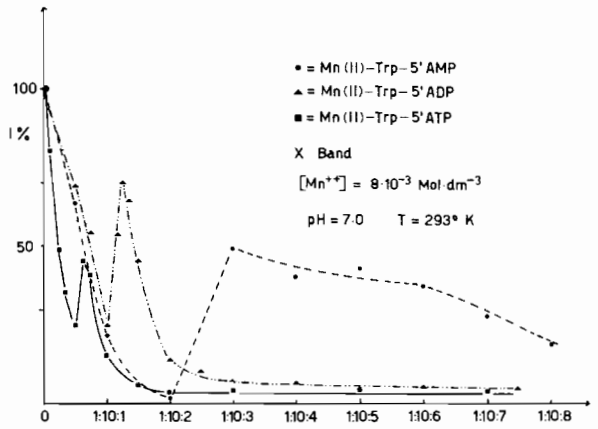

Fig. 1.

centration, the predominant species becomes Mn(II)–$L_2)_2$, E.S.R. undetectable [7].

The intensity minima of ternary systems occurring at different molar ratios point to the fundamental role of the phosphate groups in the stabilization of mixed coordination.

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About the Origin of a Novel Fluroescence Observed in Metallo-proteins

M. BACCI, R. LINARI

Istituto di Ricerca sulle Onde Elettromagnetiche del C.N.R., Florence, Italy

F. RICCHELLI, B. SALVATO

Centro Emocianine del C.N.R., Padua, Italy

Very recently [1] new fluorescence bands at 415–445 nm have been described for ceruloplasmin, tyrosinase and haemocyanin, when these copper-proteins are excited within their absorption band at 325–345 nm. The excitation spectra show the occurrence of a chromophore absorbing at *ca.* 330 nm and the fast decay time ($\leqslant$10 ns) should exclude any phosphorescence.

Although in the apo-proteins the absorption band at 325–345 nm, typical of Type 3 sites, has nearly completely disappeared, the excitation peak at 330 nm is still present and moreover the quantum yield of the fluorescence strongly increases. Therefore the absorption due to the copper(II) pair should hide the less intense residual absorption produced by the true fluorophore, while the only role of the copper is the quenching of the fluorescence.

Furthermore a quite analogous fluorescence has been found in several proteins obtained from different sources and having different catalytic functions (Table I), and in carboxylic and amino acids as well.

TABLE I. Behaviour of Proteins and Peptides under Excitation at 330 nm.

Compound	Fluorescence at 400–450 nm
Ceruloplasmin	yes
Haemocyanin	yes
Apo-haemocyanin	yes
Tyrosinase	yes
Catalase	yes
Peroxidase	yes
Cytochrome *c*	yes
Dopamine-β-hydroxylase	yes
Subtilisin	yes
Valinomycin	no
Gramicidin D	no

Measurements of the intensity of the fluorescence as a function of pH, concentration and different added metal ions, performed on solutions of pure carboxylic and amino acids, seem to indicate free carboxylate groups as mainly responsible for such a fluorescence, while an inter- or intra-molecular hydrogen bond probably also plays an important role.

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