Interactions of starch with salts of metals from the transition groups

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Abstract

Interpretation of EPR spectra of combinations of gelatinized one of amylopectin, cornstarch, waxy cornstarch, and potato starch with one of Co (II), Cr (III), Cu (II), Fe (III), and Mn (II) produced evidence for the formation of the Werner-type complexes with metal central atom and polysaccharide as the ligand. Ligation of the central atom involved lone electron pairs of the polysaccharide hydroxyl groups. Results of complexation depended on metal cation and polysaccharide as well as a form in which it was examined. Formation of complexes with granular starch was additionally confirmed by appearance of starch granules soaked in aqueous salt solutions in scanning electron microscopy. © 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Rendleman (1978) and Tomasik and Schilling (1998) described several complexes formed by starch and salts of metals from transition groups. Potato starch with random phosphoric acid moieties bound to amylopectin formed metal complexes with involvement of these moieties (Leszczyński, 1985). Recently, a group of metal starch derivatives were reported, including iron (III) (Tomasik, Jane, Spence, & Anderegg, 1995), titanium (IV) (Tyrlik, Tomasik, Anderegg, & Bączkowicz, 1997), and lanthanum (Tomasik, Schilling, Refvik, & Anderegg, 2000) atoms bound covalently to the hydroxyl oxygen atoms. They were prepared by 'rusting' reduced iron powder in starch gel and by reacting starch with corresponding metal alkoxides [Ti (IV) and La]. Preparation of starch complexes from alkali starch and salts of any metal from either non-transition (A) or transition (B) groups were patented (Stern, 1928). The same structure was assigned to these products but in view of our recent results (Lii, Tomasik, Hung, & Lai, 2002) such structure of these metal derivatives should be questionable. It was proven (Ahmad & Williams, 1999; Kostuch, Urban, & Tomasik, 2000; Lii et al., 2002) that contrary to many opinions (De Willigen, 1953; De Willigen & De Groot, 1971; Jane, 1993; Oosten, 1982, 1983) alkali metal (IA group) salts interact with starch with involvement of their anions rather than cations. On the other hand, in solutions of the salts of metals from higher non-transition groups also cations interact with starch (Lii, Tomasik, Yen, & Lai, 2001).

Interactions between salts of metals from transition groups and starch have been already investigated on $CuSO_4$ (Mellanby, 1919), silver (I) halides (Itoh, 1966), $ZnCl_2$ (Hart, 1966), HgI (Samuel, 1948), and titanium carboxylates (Langkammerer, 1949). Several Fe (III) complexes were also reported (Farbenfabriken Bayer, 1968; Krause, Bełżyńska, Jagodziński, & Krochmal, 1961; Krause & Rychlewska, 1962; Mellanby, 1919; Shi, 1989; Synowiecki, 1961; Zhang, Chen, & Zhang, 1988). In several cases complexes described were sorption complexes in which amylopectin rather than amylose was indicated as the place of sorption (Klotz, 1961; Krause, 1960; Synowiecki, 1961). The problem of penetration of the interior of starch granules by either salts or ions remained unrecognized and it became the subject of our studies.

2. Materials

Amylopectin from corn was purchased from Fluka (Switzerland). Native waxy maize starch was kindly provided by Central Laboratory of the Polish Potato
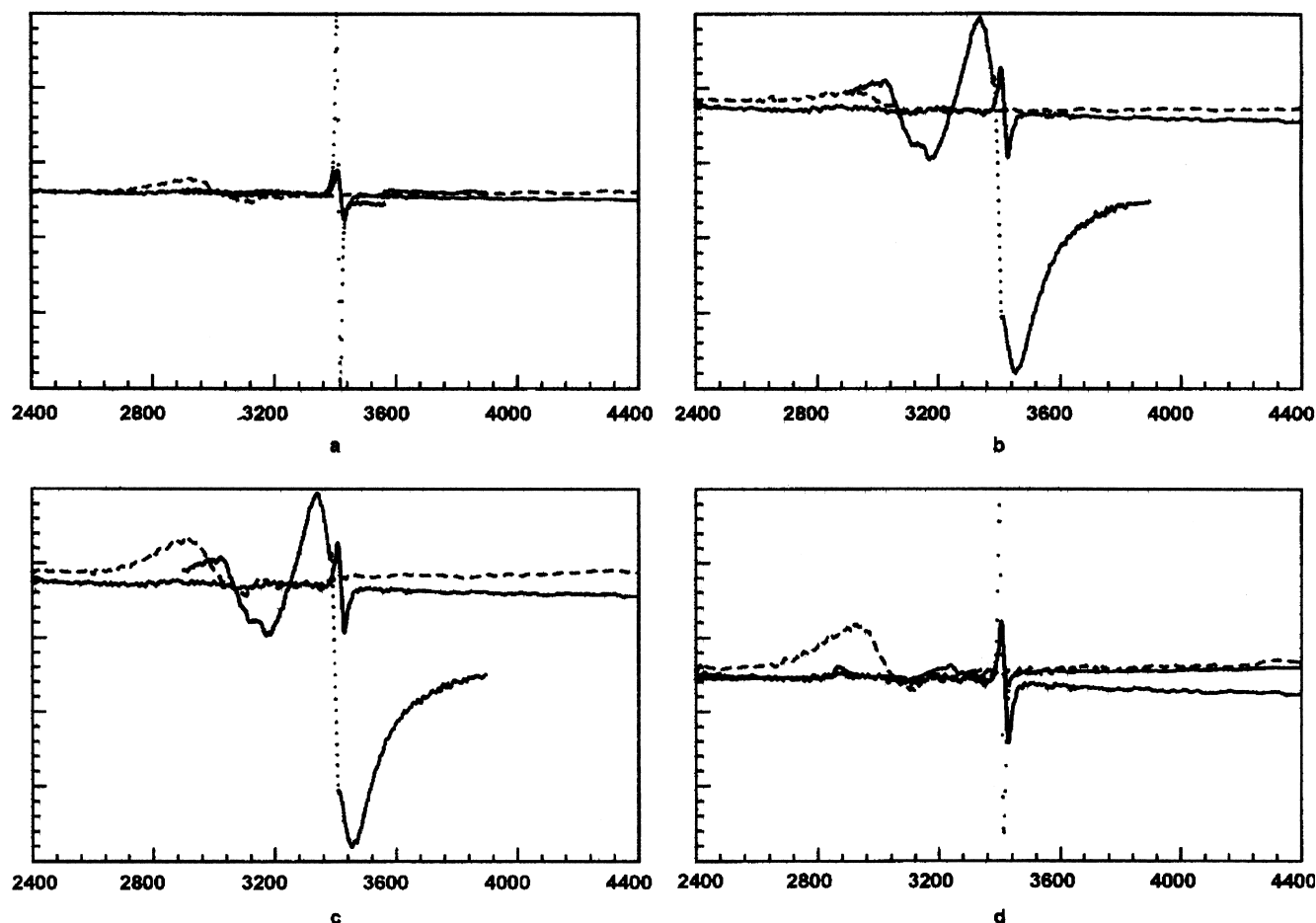
Fig. 1. EPR spectra of complexes of $CoSO_4$ with amylopectin (a), cornstach (b), waxy cornstarch (c), and potato starch (d). Solid line: spectrum of salt; pointed line: spectrum of sample from experiment B; broken line: sample from experiment C.

