

Selective hydrolysis of polymer-bound ethoxycarbonylethyl phosphonate and e.p.r. studies of copper(II) complexes with the parent resin and its derivatives

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New ion exchange/coordination resins for the selective complexation of metal ions have been obtained by selective hydrolysis of a polymer-bound ligand—ethoxycarbonylethyl phosphonate. Their properties such as water regain, phosphorus content, acid capacity and sorption properties towards copper(II) from nitric acid solutions were determined. Structures of ligand complexes with copper(II) were studied using electron paramagnetic resonance and compared to the structures of complexes formed by diphosphonate and dicarboxylate ligands. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Selective complexing agents bound to an insoluble polymeric matrix attract a lot of attention. They are used for recovery of metal ions from the environment and from industrial liquids^{1,2}, in the processing of precious metals³ and as catalysts^{4,5}. A review of such polymers was given by Reedijk⁶.

Properties of such insoluble complexing agents depend mainly on the type and structure of the immobilized ligand. Among these materials, polymers with phosphonate groups are of particular interest due to their selectivity towards heavy metal ions^{7–9}. Moreover, they retain their complexing activity under acidic conditions. This is especially true in the case of newly developed diphosphonate ligands¹⁰. Their enhanced selectivity under these conditions is a result of the close proximity of phosphonate groups. The same effect has been observed for small-molecule compounds¹¹.

The high performance of diphosphonate-containing polymers prompted investigations of the effect of neighbouring groups on their selectivity^{12,13}. The complexing properties of resins with phosphonate and carboxylate groups were described in terms of the sorption of metal ions from different solutions, but no experiments were done to find the ligand–ion complex structure.

The aim of this work is to use e.p.r. spectroscopy to find the type of coordination between copper(II) ions

and polymeric complexing agents. In order to achieve this goal, a series of polymers with phosphonate and carboxylate functionalities in both the ester and acid forms were prepared by selective hydrolysis of immobilized ethoxycarbonylethyl phosphonate.

EXPERIMENTAL

Materials

The copolymer of vinylbenzylchloride (VBC), styrene (St), and technical divinylbenzene (DVB) was prepared by suspension polymerization with 0.5 wt% of benzoyl peroxide as the initiator. The nominal cross-linking degree was 2 wt% with respect to *m*- and *p*-DVB. Polymerization was carried out in the presence of dodecane (1:1 w/w with respect to the monomers) in order to obtain porous polymer. After polymerization, the copolymer was carefully washed with hot water and acetone, dried and extracted with toluene. Fraction 60–100 mesh was used in all experiments.

Diethyl ethoxycarbonylethyl phosphonate was obtained as described by Kuhtin and Oriehova¹⁴. Thus, a 250 ml three-neck flask equipped with a dropping funnel, reflux condenser and thermometer was charged with 0.6 mol (99.6 g) of triethyl phosphite. Acrylic acid (0.6 mol, 43.25 g) was added slowly over 1 h with continuous stirring. During this time the temperature increased to 140°C. After addition of acrylic acid, the temperature increase ceased, and the mixture was heated at 120°C for an additional 3 h. Gas chromatography analysis showed that the product was 92% pure. Vacuum

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distillation afforded diethyl ethoxycarbonylethyl phosphonate, collected at 93–94°C/0.15 mmHg (purity 99+%, yield 87%).

The sodium derivative of the above compound was prepared by reacting 27.85 g (117 mmol) of it with an equimolar amount of sodium metal (2.7 g) in 150 ml of dry toluene. The reaction was started upon gentle heating of mixture, and continued until the sodium metal dissolved.

The starting material was prepared by reacting the sodium derivative of (EtO)₂P(O)CH₂CH₂COOEt with the VBC/St/DVB copolymer. Thus, 10 g of the aforementioned copolymer containing 46.8 mmol of chlorine was reacted with 117 mmol of the sodium derivative of (EtO)₂P(O)CH₂CH₂COOEt in 150 ml of dry toluene under reflux for 20 h. The resin was then separated by filtration, washed with dioxane, dioxane/water, water and finally with acetone.

The obtained resin (resin 1) was subsequently selectively hydrolysed. Thus, 1.5 g of the resin was allowed to swell in water, and added to a mixture of 30 ml of tetrahydrofuran and 30 ml of 8 M NaOH. The reaction was carried out for 48 h at room temperature to obtain a resin with a carboxylic acid functionality (resin 3). In order to obtain a resin with a phosphonic acid functionality (resin 2), 1.5 g of the starting material was reacted with 2 g of bromotrimethylsilane in 4 g of chloroform for 5 days at room temperature followed by hydrolysis of the resulting trimethylsilyl ester with water. Finally, in order to obtain resin 4, with both phosphonic and carboxylic acid functionalities, the starting material was reacted as in the case of resin 2 and then subsequently hydrolysed with 3 M NaOH at 100°C for 8 h.

