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Coordination of Transition-metal Ions by Polygalacturonic Acid: a Spectroscopic Study

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The interaction between polygalacturonic acid with Cu(II), VO(IV), Mn(II), Ni(II) and Co(II) has been studied with the aid of ESR, electronic and IR spectra. The results show that in fully hydrated gels Cu(II) and VO(IV) ions form inner-sphere carboxylate complexes, whereas $[Mn(H_2O)_6]^{2+}$ *retains its inner hydration sphere. On dehydration, all the ions are bound to carboxyl groups, whose binding mode is dependent on the nature of the ion. The changes observed in spectral parameters upon dehydration suggest the substitution of water molecules by sugar oxygen atoms in order to preserve the stereogeometry of the ions.*

Introduction

The retention of metal ions by acid polysaccharides is of considerable interest in view of its biological role in the availability of nutrients to plants [1, 2]. It has been demonstrated that ill-defined gels on the root surfaces of the plants remove nutrient cations directly from the solid phase of the soil by a contact ion-exchange process. In this mechanism metal complexes with pectins and/or acid polysaccharides are formed [3–5]. Earlier investigations of complexation of galacturonic and glucuronic acids in solution often contradict each other with respect to the binding of the ions. Some have suggested a chelate structure involving carboxyl and hydroxyl groups [6, 7]. More recently, on the basis of potentiometric measurements, an 'acetate-like' structure has been reported for the complexes with this monomeric acid at pH < 10 [8]. No exhaustive spectroscopic data have been reported for transition-metal ions binding to acid polysaccharides. Therefore, we have examined the coordination of some selected metal ions, in order to clarify on the basis of spectroscopic results, the environment of specific sites for ion uptake by polygalacturonic acid gels under acidic conditions.

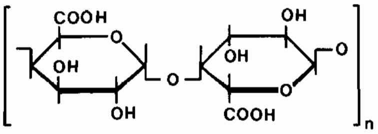

Fig. 1. Polygalacturonic acid.

Experimental

Materials

Polygalacturonic acid (J. T. Baker) (Fig. 1) was purified according to described procedures [9]. Aqueous solutions of metal ions were prepared by weight from the appropriate salt.

Preparation of the Samples

Metal ions sorption was carried out by adding weighed amounts (0.5–1 g) of the acid to a solution (~100 cm^3) with varying concentration of metal salts and allowing the suspension to equilibrate at room temperature under magnetic stirring. Therefore the samples were filtered and washed several times with water. As a rule, sorption was carried out from sulphate solutions. In some cases, in order to enhance the exchange, which is maximum around pH = 4–4.5, acetate solutions were used. The investigation showed no difference in the nature of the complexes with varying anions. The degree of cation saturation was determined as the ratio of the sorbed ions to the complete exchange capacity (CEC), after volumetric analysis of metal concentration in the aqueous phase using standard EDTA solutions. Samples with varying amounts of water were investigated: namely hydrated, air-dried and dehydrated complexes. Dehydration was carried out at 120 °C for 6 hours.

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TABLE I. Carboxylate Stretching Frequencies (cm^{-1}) in Metal–Polygalacturonates.

Metal-ion	State of the sample§	ν_{as} (CO_2)	ν_{sym} (CO_2)	Δ
Na^+	a.d.	1600 s	1410 s	190
Ca^{2+}	a.d.	1600 s	1415 s	185
Mn^{2+}	a.d., d.	1600 s	1415 s	185
Co^{2+}	a.d.	1610 s	1410 s	200
Co^{2+}	d.	1615 s	1415 s	200
Ni^{2+}	a.d., d.	1615 s	1415 s	200
VO^{2+}	a.d.	1630 s	1400 s	230
VO^{2+}	d.	1625 s	1395 s	230
Cu^{2+}	a.d.	1620 s	1405 s	215
Cu^{2+}	d.	1615 s	1400 s	215

§a.d. = air dried; d. = dehydrated.

Hydrated complexes were obtained on keeping them in water for one day.