Industry in Poznan, Poland. Potato starch was purchased from MATIZOLBUD (Zalesice, Poland). All Co (II), Cr (III), Cu (II), Fe (III), and Mn (II) were sulfates of analytical grade, from POCh Factory of Chemicals (Gliwice, Poland).

Ethanol, 96%, of analytical grade was product of POCh Gliwice, Poland.

3. Methods

3.1. Pasting of starch

Seven percent of aqueous starch suspensions (w/w) was heated at a steam bath for 1 h with continuous agitation. Starch from the paste was collected by precipitation with 96% ethanol, followed by air-dried to 12.7% water content.

3.2. Preparation of samples

Samples were prepared according to one of three procedures:

• *Procedure A*: solid polysaccharide (2 g) was blended

with solid salt (10 w/w%) and thoroughly shaken.
• *Procedure B*: solid polysaccharide (2 g) was agitated for 24 h at room temperature in 0.1 M aq. solution of a salt (30 cm^3). After that time solid was filtered off and dried in an oven at 130 °C.
• *Procedure C*: solid, gelatinised polysaccharide (0.5 g) was agitated for 24 h at room temperature with 0.1 M aq. salt solution (10 cm^3) then precipitated with ethanol (20 cm^3). Samples prepared in solutions were dried (24 h at 50 °C) prior to thermolysis. All preparations were coloured typically for given inorganic salts.

3.3. EPR spectra

The spectra were recorded for powdered samples in the X-band region (9.5 GHz, $\lambda = 3.2$ cm) at room temperature. $CuSO_4$ was taken as the standard for the spin abundance (2.4×10^{21} spins/g) and DPPH was the standard for the g-factor. The apparatus was manufactured by Politechnika Wroclawska (Poland). The spectral curves were processed using the 2.8b MicroCal Origin program.
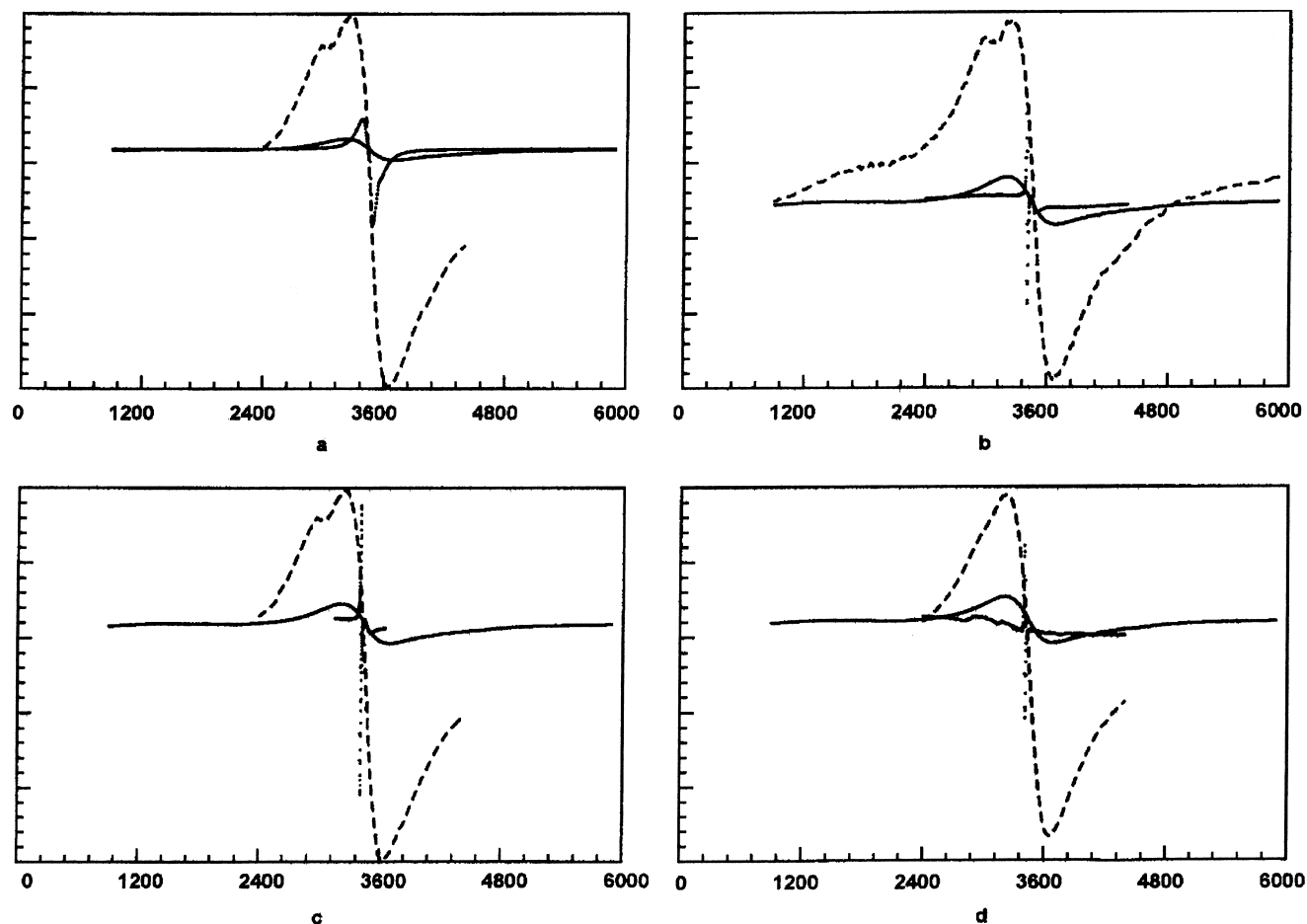
Fig. 2. EPR spectra of complexes of $Cr_2(SO_4)_3$ with amylopectin (a), cornstarch (b), waxy cornstarch (c), and potato starch (d). Solid line: spectrum of salt; pointed line: spectrum of sample from experiment B; broken line: spectrum of sample from experiment C.