Resins 5 and 6, both used to compare selectively hydrolysed resins with those containing diphosphonate and dicarboxylate ligands, were prepared by reacting the same VBC/St/DVB copolymer with the sodium salt of tetraethyl ethylenediphosphonate and with the sodium derivative of diethyl malonate followed by hydrolysis, as described by Alexandratos and Trochimczuk¹².

Methods

In order to determine the sorption capacity of resins towards copper(II) the samples were added to 10⁻⁴ N Cu(NO₃)₂ solutions in 0.1, 0.01 and 0.001 M nitric acid. Enough resin to give 0.1 mEq of acid capacity was shaken with 10 ml of the given solution for 24 h. After that time the solution was filtered, and the copper(II) concentration determined using atomic absorption on a Varian 250+ spectrophotometer with the wavelength set to 324.8 nm.

The phosphorus content was measured by digesting an approximately 20 mg sample of resin in a perchloric acid solution, followed by reaction with amidol and ammonium molybdate.

Water regain (*W*) was determined by centrifuging an excess of water from the swollen resin and drying the resin at 110°C for 24 h, and calculated as

$$W = (m_w - m_d)/m_d$$

where *m_w* is the weight of swollen polymer after centrifugation and *m_d* is the weight of polymer after drying.

The acid capacity was determined by placing 1 g of swollen resin in the H⁺ form in 100 ml of 0.1 M NaOH

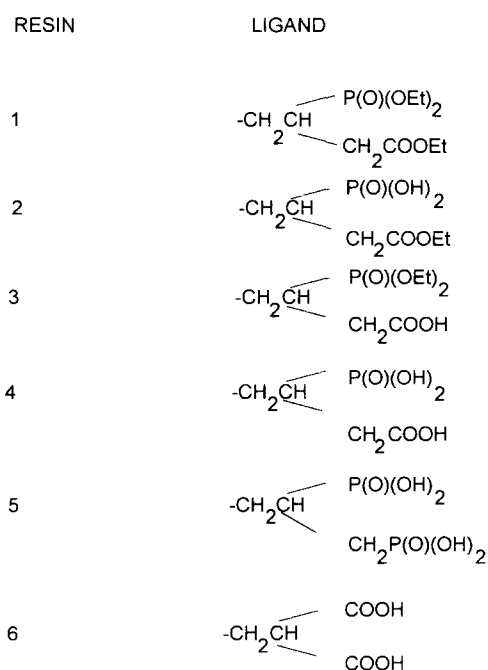


Figure 1 Structure of the investigated chelating/ion exchange resins

solution for 24 h, then titrating a 50 ml aliquot with 0.05 M sulfuric acid.

E.p.r. experiments were performed using a Bruker ESP 300E X-band spectrometer. The samples were prepared by adding an appropriate amount of swollen resin (taking into account their water regain) to 10 ml of 1 × 10⁻⁴ N Cu(NO₃)₂ solution. In every case, the copper(II):acid capacity ratio was approximately 100. HCl and/or KOH were used to adjust the pH at constant ionic strength.

RESULTS AND DISCUSSION

To obtain evidence of complex formation between copper(II) and oxygen donors of diethyl ethoxycarbonylethyl phosphonate competing in aqueous solutions with water molecules, the series of chelating/cation exchange resins providing different combinations of oxygen-containing groups (phosphonic acid, ethyl phosphonate, carboxylic acid and carboxylate ester) (Figure 1) incorporated in the same polymer matrix were investigated using an e.p.r. method.

The desired polymers were obtained by selective hydrolysis of resin 1 bearing ligands introduced by reaction of the sodium salt of diethyl ethoxycarbonylethyl phosphonate with the VBC/DVB copolymer. In the hydrolysis, the selectivity of bromotrimethylsilane towards phosphonate esters^{15,16} and their considerable resistivity towards alkaline hydrolysis¹⁷ were used. As can be seen in Table 1, resin 1 has residual acid capacity, indicating that some of the ester groups have been hydrolysed during reaction of diethyl ethoxycarbonylethyl phosphonate with sodium metal. Resins 2, 3 and 4 have acid capacities of two times, equal to and three times higher than their respective phosphorus contents. This can be used as a measure of de-esterification selectivity. A slight increase in phosphorus content (resins 2 through 4) is a result of net weight loss during hydrolysis. Water regain is almost the same for each polymer, and indicates their relatively high hydrophilicity.