Spectroscopic Measurements

X-band EPR spectra were obtained on a Varian E-9 spectrometer at about 9.15 GHz frequency, using diphenyldipicrylhydrazyl (DPPH) as standard marker. Measurements were carried out at room temperature. No difference was observed in the spectra recorded at 110 K. Electronic spectra were recorded with a Beckman Acta M IV spectrophotometer, equipped with a reflectance unit, using $BaSO_4$ as reference sample. IR spectra were recorded with a Beckman 4250 spectrophotometer in KBr phase. The electronic spectra of the disks in KBr excluded the exchange of water molecules with Br^- with this technique.

Thermal Analyses

Thermal analyses were carried out on air-dried samples, using a Dupont 990 thermal analyser at a heating rate of 10 °C min^{-1} under a nitrogen stream of 40 cm^3 min^{-1}. The measurements revealed a water content of 13–15% wt., quite independently from the nature of the ion and the loading of the samples. Water molecules were lost in the temperature range 60–130 °C.

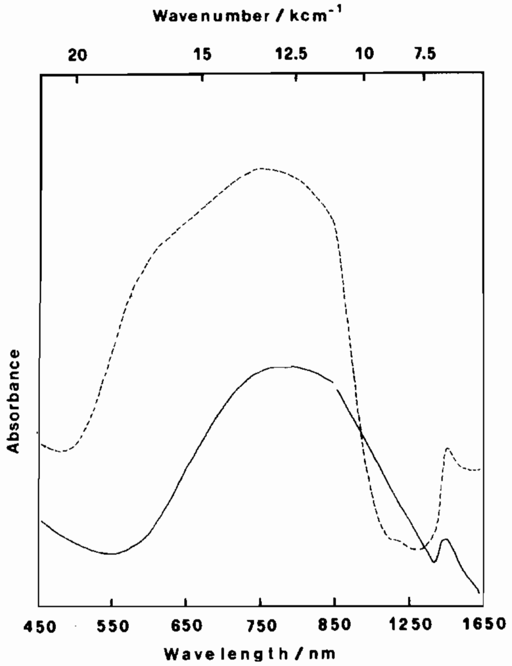

Fig. 2. Reflectance electronic spectra of air-dried (———) Cu(II) (85% of CEC)– and (-------) VO(IV) (65% of CEC)–polygalacturonates.

Results

IR and Electronic Spectra

IR spectra of polygalacturonic acid-complexes exhibit (in addition to the 1730 cm^{-1} absorption of free carboxyl groups in the partially loaded samples) two strong bands in the range 1600–1635 cm^{-1} and 1400–1410 cm^{-1}, assigned respectively to the $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ modes of carboxylate group, as listed in Table I. The mode of coordination of carboxylate groups has often been deduced from the magnitude of Δ, the difference between $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$. Monodentate coordination will shift ν_{as} to higher and ν_{sym} to lower frequencies [10]. Our results show that the Δ values of Co(II)-, Ni(II)- and Mn(II)-complexes are similar to those of Na– and Ca–polygalacturonates. It is reasonable, therefore, to assign a bidentate structure to carboxylate