3.4. Thermogravimetric, differential thermogravimetric, and differential scanning calorimetry analyses

Thermal DSC–TG (DSC, differential scanning calorimetric; TG, thermal gravimetric) analysis was carried out with the NETZSCH STA-409 simultaneous thermal analyser calibrated with standard indium, tin, zinc and aluminium of known purity (99.99%) of known temperature and enthalpy of melting. Samples (approximately 0.020 g) were heated in corrundum crucibles with non-hermetic lids. Corrundum was the standard. The heating was performed under static conditions in the air in the range of 20–450 °C with the temperature rate increase of 5 K/min. Recorded thermograms were analysed with the NETZSCH-TA-ANALYSIS programme. Measurements were duplicated. They provided the ± 0.5 °C precision in reading of temperature.

3.5. Scanning electron microscopy

Samples were dried in vacuo and then examined by using a scanning electron microscope (Zeiss DSM 950, Germany) operating at 15 keV.

4. Results

4.1. EPR studies

In this study evidence is given for the ligation of selected cations of metals from transition groups with starch. Metal cations were paramagnetic. In every case the EPR spectra were run for either granular or gelatinized cornstarch, waxy cornstarch, and potato starch, as well as plain, and gelatinized amylopectin. In the first series of experiments solid polysaccharides were thoroughly blended with solid hydrated salts. In this series of experiments no evidence could be found for interaction of polysaccharide with metal salts when the components were blended in the solid state. They could be considered as secondary control samples. g-Factor in the EPR spectra of such blends were only insignificantly different from that for plain salt.

In the second series of measurements all solid polysaccharides were agitated with 0.1 M aq.metal salt solutions. Pattern of the EPR spectra (Figs. 1–5) showed that there were clear interactions between polysaccharides and metal ions under investigation. Sharp signals in the spectra of pure salts, particularly of $CoSO_4$, should be ascribed to
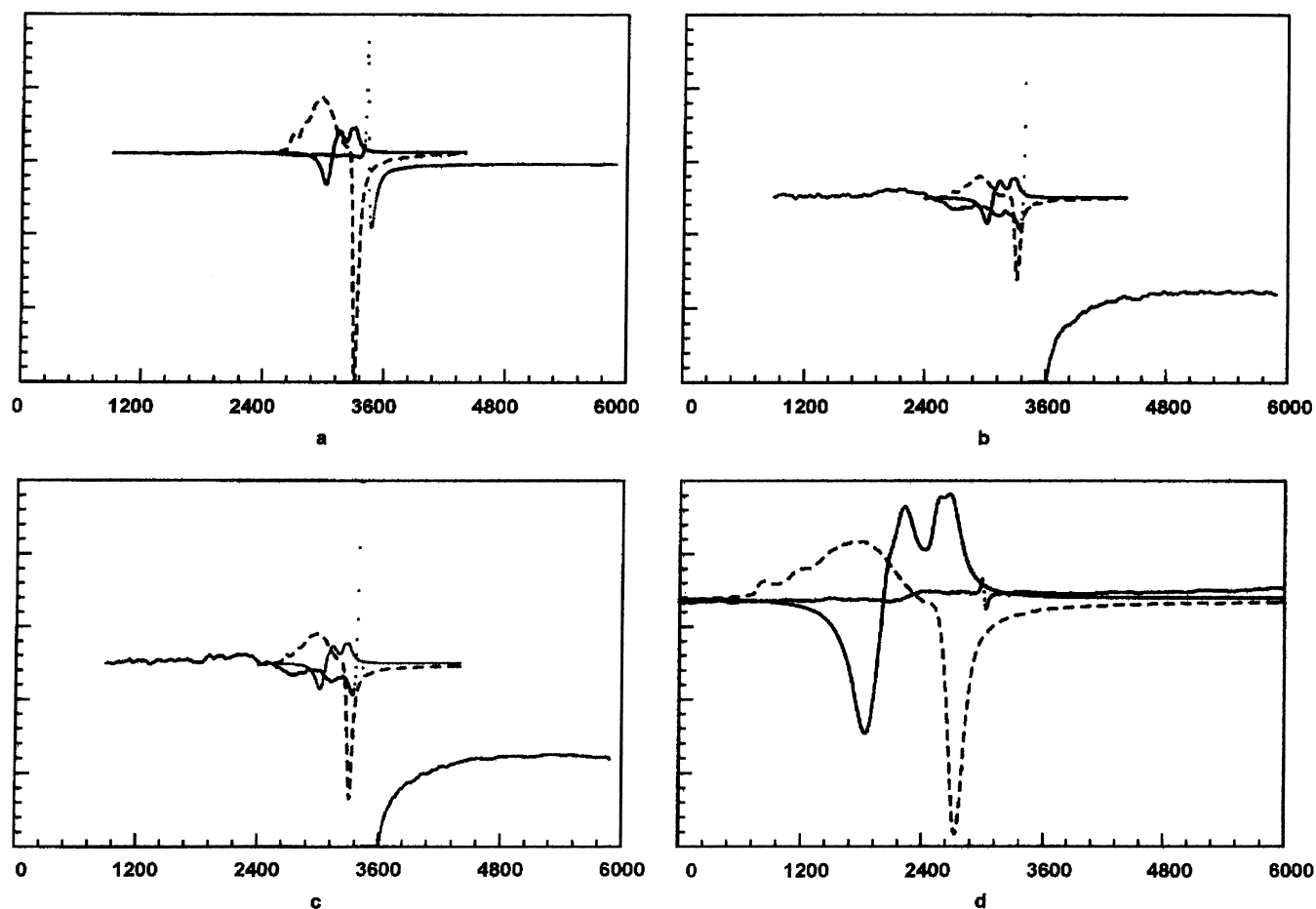
Fig. 3. EPR spectra of complexes of $CuSO_4$ with amylopectin (a), cornstarch (b), waxy cornstarch (c), and potato starch (d). Solid line: spectrum of salt; pointed line: spectrum of sample from experiment B; broken line: spectrum of sample from experiment C.