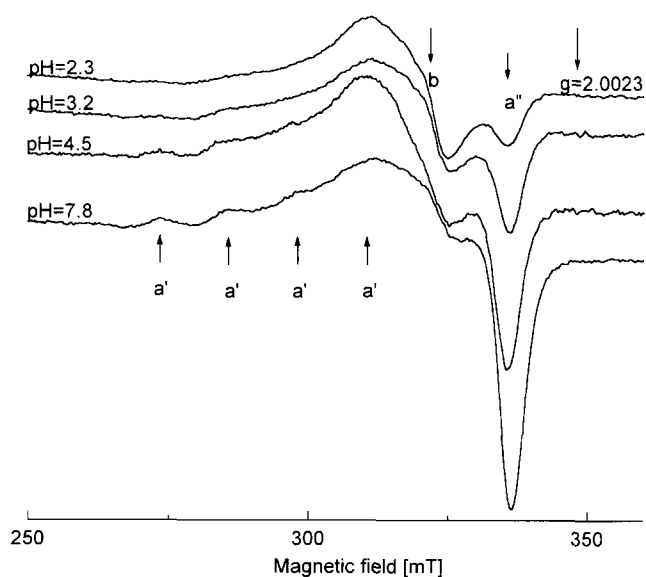
Table 1 Characteristics of selectively hydrolysed resins

Resin	Type of group		P content (mmol g ⁻¹)	Acid capacity (mmol g ⁻¹)	Water regain (g g ⁻¹)
	Carboxylic acid	Phosphonic acid			
1	Ester	Ester	1.88	0.15	1.32
2	Ester	Acid	1.92	3.90	1.25
3	Acid	Ester	1.87	1.88	1.35
4	Acid	Acid	2.02	5.97	1.26
5	Diphosphonic acid		2.98	6.10	1.42
6	Dicarboxylic acid		0.00	3.72	1.37

Table 2 Copper(II) uptake from 0.01 M nitric acid solution by selectively hydrolysed resins

Resin	Distribution coefficient, <i>D</i>	Log <i>D</i>	mg Cu ^{II} (g dry resin) ⁻¹
1	219	2.34	0.51
2	679	2.83	1.00
3	245	2.38	0.54
4	1905	3.28	1.45
5	+∞	+∞	> 2.10
6	27	1.43	0.08

Such polymers were placed in contact with copper(II) solutions in 0.1, 0.01 and 0.001 M nitric acid. From the 0.1 and 0.001 M nitric acid solutions, under experimental conditions, no uptake of copper ions and complete uptake were observed, respectively. It can be concluded that under highly acidic conditions, competition from protons is too strong, whereas in 0.001 M nitric acid solution both phosphonate and carboxylate functionalities are active. In Table 2, distribution coefficients of copper(II) between resins and 0.01 M nitric acid solution are presented. As can be seen at this pH, the amount of copper complexed and/or exchanged by the ligand strongly depends on the type of ligand functionality (ester/acid). Resins 1 and 3 have similar complexing/ion exchange capacity. Since the difference in ligand structure is such that resin 3 possesses a carboxylic acid moiety instead of a carboxylic ester group one can assume that all the copper(II) is bound through the phosphoryl oxygen or is a result of ion exchange activity due to the residual acid capacity displayed by resin 1. To check the latter possibility, resin 6, with two carboxylic acid groups, was used. The results of the sorption study indicate that the distribution coefficient, *D*, is 10 times lower than for resins 1 and 3, which gives reason to assume that all the copper(II) is bound to them through the phosphoryl oxygen rather than through ion exchange on carboxylic acid groups. Removal of ester groups from phosphonate (resin 2) results in a three-fold increase in *D*. This increase can be ascribed to ion exchange properties of phosphonic acid. A further increase in copper(II) uptake was observed for resin 4 in which both types of esters have been hydrolysed. The highest removal of metal ions from 0.01 M nitric acid solution was observed for resin 5, with the diphosphonic acid ligand, and can be rationalized by its higher acidity when compared with either dicarboxylic acid or carboxyethylphosphonic acid. The type of interactions between copper(II) and ligands attached to the polymer matrix can be observed using the e.p.r. method. The donor properties of the phosphonic acid group towards copper(II) are known to be slightly