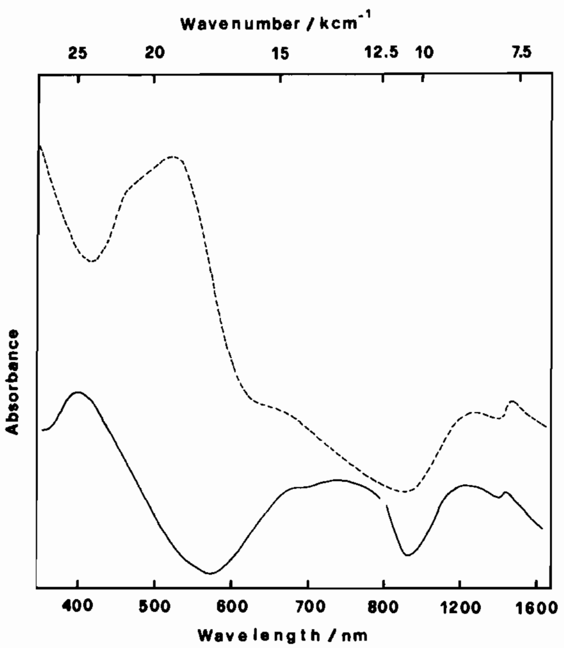

Fig. 3. Reflectance electronic spectra of air-dried (———) Ni(II) (82% of CEC)– and (--------) Co(II) (70% of CEC)–polygalacturonates.

groups in Co(II)-, Ni(II) and Mn(II)-complexes. Their frequency values agree with those reported for other M(II)–carboxylates whose bidentate coordination mode is note from crystal structures [10, 11]. Instead, the higher Δ values observed for Cu(II)- and VO(IV)-complexes suggest carboxylate groups less symmetrically bound to the ion or monodentate coordination through an oxygen atom only. Dehydration produced only slight variations in carboxylate stretching frequencies.

The electronic spectrum of copper–polygalacturonate (Fig. 2) is characterized by a broad structureless band showing a maximum around 12.7 kK. The position and the shape of the absorption suggest a moderately distorted octahedral geometry, with parameters only slightly different from those of the hexaquocation(II) [12].

The electronic spectrum of Co(II)-complex (Fig. 3) is typical of a pseudo-octahedral configuration. By assuming O_h symmetry, the bands occurring at 8.1, 14.8 and 19.2 kK may be assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. A tetragonal distortion is, however, suggested by the splitting of the octahedral $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. Similarly, Ni(II)-complex exhibits absorption bands typical of an hexacoordinate ion (Fig. 3), occurring at 8.1 kK (ν_1: $^3A_{2g} \rightarrow {}^3T_{2g}$), 13.5 kK ($\nu_2$: $^3A_{2g} \rightarrow {}^3T_{1g}$), 14.5 kK ($^3A_{2g} \rightarrow {}^1E_g$) and 24.7 kK ($\nu_3$: $^3A_{2g} \rightarrow {}^3T_{1g}$ (P)). Shoulders arising mainly on ν_3 and ν_1 transitions are, however representative of a deviation from regular geometry. Dq values, of Co(II)- and Ni(II)-complexes, compared with those of hexaquocations(II) [13, 14], are slightly lower. All these spectra showed little variations upon dehydration of the samples. This provides striking evidence that anhydrous compounds are still hexacoordinated. The spectrum of oxovanadium(IV)-complex exhibits in the visible region a broad maximum centered at about 13.0 kK with a shoulder at 16 kK (Fig. 2). The two bands are usually assigned respectively to $^2B_2 \rightarrow {}^2E$ (ν_1) and $^2B_2 \rightarrow {}^2B_1$ (ν_2) transitions in C_{4v} symmetry [14]. In dehydrated samples absorption was notably broadened and the shoulder shifted to about 15.4 kK. Because ν_2 absorbance energy is equivalent to 10 Dq, these changes evidence a decrease of the in-plane ligand field experienced by metal ion.

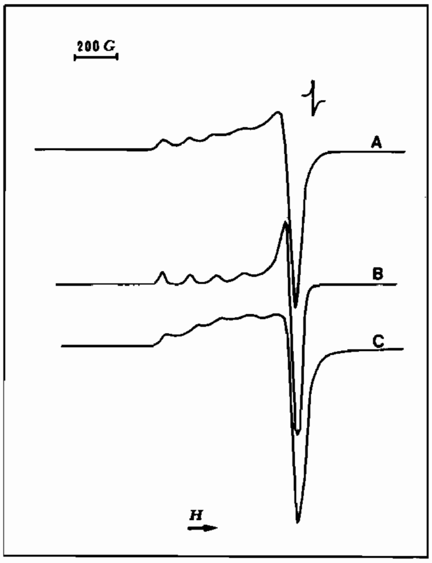

Fig. 4. Room temperature ESR spectra of exchanged Cu^{2+} (~1% of CEC) ion in polygalacturonic acid: (A) air-dried sample; (B) hydrated sample; (C) dehydrated sample.

