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EPR and Mössbauer Spectroscopic Studies on Metal Complexes of Pectic Acid and their Derivatives

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Foods are more and more deficient in Mg and trace metals, due to the use of increasing amounts of NPK fertilisers, liming and high costs of trace metal fertilization as well as to the purification and refinement of raw nutriments. Recently, for the substitution of these metals, instead of inorganic salts or artificial metal chelates, metal complexes of biopolymers have been used [1], which, administered *per os* to vertebrates, can be absorbed and utilized without harmful side effects. Metal bonds in biopolymers are presumably similar to those in foods, and therefore will be studied by EPR and Mössbauer spectroscopy.

Pectic acid (PAH), which contains polygalacturonic acid and some neutral carbohydrates, *e.g.*, rhamnose, was prepared by the alkaline hydrolysis of pectin [1]. Derivatives of PAH as pectic acid dinitrate $(PA)(NO_3)_2H$ and pectic acid disulphate $(PA(SO_4)_2H_3$ were obtained by treatment of PAH with conc. HNO_3 [2] and with the N,N-dimethyl formamide-sulphur trioxide complex [3a, b], respectively. We have produced metal pectates as insoluble colour gels by the reaction of PAH with Cr(III)-, MoO(III)-, Fe(III)-, Mn(II)-, VO(II)-, Cu(II)-, Fe(II)-, Co(II)- or Ni(II)-sulphate in aqueous solutions [1] and metal complexes of PAH derivatives as water soluble compounds.

The EPR data of PAH gel doped with Mn^{2+}, Cu^{2+} and VO^{2+} ions show outer-sphere arrangement (Table I) similar to Ca alginate and agarose gels [4] doped with Mn^{2+} and Cu^{2+} ions. In the case of $(PA)(SO_4)_2H_3$ doped with Mn^{2+}, Cu^{2+} and VO^{2+} ions we have also found outer-sphere complexes in the hydrated (freeze dried) state. $(PA)(NO_3)_2H$ doped with Mn^{2+} ions also forms an outer-sphere complex, however, with Cu^{2+} ions it results in an inner-sphere complex and with VO^{2+} ions it gives both types of complexes: (1) outer-sphere and (2) inner-sphere arrangements (Table I). After dehydration (at 105 °C) of fully hydrated samples with an outer-sphere arrangement, EPR parameters will change due to transition of (1) to (2), however, in the case of inner-sphere complexes practically no change in EPR parameters can be observed [5a,b, 6].

TABLE II. Mössbauer Parameters for Iron(II) and Iron(III) Compounds at the Temperature of Liquid Air.

Compound	I.S. (mm s^{-1})	Q.S. (mm s^{-1})
$FeSO_4 \cdot 7H_2O$	1.48	3.4
Fe(II)alginate	1.42	3.21
$Fe(PA)_2$	1.40	3.15
$Fe_3[PA(SO_4)_2]_2$	1.37	3.08
$Fe[PA(NO_3)_2]_2$	1.40	3.05
Fe(II)-Dowex-Al Chelating Resin	1.30	2.91
$Fe(PA)_3$	0.45	0.90
$Fe[PA(SO_4)_2]$	0.40	0.60
$Fe[PA(NO_3)_2]_3$	0.46	0
$Fe_2(SO_4)_3$	0.65	0

The quadrupole splitting (Q.S.) value in the Mössbauer spectra of freeze dried iron(II) pectate also shows an outer-sphere arrangement (Table II). After dehydration (at 105 °C) the value of Q.S. decreased from 3.15 to 2.91 mm•s^{-1} [7, 8]. In the case of PAH derivatives the Q.S. values decreased with the decrease of water content in the first coordination sphere of iron(II). The Q.S. values of

TABLE I. EPR Data for Mn^{2+}, VO^{2+} and Cu^{2+} Ions Doped in Various Samples.

Metal ion	Mn^{2+}		VO^{2+}			Cu^{2+}		
Host lattice	A_{iso} (G) hpf split.	$\Delta\nu$ (G) line width	A_{iso} (G)	$A_\parallel$ (G)	$A_\perp$ (G)	$g_\parallel$	$g_\perp$	$A_\parallel$ (G) hpf split.
			hpf-splitting			spect. split.		
H_2O	−95.0	30.4	119.7	203	78	2.422	2.087	−118.5
PAH	−96.0	64; 28	112.2	195.6	70.5	2.403	2.081	−120
$PA(SO_4)_2H_3$	−94.7	41; 61; 82	113.9	195.2	73.2	2.376	2.089	−131
$PA(NO_3)_2H$	−91.8	36	(1) 114.4 (2) 108.5	196.1 187.8	73.6 68.9	2.318	2.070	−154
Oxalate	−91.1	22.9	103	180	65	2.318	2.071	−151.5

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

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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	–	–	–	–	ν_{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