**Figure 2** E.p.r. spectra of the copper(II)-resin 1 system as a function of pH at room temperature

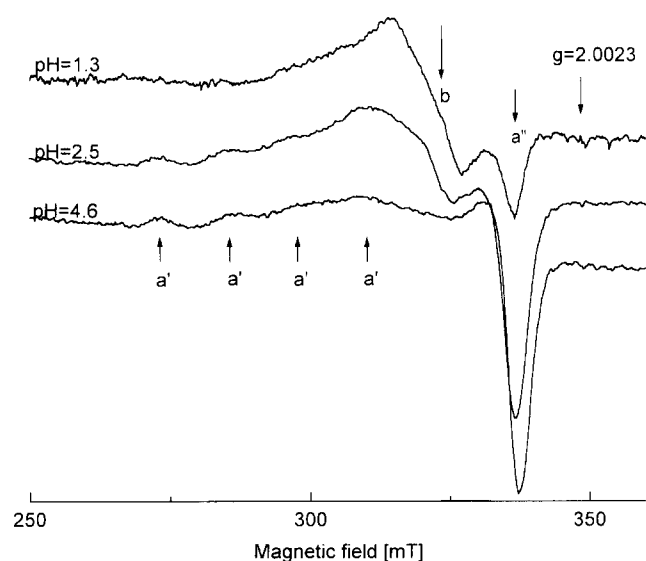
stronger than those of water molecules and weaker than those of carboxyl groups, which is the reason for the small differences between the e.p.r. spectral parameters of the copper(II) complexes with both types of functional groups attached to the ion exchange resins^{18,19}.

The e.p.r. spectra of copper(II) complexed by the polymeric ligands (resins 2–6) exhibit very well-resolved anisotropic copper hyperfine structure at room temperature. This fact indicates that copper(II) ions are well dispersed and diluted by the diamagnetic polymeric matrix. Furthermore, an anisotropic character of the spectra at room temperature gives a direct proof of copper(II) complex immobilization, which can be the case only when metal ion is bound to the functionalized polymer¹⁸.

Specific interactions are observed between copper(II) and polymer ligand 1 on the basis of room temperature spectra. It is shown in Figure 2 that the almost isotropic spectrum at a lower magnetic field (b) overlaps onto the anisotropic spectrum (a), consisting of lines a' and a''. Increasing the intensity of signal a' in a perpendicular region as well as improved resolution of copper hyperfine lines a' in a parallel region indicate a larger contribution of the anisotropic spectrum as the pH becomes higher. The results demonstrate clearly that tumbling copper(II)-aqua complexes are in equilibrium with copper(II) ions bound to the phosphoryl oxygen of the phosphonate ester. The equilibrium is shifted towards increasing efficiency in copper(II) coordination at higher

Table 3 E.p.r. spectral parameters of copper(II)-resin systems at 77 K

Resin	pH	A_{\parallel}	g_{\parallel}
1	3-10	137	2.400
2	3.1	137	2.410
	5-10	147	2.374
3	2-3	137	2.415
	5-10	146	2.382
4	4.5	134	2.405
	6	145	2.390
	9	144	2.384
	11	148	2.370
5	2	137	2.409
	3	131	2.400
	4.5	128	2.408
	6-8	127	2.390
	10	136	2.397
6	3-9	162	2.346
	10	166	2.336

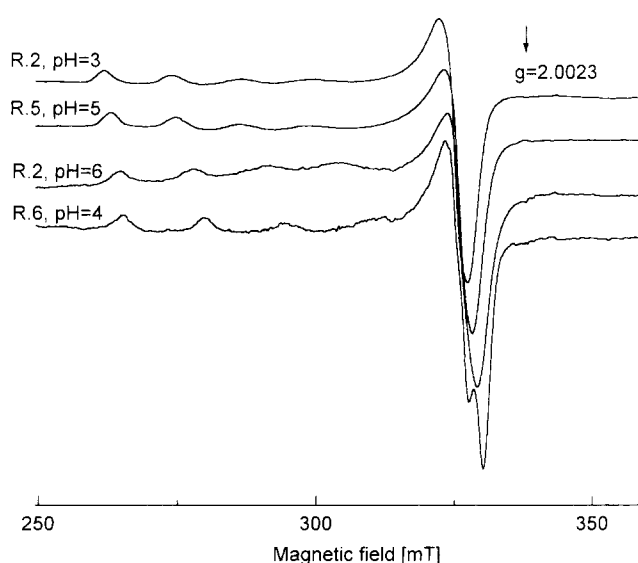
**Figure 3** E.p.r. spectra of the copper(II)-resin 2 system as a function of pH at room temperature

pH. The e.p.r. spectral parameters of the polymers with different functional groups are collected together in *Table 3*.