Electron Spin Resonance Measurements

The room temperature spectra of polygalacturonic acid loaded with Cu^{2+} and washed free of excess ion are shown in Fig. 4. In the air-dried samples, at small degrees of ion sorption, anisotropic axial spectra are observed. The spectral parameters ($g_\parallel$ = 2.389, $g_\perp$ = 2.070 and $A_\parallel$ = 120 G) are characteristic of a copper environment with a relatively strong axial perturbation [12]. These values are close to those of copper complexes with water molecules coordinated in the metal plane and carboxylate groups in the axial positions (15, 16). On increasing the ion concentration a symmetrical line with g_{av} = 2.18 and δH = 230 G appears. This must be caused by a weak exchange among closely spaced Cu^{2+} ions. The hydration of the samples did not modify the spectrum ($g_\parallel$ = 2.390, $g_\perp$ = 2.070, $A_\parallel$ = 122 G and $A_\perp \sim$ 20 G). No 'solution-like'

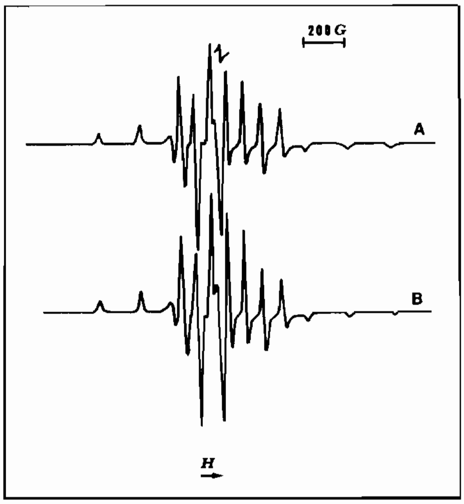

Fig. 5. Room temperature ESR spectra of exchanged VO^{2+} (~1% of CEC) ion in polygalacturonic acid: (A) air-dried or hydrated sample; (B) dehydrated sample.

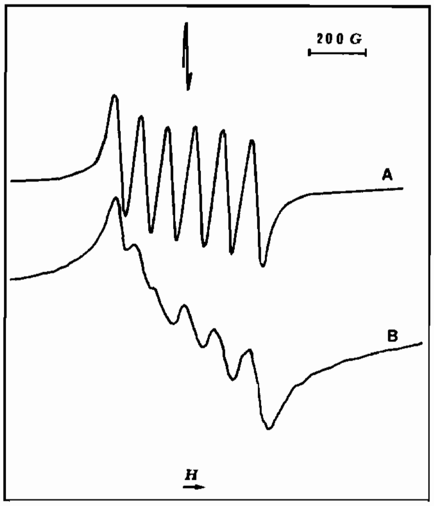

Fig. 6. Room temperature ESR spectra of Mn^{2+} (~0.5% of CEC) doped in Ca(II)–polygalacturonate: (A) hydrated sample; (B) air-dried sample.

Cu^{2+}-spectrum was observed. This evidences that ion-sorption is accompanied by the formation of an inner-sphere complex. Dehydration at 120 °C produced an increase of $A_{\parallel}$ (135 G) and a decrease of $g_{\parallel}$ (2.366) and $g_{\perp}$ (2.067) in comparison with hydrated and air-dried samples. Such a trend is expected when the axial perturbation in the copper environment becomes less important (increase in tetragonal character) without producing a planar geometry [12]. Dehydration produces, in addition to the anisotropic spectrum, an isotropic resonance also at low ion concentrations. This is explainable by the presence of exchange associates groups after drying.