defects in solid salt lattice rather than to unpaired spins in corresponding metal ions. Corresponding signals in the spectra of samples of polysaccharides blended with aqueous solutions turned usually into typical spectra of ligated metal ions. This effect was particularly pronounced when metal ions were ligated by pasted polysaccharides. Granular, i.e. non-pasted polysacchrides could form complexes either by a sorption of metal ions on the granule surface or by penetration of ions into interior of starch granules. Since anions are capable of such penetration rather than cations (Lii et al., 2002) such complexes could have character of ion pairs with negatively charged salt anion containing granules and assisting cation. Sharp signals in the spectra of Cr (III) and Fe (III) sulfates suggested that these salts crystallized in starch forming defected lattices responsible for such pattern of the spectra. Inspection of g-factors in Table 1 pointed that this might happen also in case of cobalt salt with potato starch whereas cornstarch and waxy cornstarch ligated the cobalt cation.

In other cases g-value exceeded 2.200. It should be noted that contrary to potato starch (Baldwin, Adler, Davies, & Melia, 1994) cornstarch and waxy cornstarch had their outer shell perforated by micro-pores (Huber & BeMiller, 1997).

g-Factor in the spectra of these complexes split into a higher g-parallel and lower g-perpendicular. It could be strong evidence that on contact with starch some changes took place in the coordination sphere of the central metal atom and resulting complexes took tetrahedral symmetry. Using the same arguments formation of complexes of all granular starches and amylopectin with Cu (II) and Mn (II) could be postulated because original splits into g-parallel and g-perpendicular signals of pure salts ceased in the spectra of these salts after contact of aqueous salt solutions with these polysaccharides. A high g-value found in the spectrum of manganese salt with granular waxy cornstarch could not be considered as any evidence for the complex formation because this g-value and splitting were practically identical as in the spectrum of pure salt. Solid amylopectin did not form complexes when contacted with Co (II), Cr (III) and Fe (III) cations (Experiment A). In solid amylopectin lone electron pair orbitals of the hydroxyl groups capable of coordination were involved in the formation of intra- and inter-molecular hydrogen bonds. The energy of interactions with these metal cations could not break these hydrogen bonds. Complexes formed on blending are assumed to have the high-spin character. Such postulate could be rationalised
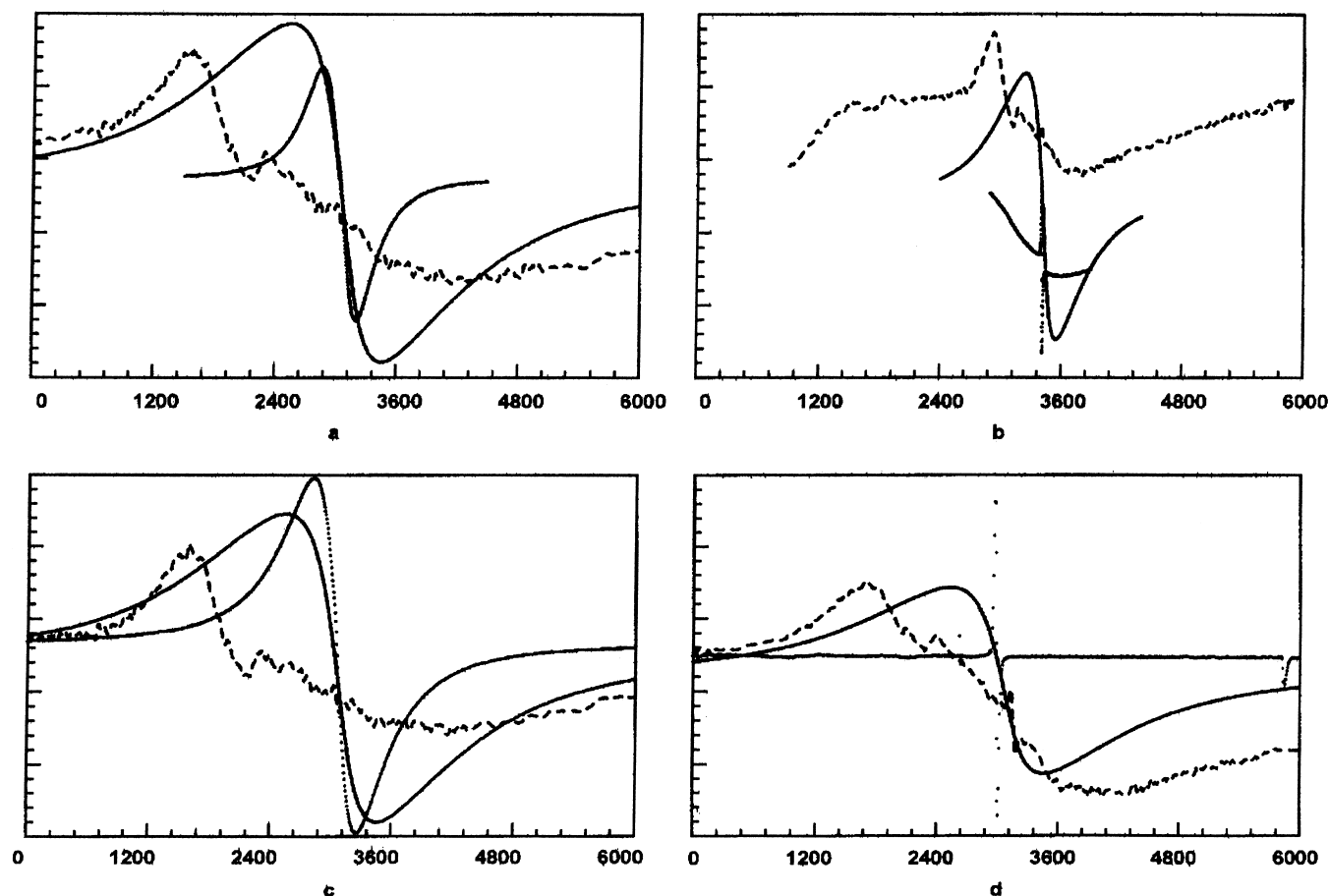
Fig. 4. EPR spectra of complexes of $Fe_2(SO_4)_3$ with amylopectin (a), cornstarch (b), waxy cornstarch (c), and potato starch (d). Solid line: spectrum of salt; pointed line: spectrum of sample from experiment B; broken line: spectrum of sample from experiment C.