Furthermore, e.p.r. spectra at room temperature demonstrate a stronger coordination ability of resin 2 (containing phosphonic acid groups) in comparison with the parent resin (resin 1); the anisotropic spectrum appears and reaches the highest contribution at significantly lower pH (*Figure 3*).

Analysis of the e.p.r. anisotropic parameters A_{\parallel} and g_{\parallel} , which are especially sensitive to the nature of the donor atoms coordinated in the plane around copper(II)²⁰, leads to the conclusion that the complexation ability of the ion exchangers strongly depends on pH of the solutions being in equilibrium with the polymers; the different donor properties of the particular resin are pronounced in the e.p.r. spectra (*Figure 4* and *Table 3*).

E.p.r. parameters of copper(II) immobilized on resin 1 are close to those usually observed for copper-aqua complexes (*Table 3*). It suggests that copper(II) coordination (proved earlier by room temperature e.p.r. spectra) is realized through the phosphoryl oxygen of the phosphonate ester with similar donor properties to water molecules. This type of interaction was observed

**Figure 4** E.p.r. spectra of copper(II)-resin systems at 77 K

for copper(II) and tetraisopropyltetramethylenebisphosphate²¹. It appears also that copper(II) binding is facilitated by a greater extent of neutralization of the protons competing with copper(II) ions.

E.p.r. parameters of the copper(II)-resin 2 system in the pH range 1-3 are almost equal to these found for the copper(II) complex with four water molecules in the metal plane¹⁷. Hence, the immobilization of copper(II) ions on resin 2, indicated by room temperature spectra, should be interpreted as arising from the binding of phosphonic acid groups at axial positions. At low pH the coordination of the functional groups to copper(II) ions is usually followed by subtraction of the protons from the OH groups.

The characteristic increase of A_{\parallel} and decrease of g_{\parallel} between pH 7 and 10 correspond to an increasing strength of interaction between the metal and equatorial ligands as the result of substitution of water molecules surrounding copper(II) ions by deprotonated phosphoryl groups.

The similarity between the e.p.r. parameters for the species formed by resins 2 and 3 with copper(II) in the pH range 5-10 suggests the same coordination mode of the acid groups. The spectral parameters show that at least one functional group is bound in the plane; the remaining coordination positions are filled by water molecules. A higher sorption ability of the phosphonic group at pH 2 should be assigned to its greater dissociation degree (promoting earlier interaction with copper(II) ions) than for carboxylic groups. The further increase in copper(II) sorption ability for resin 4 at pH 2 suggests that the phosphonic acid group occupying the axial position is bound to a second copper(II) ion, whereas part of the carboxylic group may be coordinated in the metal plane. Due to the opposite effect of these interactions on the A_{\parallel} and g_{\parallel} parameters, their values are close to those observed for copper(II) surrounded by water molecules. The involvement of more than one acid molecule in the metal coordination plane at higher pH appears to be probable in view of a characteristics change in the e.p.r. parameters.

The significantly different coordination properties of resin 5 (with two phosphonic groups) in comparison with resin 2 (with one phosphonic group) are manifested by

e.p.r. spectral properties. The strongest copper(II) sorption (see Table 2) ability of resin 5 and its A_{\parallel} value being lower than for the aqua complex imply a significant weakening of the equatorial copper–ligand bonds due to interaction with phosphonic acid groups in the axial position²². A second phosphonic acid group may be involved in bonding to the neighbouring copper(II) ion to a greater extent than in the case of resin 4, resulting in an accordingly higher copper(II) sorption. At pH values higher than 10, phosphonic acid groups are activated to occupy the equatorial position, as is reflected in the increase in the A_{\parallel} and the decrease in the g_{\parallel} parameters.

Unique ligand properties are displayed by resin 6; each carboxylic group is attached to same carbon atom of the pendant group, giving it a higher ability to operate as a chelating agent in comparison with known polyacrylic acids¹⁹. Due to weaker acidity in comparison to the phosphonic acid groups, their copper(II) uptake is the lowest of all the investigated polymers at pH 2. On the other hand the stronger donor strength of the carboxylic groups leads to a significant increase in equatorial metal–ligand interactions, indicated by distinctly different spectral e.p.r. characteristics (Figure 4 and Table 3): unexpectedly high A_{\parallel} and low g_{\parallel} parameters. These results indicate considerable stability of the chelate rings. Four oxygen donors around copper(II) originate from two functional groups ($-\text{CH}(\text{COOH})_2$) interacting through deprotonated oxygens or from one ($-\text{CH}(\text{COOH})_2$) group coordinating through both types of oxygen.

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