The ESR spectra of VO(IV)-complexes in different hydration states are shown in Fig. 5. As for copper samples, anisotropic spectra with coincident spectral parameters ($g_{\parallel}$ = 1.990, $g_{\perp}$ = 1.938, $A_{\parallel}$ = 195 G and $A_{\perp}$ = 73 G) are observed in hydrated and air-dried complexes. By a comparison with hyperfine splitting values of $[VO(H_2O)_5]^{2+}$ ($A_{\parallel}$ = 203 G and $A_{\perp}$ = 78 G) and $[VO(C_2O_4)_2]^{2-}$ ($A_{\parallel}$ = 188 G and $A_{\perp}$ = 65 G) [17], the observed values may be explained by an in-plane ligand field of intermediate strength. This suggests that VO^{2+} in the polyacid is coordinated by two carboxylate groups but remains partially hydrated. In order to verify the hydration of the ion, we have suspended a dilute sample (0.5% of CEC) in D_2O. The reduction in hf line-widths registered in comparison to the spectrum in H_2O is indicative of the water binding to metal. The difference (~3.5 G) in the line-width of $M_I = +\frac{1}{2}$ perpendicular resonance may be caused by two equatorially coordinated water molecules, in agreement with the 1.6 G value per water molecule recently proposed [18]. Dehydration produced meaningful changes in the state of the ion ($g_{\parallel}$ = 1.985, $g_{\perp}$ = 1.931, $A_{\parallel}$ = 204 G and $A_{\perp}$ = 76 G). These parameters suggest the weakening of σ-releasing properties of the in-plane ligands and, in agreement with electronic data, are representative of a variation in VO^{2+} coordination sphere. The room temperature ESR spectra of Mn(II)-exchanged gels (Fig. 6) reveal, in hydrated environment, a 'solution-like' nature (A_{iso} = 93 G). This behaviour is similar to that of the ion in fully hydrated smectites and humic acids [19, 20]. Upon partial or complete dehydration, the Mn^{2+} signals are weaker and more diffuse than in hydrated samples. In order to eliminate dipolar broadening we have doped Mn^{2+} in Ca(II)–polygalacturonate. Also in this case, dehydration caused a broadening of hyperfine structure, attributable to reduced rotational mobility of the ion [21]. These features reveal that ion aquo-shells are not destroyed during the sorption process. Only drying loads to the formation of rigid-limit species, associated to the dehydration of the cation.

Discussion and Conclusions

The reported data evidence that sorption of the examinated ions by polygalacturonic acid is accompanied by the formation of stable carboxylate complexes. Their insolubility in water makes reasonable the hypothesis that ions act as cross-linking agents in the polymer network [9]. The specific interactions between ions and polysaccharide chains are dependent from the nature of the ions and the water content. In fully hydrated Cu(II)– and VO(IV)–gels inner-sphere complexes are formed. On the contrary, Mn^{2+} ion is retained as aquo-ion. Air-drying allows all the ions to form inner-sphere complexes. It is noteworty to evidence that Cu(II) and VO(IV) environments are not modified upon air-drying. It can be suggested that, in this state, Co(II), Ni(II) and Mn(II) ions satisfy the geometrical requirements for hexacoordination, being surrounded by bidentate carboxylate groups and two axial water molecules. On the contrary, in VO(IV)- and Cu(II)-complexes two carboxylate groups act as unidentate ligands. The octahedral environment is completed by water molecules. Changes observed in ESR spectra of the latter ions suggest modified environments in dehydrated samples. Excluding direct intermolecular interactions, not evidenced by spectral results and unlikely because of sterical hindrances, we may suppose that water molecules are substituted by weaker interacting groups. From an examination of molecular models, a reasonable hypothesis is the binding of sugar ring- or glycosidic-oxygens. This may also explain the invariance in the geometry of Ni(II)- and Co(II)-complexes after dehydration. In fact for these ions differences in the distortion power of similar O-donor ligands are difficult to be rationalized only on the basis of reflectance spectra. Difference may be suggested in the behaviour of Cu(II) and VO(IV) dehydrated complexes. If for VO(IV)-complex ESR data might be in accord with a square pyramidal structure, the tetragonally distorted octahedral Cu(II) geometry is explained only by taking into account four sugar oxygens in the ion coordination sphere. The flexibility of polymeric system allows the formation of 'cages' between sugar rings in which ions are arranged in irregular way, as demonstrated by the isotropic ESR resonance. Anhydrous state is not important in nature, where hydrated environments are prevalent; so our results suggest that in hydrated systems the exchange-sites of polygalacturonic acid are probably accounted for only by carboxyl groups. Further, our conclusions support those drawn by Khon [22], who, on the basis of theoretical considerations, suggested that in pectates calcium ions are bound to carboxyl groups by electrostatic forces, excluding the chelate intramolecular binding proposed by Schweiger [23, 24]. Lakatos *et al.* also [25] considered pectates as outer-sphere complexes. However this behaviour cannot be assumed as a general rule. According to the ion properties, the electrostatic attraction may be able to overcome the metal–H_2O bonds, affording the insertion of carboxylate groups in the inner hydration sphere of the cations. On this point of view, the strong affinity of Cu(II) for these systems [3], in comparison with alkaline and alkaline-earth cations, can be attributed to the covalence in the metal bond with carboxylate groups.