by a formal similarity of polysacharides and water as well as alcohols. Thus, polysaccharides should ligate central metal atoms with involvement of the lone electron pair orbitals of the hydroxyl groups.

Gelatinised polysaccharides formed high-spin complexes with all metal cations under study (Table 1).

Values of g-factor in the relevant spectra of the samples prepared from solid polysaccharides and salt solutions suggested changes in the coordination sphere of the central metal atoms. Whenever splitting of the signal was observed [some Co (II), Cr (III), Cu (II), and Fe (III) complexes] higher g-parallel and lower g-perpendicular spoke for unpaired electron localised in the d_z2 orbital and tetrahedral symmetry around this central atom. Ligation of Mn (II) atom was manifested by a vanishing of the original splitting of the signal of Mn (II) in the spectrum of pure salt. Strong decrease in the signal of the Mn (II) ion in the sample prepared from granular potato starch indicated that that ion weakly orbed on the surface of that kind granules. Changes in the intensity of the signal of Fe (III) in the spectrum of granular cornstarch could be interpreted in similar manner. Attention should be paid to the spectra of Co (II) complexes. In several cases these spectra are well shaped and intensive in spite the measurements were carried out at room temperature. Frequently, spectra of cobalt complexes are available just from the measurements in liquid nitrogen.

4.2. Thermogravimetric and differential scanning calorimetric studies

Documented by varying EPR-spectral pattern changes in the coordination sphere of the central atoms upon their contact with pasted polysaccharides could originate from changes in the hydration of the central atom. Thermogravimetric and differential scanning calorimetric analyses of these complexes showed that except Cr (III) complex there was only residual amount of water either in the coordination sphere of the central atoms or/and in the starch matrix (Table 2).

Chromium sulfate octadecahydrate lost all water molecules up to 110 °C (Rollinson & Bailar, 1946) whereas the weight loss from the starch complex of Cr (III) begun at 129 °C (Table 2). Thus, one might accept that starch was able to repulse all water molecules from the coordination sphere of that central atom. Copper sulfate pentahydrate dehydrated into monohydrate to 110 °C (Macintyre, 1992) in order to turn into anhydrous salt at 250 °C. Since the weight loss from the complex begun at 188 °C only one
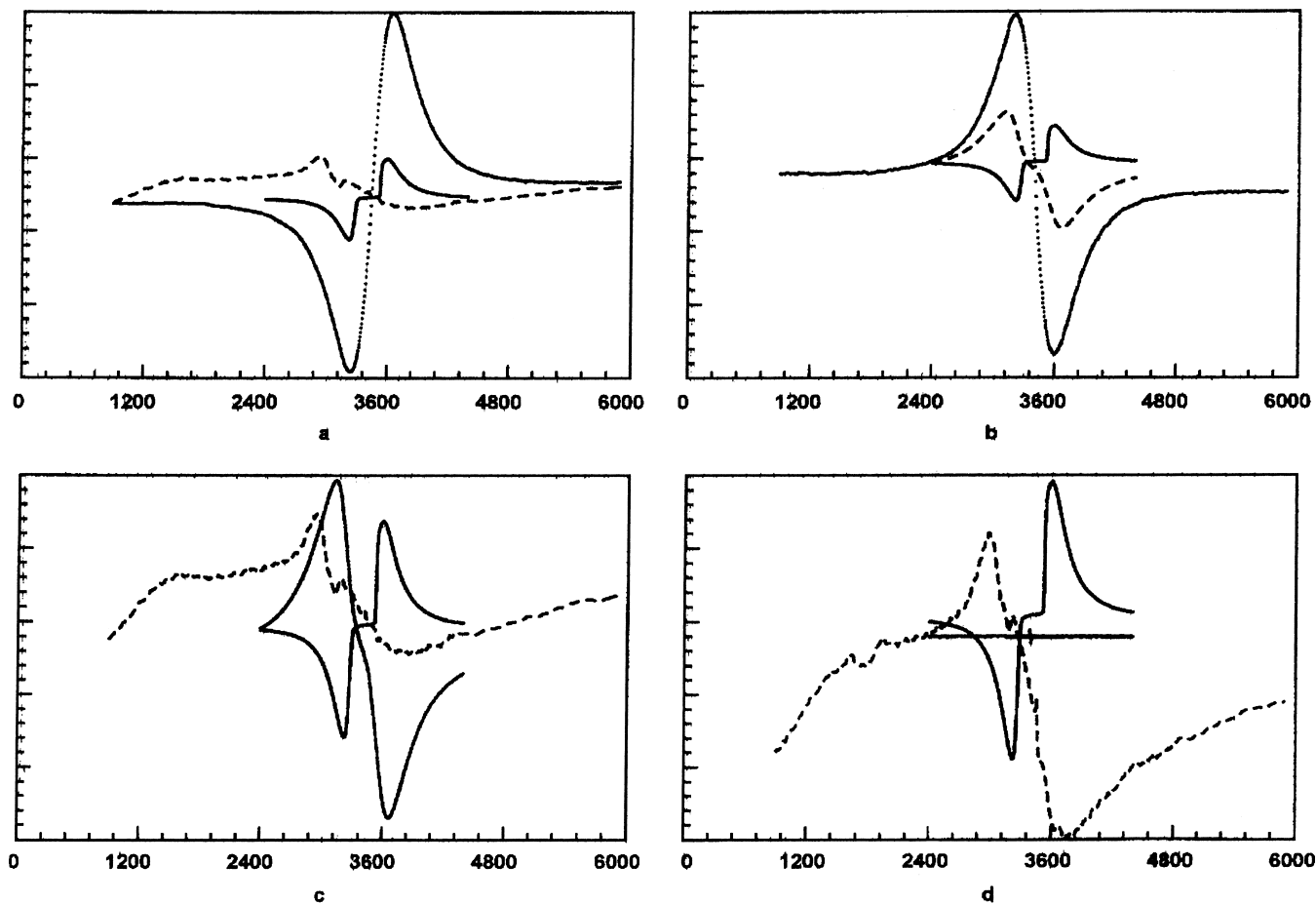
Fig. 5. EPR spectra of complexes of MnSO$_4$ with amylopectin (a), cornstarch (b), waxy cornstach (c), and potato starch (d). Solid line: spectrum of salt; pointed line: spectrum of sample from experiment B; broken line: spectrum of sample from experiment C.

