iron(III)-complexes show inner-sphere coordination with polynuclear structure [7, 8].

The structure of inner-sphere complexes will be studied by IR spectroscopy (see next paper).

According to animal and human investigations, Mg and transition metal complexes of PAH in gel or dehydrated form are suitable for *per os* treatment of iron-deficient anaemia, Mg-deficient ischemic heart diseases [9] and all trace-metal deficient diseases. $Fe[(PA)(NO_3)_2]_3$ was applicable for parenteral, *i.e.*, intravenous administration of iron(III) to pigs. Unfortunately, however, $Fe[(PA)(SO_4)_2]_3$ was found to be toxic.

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Infrared Spectroscopic Study on Metal Pectates

B. LAKATOS, S. HOLLY and J. MEISEL

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1025 Budapest, Hungary

According to EPR and Mössbauer spectroscopical measurements, some 3d-transition metal pectates in fully hydrated colour gel states form outer-sphere coordination complexes [1]. These outer-sphere complexes were transformed to inner-sphere coordination complexes with water elimination and change of colour after dehydration at 105 °C. The comparison of the IR-spectra of these dehydrated metal complexes with those of pectic acid may provide some information on the inner-sphere coordination structure.

The dehydrated samples were pulverized and compressed into disks, after being stirred for 3 min in a vibrator with KI. IR-spectra were recorded on a Perkin Elmer Model 225 spectrophotometer.

TABLE I. Characteristic IR Absorption Frequencies of Pectic Acid and Dehydrated Metal Pectates.

Band maxima (cm^{-1})					Assignment
Pectic acid	Ca-pectate	Mg-pectate	Mn-pectate	Cu-pectate	
3450vs	3450vs	3430vs	3400vs	3440vs	ν_{OH}
2930m	2930m	2930m	2930m	2920m 2940m	ν_{CH}
2600w	–	–	–	–	
1745vs	–	–	–	–	$\nu_{CO}(COOH)$
–	1613vs	1632vs	1619vs	1620vs	$\nu_{as}(COO^-)$
–	1420vs	1426vs	1415vs	1410vs	$\nu_s(COO^-)$
1400s	–	–	–	–	
1330s	1332s	1330s	1328s	1326s	β(COH)
1216s	1235m	1234m	1228m	1232m	β(COH)
1140s	1145s	1145s	1142s	1145s	ν_{C-O} and ν_{C-C}
1096vs	1094vs	1094vs	1092vs	1094vs	
1070s	1072m	1074m	1072m	1070m	
1045s	1046m	1042m	1042m	1044m	
1016vs	1014s	1012s	1012m	1012m	
948s	958s	956s	956s	954s	α(1–4) and ring skeletal
886m	894m	890w	888w	888w	β(CH) and ν_{COC}
828m	836m	832m	830m	830w	
786w	816w	812w	812w	816w	$\beta(COO^-)$
735w	766w	762w	760w	762w	ring-breathing
630m	646m	638m	634m	636m	γ_{OH}

Key to intensities: vs = very strong, m = moderate, w = weak.

The observed characteristic frequencies of IR-spectra of dehydrated metal pectates and pectic acid can be seen in Table I.

Within the range of 4000–2800 cm^{-1} and 1400–1000 $cm^{-}1$ no significant difference can be detected in the IR absorption spectra of dehydrated metal pectates and pectic acid. Thus we came to the conclusion that probably no direct chemical bond exists between metal ions and carbohydrate OH groups of the pectic chain.

Contrary to this, the intensity of the ν_{CO} stretching frequency of the carboxylic group of pectic acid at 1745 cm^{-1} decreases with the increase in the amount of metal ions substituting carboxylic hydrogen ions. According to the degree of substitution, two intensive bands can be simultaneously observed within the range of 1660–1580 cm^{-1} and 1430–1400 cm^{-1}. The former band may be assigned to antisymmetric $\nu_{as}(COO^-)$ stretching vibration of carboxylate groups and the latter band to symmetric $\nu_s(COO^-)$ stretching. As the difference (Δ) between the frequencies of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is greater in the case of the covalently complexed carboxylate ion than in the uncomplexed anion (see Table II), an unidentate metal–carboxylate bond [2a, b] could be proposed in the case of dehydrated

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

H. KOSŁOWSKI

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

M. BEZER, L. D. PETTIT

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

S. DJAMIL and M. BATAILLE

Laboratoires de Chimie Biologique et Chimie Macromoleculaire, Université des Sciences et Techniques de Lille, 59-655 Villeneuve d'Ascq, Cedex, France

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.