1 H. Kozłowski, M. Bezer, L. D. Pettit, M. Bataille and B. Hecquet, *J. Inorg. Biochem.*, (in press).
2 G. Formicka-Kozłowska, H. Kozłowski, I. Z. Siemion, K. Sobczyk, and E. Nawrocka, *J. Inorg. Biochem., 15*, 201 (1981).
3 H. Kozłowski, G. Formicka-Kozłowska and L. D. Pettit, *J. Pure Appl. Chem.*, (in press).

U16

Spectroscopic Studies of Cu(II) Complexes with Proline and Lysine Containing Octapeptide

G. FORMICKA-KOZŁOWSKA, D. KONOPIŃSKA, H. KOZŁOWSKI

Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

and B. DECOCK-LE REVEREND

Lab. de Chimie Macromoléculaire, Université des Sciences et Techniques de Lille, 59-655 Villeneuve d'Ascq, Cedex, France

Recent studies on Cu(II) complexes with proline containing peptides have shown that the proline residue may act as a 'break-point' in the peptide sequence unless it is on a N-terminal position [1, 3].

The lysine residue, on the other hand, may in specific cases bind the metal ion *via* its lateral NH_2 group [2]. The dog double tuftsin octapeptide, Thr–Lys–Pro–Lys–Thr–Lys–Pro–Lys, contains both Pro and Lys residues and its coordination ability was checked in the system with cupric ions.

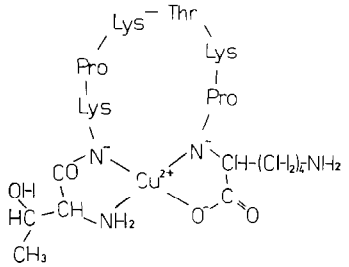

Fig. 1. Proposed structure of the 3N complex.

The EPR, absorption and CD spectra of Cu(II) octapeptide solutions suggest the presence of three different species formed at 3–10 pH range (Table I). The charge transfer region in the CD spectra in which two CT bands are observed at 280 nm ($\Delta\epsilon = -1.7$ for pH 10) and 325 nm ($\Delta\epsilon = +0.4$, pH 10) indicates the involvement of N-terminal NH_2 group (Thr) and one or two amide nitrogen donors [1–4]. The involvement of the lysine NH_2 lateral group seems to be less likely since no CT band for such coordination mode (at 250–270 nm, see ref. 2) could be observed.

The detailed considerations of the structure and the binding mode in 3N species (Table I, ref. 1, 4) lead to the unusual conclusion that the Cu(II) ion binds two octapeptide terminals (NH_2, N^- of N-terminal and N^-, COO^- of C-terminal) and that five central amino acid residues create a loop-like structure. It seems that octapeptide itself has a bent structure which could be additionally stabilized by the metal ion coordination.

TABLE I. Spectroscopic Characterization of Complex Species Formed in Cu(II) Thr–Lys–Pro–Lys–Thr–Lys–Pro–Lys System.

Species	d–d transition		CD		EPR	
	λ, nm	ε	λ (nm)	(Δε)	$A_\parallel$ (G)	$g_\parallel$
1N	750	25	780sh	(–)		
			760	(–0.02)		
2N	610	100	690sh	(–)	162	2.300
			640	(–0.28)		
3N	550	170	560	(–0.45)	170	2.212
			460	(+0.04)		

The results obtained may indicate the new way of synthesis of the model systems in which metal ion is bound *e.g.* to protein without formation of the subsequent 5- or 6-membered chelate rings characteristic for low-molecular weight models. It seems also to be evident that proline residue, even if not bound directly to metal ion, plays a critical role in the metal–peptide complexation mode.

1 H. Kozłowski, M. Bezer, L. D. Pettit, M. Bataille and B. Hecquet, *J. Inorg. Biochem.* (in press) and references therein.
2 S. Salardi, L. Tosi, A. Garnier-Suillerot, C. Toniolo, B. M. Bonora and F. Marchiori, *Biopolymers, 21*, 1229 (1982) and references therein.
3 G. Formicka-Kozłowska, H. Kozłowski, M. Bezer, L. D. Pettit, G. Kupryszewski and J. Przybylski, *Inorg. Chim. Acta, 56*, 79 (1981) and references therein.
4 G. Formicka-Kozłowska, D. Konopińska, H. Kozłowski and B. Decock-le Reverend, *Inorg. Chim. Acta, 78*, L47 (1983).

U17

Interaction of Metal Ions with Peptide Hormones

GRAZYNA FORMICKA-KOZŁOWSKA

Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

LESLIE D. PETTIT

School of Chemistry, University of Leeds, LS2 9JT Leeds, U.K.

Among our studies concerning the coordination chemistry of naturally occurring peptides we have