water molecule could retain in the coordination sphere of Cu (II) in the starch complex. Hydrated Co (II), Fe (III), and Mn (II) sulfates lost all but one of their water of crystallisation up to 71, 140 and 100 °C, respectively. Full dehydration took place above temperatures noted for the beginning of the weight loss of the starch complexes with these metals (Macintyre, 1992) (Table 2). Therefore, also in these complexes retention of a single water molecule in the coordination sphere of these metals could be assumed.

It should be noted that in the thermogram (differential thermogravimeter, DTG) of pasted native potato starch after removal of water reflected by endothermic peak centered at 71 °C the subsequent effect at 260 °C associated with glassy transition followed by decomposition (Kapuśniak, Cie- sielski, Kozioł, & Tomasik, 1999) was also endothermic. In corresponding DTG-gram of complex with Cr (III) the first, effect which begun at 129 °C (TG) and centered at 149 °C (DTG) could correspond to the elimination of water from the coordination sphere of the central atom. This conclusion was consistent with presented above interpretation of EPR spectrum of that complex. In the spectrum the copper complex the first thermal effect was endothermic and it could be related to decomposition of starch without participation of the central metal atom. The first, exothermic

effects in the thermograms of Co (II), Fe (III), and Mn (II) complexes suggested beginning of some either redox reactions or metal ion catalysed air-oxidation in these steps of starch decomposition.

4.3. Elucidation of the structure of complexes

In the complexes with polysaccharides the Co (II) ion had the $d_{xy}2$, $d_{xz}2$, $d_{yz}2$, $d_{x}2-_{y}21$ configuration (Table 1). Because of high spin density at the Co atom it was coupled with the ligand. A large shift of the g-factor results from magnetic induction causing coupling of the $d_{x}2-_{y}2$ and d_{xy} orbitals.

In the complexes with the Cr (III) electrons of the central atom resided in the d_{xy}, d_{xz}, and d_{yz} orbitals. In the spectra (Table 1) splitting of g-factor was observed. It might be due to additional coupling of ligand with metal because of polarisation of σ-electrons of the metal–ligand bond. g- Parallel as well as small split of g-perpendicular might suggest asymmetry in arrangement of equatorial ligands. Result for the complex of potato starch with Cr (III) is in concordance with conclusion driven from the EPR spectrum of this complex. For unknown reason potato starch as the

Table 1
Action of metal sulfates on polysaccharides in terms of g-factor and number of unpaired spins

