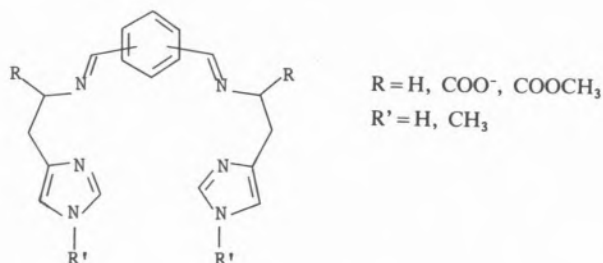
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MONONUCLEAR AND BINUCLEAR COPPER(I) AND COPPER(II) COMPLEXES DERIVED FROM L-HISTIDINE AND L-*N*⁷-METHYLHISTIDINE

The imidazole groups of histidine residues appear systematically involved in metal binding at the active site of copper proteins and enzymes, parti-

cularly those that function as oxygen carriers or promote some kind of oxygen activation [1]. Recently some copper(I) complexes containing the imidazole groups of histamine or histidine residues have been reported, also by us, to exhibit an apparent partially reversible oxygenation behavior in solution [2,3]. Though, in general, the oxygenated species in these or other systems [4] do not mimic the spectral features of the corresponding protein derivatives.

We have synthesized a series of mononuclear and binuclear copper(I) and copper(II) complexes of the ligands derived from the condensation of phthalic dicarboxaldehydes and two molecules of histamine, L-histidine, or their *N*⁷-methylated derivatives:



The binuclear copper(I) complexes are formally two-coordinate, while additional ligand molecules are required to obtain the corresponding copper(II) complexes. By changing the type of substitution of the xylil residues and the nature of the additional ligands we expect to vary the distance between the metal ions in the binuclear complexes, while the substituents R and R' affect the donor properties and charge of the ligands. The characterization of the complexes and the reactivity to dioxygen and other molecules of the copper(I) systems will be discussed.

REFERENCES

- [1] T.G. SPIRO (ed.), «Copper Proteins», Wiley, New York, 1981.
- [2] M.G. SIMMONS, C.L. MERRILL, L.J. WILSON, L.A. BOTTOMLEY, K.M. KADISH, *J. Chem. Soc., Dalton Trans.*, **1827** (1980).
- [3] L. CASELLA, M.E. SILVER, J.A. IBERS, *Inorg. Chem.*, **23**, 1409 (1984).
- [4] K.D. KARLIN, R.W. CRUSE, Y. GULTNEH, J.C. HAYES, J. ZUBIETA, *J. Am. Chem. Soc.*, **106**, 3372 (1984).



PS5.7 — MO

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CO-ORDINATION ABILITY OF AN *N*-TERMINAL TETRAPEPTIDE FRAGMENT OF FIBRINOPEPTIDE A

Spectroscopic and potentiometric studies of the interaction of Cu(II) with an *N*-terminal fragment of fibrinopeptide A have shown considerable specificity of an aspartic acid residue (Asp-2) in

metal ion binding. In the system Cu(II) — Ala-Asp-Ser(Bzl)-Gly four distinct species are formed involving all together the NH₂ group (Ala) and three amide nitrogens (see Fig. 1). Correlation of the spectroscopic and potentiometric data (Table I) allows assignment of the species CuL to co-ordination between Cu and NH₂(Ala) and the neighbouring peptide oxygen, CuH₋₁L to NN co-ordination (NH₂, N⁻), CuH₋₂L to NNN co-ordi-

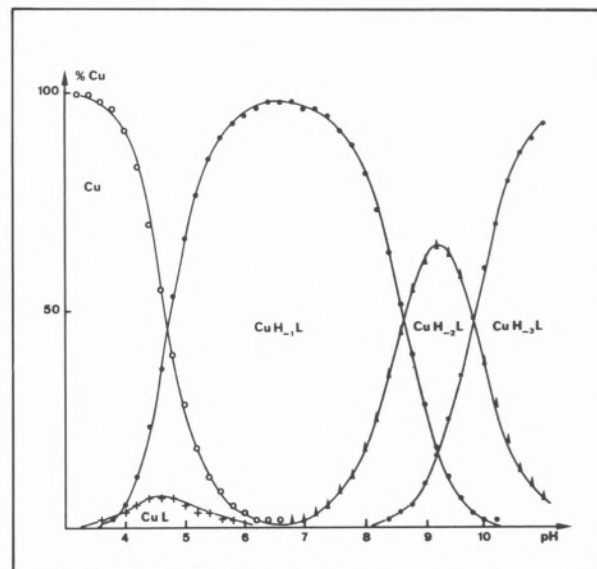


Fig. 1

The distribution of species as a function of pH for solutions containing Copper(II) and Ala-Asp-Ser(Bzl)-Gly with 1:1 metal to peptide molar ratio.

Table I

Formation constants and spectroscopic data of proton and Cu(II) complexes with Ala-Asp-Ser(Bzl)-Gly

Species	log β (or K)	Absorption spectra d-dλ _[nm] (εl. M ⁻¹ cm ⁻¹)	CD spectra λ _[nm] (Δε)	EPR spectra g A (G)
LH	8.332(NH ₃ ⁺)			
LH ₂	3.700(βCOOH)			
LH ₃	2.510(αCOOH)			
CuL	6.18			
CuH ₋₁ L	2.28	635(84)	618(+0.09)B + E ^{a)} 298(-0.78)N ⁻ → Cu(II) ^{b)} 264(+0.58)NH ₂ → Cu(II) ^{b)}	2.245 192
CuH ₋₂ L	- 6.39	625(130)	590(-0.26)B + E 298(-0.48)N ⁻ → Cu(II) 259(+1.9)NH ₂ → Cu(II)	
CuH ₋₃ L	-16.2	510(180)	520(-1.8)B + E 300(+0.84)N ⁻ → Cu(II) 272(-0.4)NH ₂ → Cu(II)	2.179 210

a) d-d transitions. b) charge transfer transitions.