TABLE II. Carboxylate Stretching Frequencies (cm^{-1}) of Dehydrated Metal Pectates and the Difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$.

Metal ion	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta = \nu_{as} - \nu_s$
Al^{3+}	1656vs	1420vs	236
VO^{2+}	1635vs	1400vs	235
Cr^{3+}	1630vs	1408vs	222
Fe^{2+}	1623vs	1412vs	211
Co^{2+}	1626vs	1415vs	211
Zn^{2+}	1625vs	1415vs	210
Ni^{2+}	1622vs	1412vs	210
Cu^{2+}	1620vs	1410vs	210
Mg^{2+}	1632vs	1426vs	206
Mn^{2+}	1619vs	1415vs	204
Ca^{2+}	1613vs	1420vs	193
Na^+	1613vs	1413vs	200

3d-transition metal and aluminium pectates in contrast to the bidentate bond [3].

Three interesting changes can be seen in the 'finger print' range of 1000–600 cm^{-1}. The band at 946–950 cm^{-1}, which can be assigned to pyranose ring skeletal mode displacement involving α-(1–4) linkage [4], shifts to higher frequencies within the range of 956–960 cm^{-1}. This change may be brought about by the bond between metal ion and glycosidic oxygen atom, which results in the stretching of the $C(1)–O_{glycos.}–C(4')$ angle and in higher frequencies.

The weak band at 790 cm^{-1} which could be assigned to the deformation of OCO^- bending [5], shifts to range of 812–816 cm^{-1}, depending on the polarizing properties of bonded metal ions. This shift is due to the covalent metal–carboxylate bond.

Finally the weak band at 735 cm^{-1}, which could be assigned to ring breathing vibration, shifts to the band at 762–766 cm^{-1} in the presence of metal bonds. This shift is probably caused by the metal bond to the ring oxygen atom.

Similarly, the ring oxygen atom and Ca^{2+} ion bond was assumed by Walkinshaw and Arnott [6] for the speculative model of calcium pectate on the basis of the X-ray fiber diffraction pattern. In the case of calcium alginate a glycosidic and a ring O and Ca^{2+} bond was proposed by Angyal [7].

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U15

Spectroscopic and Potentiometric Studies on Coordination Abilities of Tetrapeptides Containing Proline and Tyrosine or Phenylalanine

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The insertion of proline residues, a 'break-point' [1–3] in the second position of a tetrapeptide divides the ligand molecule into two fragments which are potentially able to interact with metal ions independently, *i.e.* the N-terminal aminoacid (*e.g. via* NH_2, CO) and two C-terminal aminoacid residues (*via e.g.* $2N^-$, COO^-). The introduction of tyrosine to such a peptide sequence complicates solution equilibria distinctly [1, 3]. Phenylalanine, which is not able to use its side-chain for the direct metal ion binding, is a good analogue for tyrosine and both residues were used for the synthesis and the study of the coordination abilities of tetrapeptides.

The spectroscopic and thermodynamic studies of cupric complexes with tetrapeptides: Gly–Pro–Gly–Tyr, Gly–Pro–Tyr–Gly, Tyr–Pro–Gly–Gly, Gly–Pro–Phe–Gly, Gly–Pro–D–Phe–Gly and Phe–Pro–Gly–Gly have shown that the metal peptide interaction always starts at the N-terminal (NH_2, CO donors). The tyrosine residue may involve its side-chain OH in the metal ion binding with formation of monomeric or dimeric species. The complex equilibria strongly depend on the position of tyrosine residue in the peptide sequence. The lack of the direct involvement of phenylalanine side-chain in the direct metal ion coordination leads to much simpler equilibria. The presence of proline residue in the ligand molecule causes very unusual coordination modes in the formal complex species with formation of unusually large chelate rings.

The combination of spectroscopic and potentiometric approaches led to the satisfactory description of very complicated systems which may be used as reasonable spectroscopic and structural models for biosystems.

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U16

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

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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.

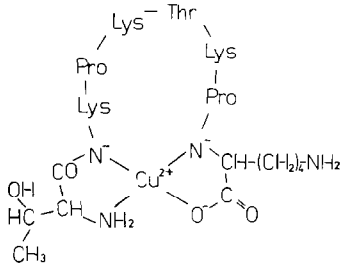

Fig. 1. Proposed structure of the 3N complex.

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.

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Interaction of Metal Ions with Peptide Hormones

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