Polysaccharide	Preparation procedure[a]	g	Unpaired spin $n \times 10^{15}$ spins/g[b]	Remarks
$CoSO_4$[c]				
Amylopectin	B	1.999(0.001)	3.6(1%)	
	C	2.456(0.001)	1.8(2%)	
Cornstarch	B	2.331(0.002)	7.2(2%)[d]	$g^{\parallel}$
		2.018(0.001)		$g^{\perp}$
	C	2.462(0.001)	2.1(1%)	
Waxy cornstarch	B	2.238(0.002)	7.2(3%)[d]	$g^{\parallel}$
		2.010(0.001)		$g^{\perp}$
	C	2.458(0.001)	3.2(1%)	
Potato starch	B	1.999(0.001)	2.8(2%)	
	C	2.540(0.002)	3.6(2%)	
$Cr_2(SO_4)_3$[c]				
Amylopectin	B	1.990(0.003)	7.8(6%)	
	C	2.256(0.002)	15.4(2%)[d]	$g^{\parallel}$
		2.000(0.004)		$g^{\perp}$
Cornstarch	B	1.990(0.001)	2.6(1%)	
	C	2.310(0.003)	13.0(2%)[d]	$g^{\perp}$
		1.989(0.002)		$g^{\perp}$
Waxy cornstarch	B	1.992(0.002)	1.8(1%)	
	C	2.341(0.003)	9.5(6%)[d]	$g^{\parallel}$
		1.988(0.002)		$g^{\perp}$
Potato starch	B	1.992(0.005)	1.8(5%)	
	C	1.990(0.003)	5.6(4%)	
$CuSO_4$				
None (pure salt)		2.099(0.001)	95(3%)[d]	$g^{\parallel}$
		2.407(0.003)		$g^{\perp}$
Amylopectin	B	2.001(0.003)	4.9(3%)	
	C	2.426(0.003)	17.8(3%)[d]	$g^{\parallel}$
		2.048(0.002)		$g^{\perp}$
Cornstarch	B	2.003(0.001)	12.1(6%)	
	C	2.435(0.003)	12.2(3%)[d]	$g^{\parallel}$
		2.045(0.002)		$g^{\perp}$
Waxy cornstarch	B	2.002(0.004)	11.8(2%)	
	C	2.434(0.003)	14.4(3%)[d]	$g^{\parallel}$
		2.039(0.002)		$g^{\perp}$
Potato starch	B	1.999(0.002)	2.8(2%)	
	C	2.441(0.003)	7.6(3%)[d]	$g^{\parallel}$
		2.023(0.002)		$g^{\perp}$
$Fe_2(SO_4)_3$				
None (pure salt)		2.002(0.001)	109(4%)	
Amylopectin	B	2.001(0.004)	8.4(5%)	
	C	2.418(0.003)	1.8(1%)	
Cornstarch	B	2.005(0.001)	1.0(4%)	
	C	2.426(0.003)	4.6(3%)	
Waxy cornstarch	B	2.001(0.002)	8.7(2%)	
	C	2.430(0.005)	3.7(3%)	
Potato starch	B	2.000(0.005)	2.2(2%)	
	C	2.446(0.003)	4.3(6%)[d]	$g^{\parallel}$
		1.994(0.002)		$g^{\perp}$
$MnSO_4$				
None (pure salt)		2.251(0.004)	32(2%)	
		1.847(0.002)	35(3%)	
Amylopectin	B	2.002(0.002)	12.6(3%)	
	C	2.400(0.003)	1.2(2%)	
Cornstarch	B	2.001(0.002)	13.7(6%)	
	C	2.246(0.003)	4.2(2%)	
		1.894(0.002)	4.1(1%)	
Waxy cornstarch	B	2.249(0.004)	4.4(2%)	

Table 1 (continued)

Polysaccharide	Preparation procedure[a]	g	Unpaired spin $n \times 10^{15}$ spins/g[b]	Remarks
Potato starch		1.840(0.003)	4.7(2%)	
	C	2.318(0.007)	3.1(2%)	
	B	2.008(0.004)	7.1(2%)	
	C	2.001(0.003)	0.4(5%)	

[a] B: Original polysaccharide agitated in 0.1 M aq. salt solution; C: Gelatinized polysaccharide agitated in 0.1 M aq. salt solution.

[b] Estimation error is given in parentheses.

[c] The signal of $g = 1.998$ (consult Figs. 1 and 2) probably reflects a defect in the lattice of the crystalline salt.

[d] Jointly for parallel and perpendicular g-factor.

ligand could not push water out of the coordination sphere of Cr (III) atom.

In the spectra of complexes of Cu (II) with gelatinized polysaccharides the central atom had the $d_{xy}2$, $d_{xz}2$, $d_{yz}2$, $d_{x^2-y^2}2$, $d_{z^2}1$ configuration. g-Factor (Table 1) split into g-parallel and g-perpendicular. When g-parallel is lower than g-perpendicular as it took place in hydrated $CuSO_4$ unpaired spin might be localised on the $d_{x^2-y^2}$. Otherwise unpaired spin should be localised on the d_{z^2} orbital. The latter situation with g-perpendicular being close to that for free electron and magnitude of g-parallel enhanced was caused by a similar metal–ligand coupling as in complexes with Cr (III). Tetrahedral symmetry around the central atom might be assumed because of either already existing or induced by the Jahn–Teller effect distortion. Coupling of the $d_{z^2}1$ orbital with either $d_{xz}2$ or $d_{yz}2$ orbital might be also taken into account. Thus, also square-planar trigonal bipyramide could not be excluded.

For complexes of Fe (III) and Mn (II) high-spin character ($S = 5/2$) might be deduced but the character of the ligand made such assumption unlikely and low-spin character ($S = 1/2$) should dominate. In the spectra of complexes with both metal ions splitting of g-factor was observed (Table 1). Thus, unpaired spin was significantly delocalised from the central atoms to the ligand. Assuming that they were low-spin complexes the configuration of the central atoms was $d_{xy}2$, $d_{xz}2$, $d_{yz}2$. Large shift of g-factor resulted from cancellation of degeneration of the d_{xz} and d_{yz} orbitals. For this sake the d_{yz} orbital was above the d_{xz} orbital.

In Table 1 also concentration of unpaired spins are reported. These data should be related to the presence of metal atoms bound to given polysaccharides by coordination, sorption and, in the case of potato starch, covalently to phosphoric acid moieties where they exchanged atoms residing therein in original starch. Inspection of these data revealed that each polysaccharide possessed its own specific affinity to the same metal ion and there was different affinity among metal ions to a given ligand. Generally, a total amount of a given metal atom trapped was higher for solid polysaccharides showing importance of surface sorption and, in case of granular starch, penetration of ions into starch granules.