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References

1 A. Veis, 'Biological Polyelectrolytes', M. Dekker, New York (1970).

2 R. A. A. Muzzarelli, 'Natural Chelating Polymers', Pergamon Press, Oxford (1973).

3 R. Ramamoorthy, *J. Theor. Biol.*, *66*, 527 (1977).

4 G. G. Leppart and J. R. Colvin, *J. Polmer Sci. (Part C)*, *36*, 321 (1971).

5 H. Jenny, *Pl. Soil*, *25*, 625 (1966).

6 T. Anthonsen, B. Larsen and O. Smidsørd, *Acta Chem. Scand.*, *26*, 2988 (1972); *ibid.*, *27*, 2671 (1973).

7 H. Grasdalen, T. Anthonsen, B. Larsen and O. Smidsrød, *Acta Chem. Scand.*, *B29*, 17, 99 (1975).

8 C. Makridou, M. Cromer-Morin and J. P. Scharff, *Bull. Soc. Chim. Fr.*, 59 (1977).

9 H. H. G. Jellinek and P. A. Chen, *J. Polymer Sci. (Part A-1)*, *10*, 287 (1972).

10 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', J. Wiley, New York (1963).

11 K. Nakamoto and P. J. McCarthy, 'Spectroscopy and Structure of Metal Chelate Compounds', J. Wiley, New York (1968).

12 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, *5*, 143 (1970).

13 C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes', Pergamon Press, London (1962).

14 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam (1968).

15 G. Nyberg, *J. Phys. Chem.*, *75*, 2228 (1971).

16 F. Dejehet, R. Debuyst, B. Ledieu, J. P. Declercq, G. Germain and M. Van Meerssche, *Inorg. Chim. Acta*, *30*, 197 (1978).

17 L. J. Boucher, E. C. Tynan and T. F. Yen, 'Electron Spin Resonance of Metal Complexes', Plenum Press, New York (1969).

18 N. F. Albanese and N. D. Chasteen, *J. Phys. Chem.*, *82*, 910 (1978).

19 M. B. McBride, *Soil Science*, *126*, 200 (1978).

20 M. B. McBride, T. J. Pinnavaia and M. M. Mortland, *Am. Mineral.*, *60*, 66 (1975).

21 L. Burlamacchi, *J. Chem. Phys.*, *55*, 1205 (1971).

22 R. Kohn and I. Furda, *Collect. Czech. Chem. Commun.*, *33*, 2217 (1968).

23 R. G. Schweiger, *J. Org. Chem.*, *29*, 2973 (1964).

24 R. G. Schweiger, *Kolloid Z.*, *208*, 28 (1966).

25 B. Lakatos, T. Tibai and J. Meisel, *Geoderma*, *19*, 149, 319 (1977).