Table 2
Results of TG, DTG and DSC analyses of pasted potato starch and its metal complexes

Sample	TG		DTG	DSC
	Temp. (°C)	Total weight loss (%)	Temp. (°C)	Temp. (°C)
Potato starch	34	0.0	71	70 (endo)
	132	16.7		
	243	18.5	285	260 (endo)
	307.5	61.6		282 (endo)
				340 (exo)
Co (II) complex	178	2.8	231	181 (exo)
			318	181 (exo)
			319	211 (exo)
	262	40.5	399	297 (exo)
				339 (exo)
	356	62.1		402 (exo)
Cr (III) complex	129	0.5	155	142 (endo)
	244	32.6	384	213 (exo)
	358	79.7	396	359 (exo)
				396 (exo)
Cu (II) complex	155.5	2.6	207	188 (endo)
	256	41.0	329	248 (exo)
	328	97.0		280 (endo)
				330 (exo)
Fe (II) complex	132	0.2	180.5	161 (exo)
	240	32.5	373	380 (endo)
Mn (II) complex	176	1.2	243	239 (exo)
	281	32.1	345	
	371	53.4	434	396 (exo)

4.4. SEM studies

Formation of complexes by granular starch was additionally confirmed by means of SEM. Starch granules soaked in water for several hours swelled and cracked and/or leached the content of their interior into water. Leaching from starch granules was demonstrated in the paper of Gallant, Bouchet, and Baldwin (1995). Such exudations could be removed from the surface of granules by a vigorous agitation of suspensions. After such treatment surface of granules remained smooth. In our recent paper we reported (Lii et al., 2002) that NaCl present in such suspensions retarded cracking of granules. Now, we confirmed this observation. We could not observe under SEM any cracked starch granules after soaking them in solutions of transition metal sulfates. Prior to separation of granules from suspensions they were vigorously agitated
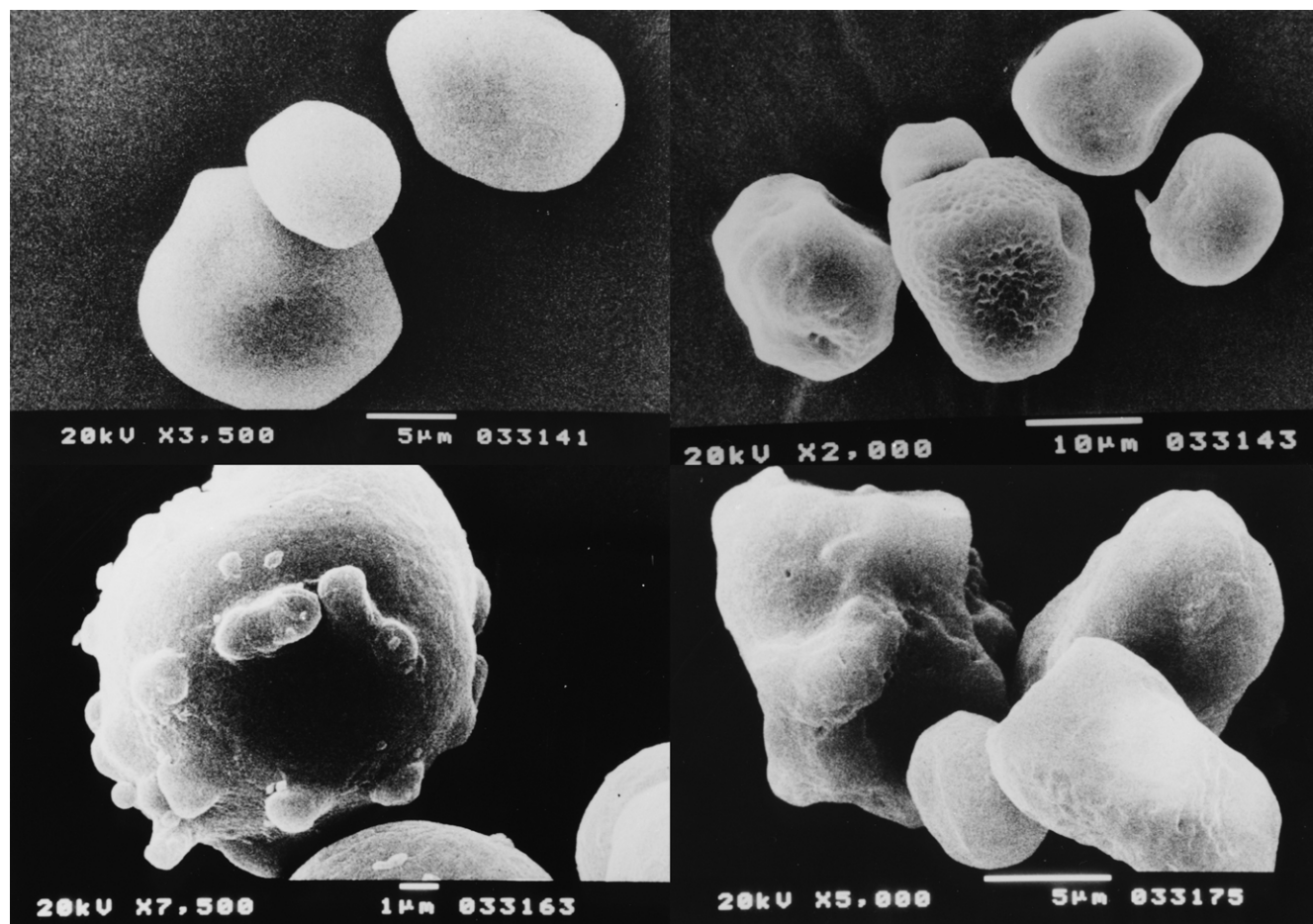
Fig. 6. SEM of potato (upper left) and maize (upper right) starch granules 24 h soaked in water at room temperature on agitation then isolated and dried in vacuum dessicator. Correspondingly, bottom left and right photographs present potato and maize starch granules, respectively, after 24 h soaking on agitation at room temperature in 0.1 M solution of $CuSO_4$. After soaking granules were washed with water and dried in vacuum dessicator.

and washed three times with water then dried. There could be visible abundant, not removed exudations on the granule surface. Fig. 6 presents starch granules after soaking in water and in $CuSO_4$ solution then agitated prior to isolation.

After soaking and washing starch granules retained a pale colour of salts. It was the evidence that after such treatment salts still resided on the granule surface. Simultaneously, it a poor aqueous solubilities of Fe (III) (Tomasik et al., 1995), Ti (IV) (Tyrlik et al., 1997), and La (Tomasik et al., 2000) complexes of starch were reported. Therefore, assumption that observed, poorly removable exudations on the surface of granules might be starch metal complexes was sound.

5. Conclusions

Granular and gelatinized starches ligated metal anions of the transition group elements and formed Werner-type complexes in which orbitals of lone electron pairs of the hydroxyl groups of starch dated electrons.

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