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Coordinating properties of polymers with N-substituted diamides of malonic acid towards Cu(II); EPR studies

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Abstract

New chelating resins containing N-substituted diamides of malonic acid have been contacted with various Cu(II) solutions and the structural parameters of complexes formed have been investigated using the EPR method. Correlation between EPR spectra obtained and Cu(II) uptake shows that two main factors are influencing the ability of the ligand to coordinate metal ion. The first is the length of the pendant group (distance from the backbone chain) facilitating ligand accessibility and the second is the ligand potential to create a chelate ring with Cu(II). This effect is dominant in resins with N-substituted diamides of malonic acid, in which neighbouring ligands can cooperate efficiently. At higher pH, unusually stable Cu(II) complexes are formed by resins with 2-aminoethyl and 2-aminomethylpyridine substituted diamides of malonic acid due to the involvement of deprotonated amide nitrogen and formation of tetradentate ligands. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Interest in investigations of metal polymer complexes is still strong due to the variety of applications of such systems. Examples include: waste water treatment, organic synthesis [1], hydrometallurgy [2] and recovery of trace metal elements [3]. Among polymers those containing nitrogen as donor atoms have been synthesised and used in complexation of transition metal cations. Various nitrogen containing ligands such as oligoethyleneimines [4,5] vinylamine [6], triazoles [7] and imidazole derivatives [8] have been used in preparation of resins. In previous work synthesis of new chelating resins with N-substituted diamides of malonic acid (Fig. 1) by modification of vinylbenzyl chloride-divinylbenzene copolymer has been presented as well as uptake of different metal ions from metal ion mixtures [9]. It was found that bis-type resins exhibited significantly higher uptake of metal cations, including Cu(II), than was observed for reference mono-resins containing respective N-substituted amides of monocarboxylic acid.

These results prompted the present work, where we have used EPR spectroscopy to investigate the coordination behaviour of –C(O)NH–R ligands (L) placed next to each other or located separately towards Cu(II). EPR is a very convenient tool in investigations of Cu(II) complexes formed by ligands attached covalently to polymers. It allows for determination of type of complex and donor set around the central atom. An additional advantage of polymer–metal complexes as a subject of EPR studies is that copper(II) interacting with ligands inside polymers is already ideally dispersed and diluted by the diamagnetic polymeric matrix thus showing very well resolved anisotropic hyperfine structure even at room temperature. EPR method has been used before to investigate macromolecule–metal complexes [10–12].

The aim of this work is to determine types of complexes formed between Cu(II) and resins containing N-substituted amides as ligands.

2. Experimental

The investigated and reference resins were prepared by suspension polymerisation of vinylbenzyl chloride/2 wt.% divinylbenzene using benzoyl peroxide as initiator.

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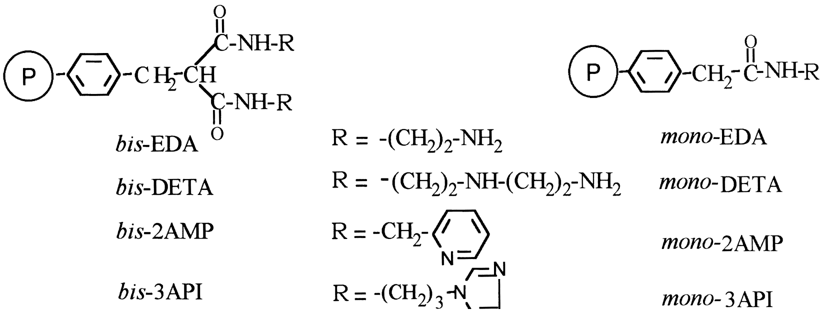

Fig. 1. Scheme of investigated and reference resins.

Polymerisation was followed by modification with diethyl malonate and by subsequent aminolysis with appropriate amine. Details of resin preparation have been presented elsewhere [9].

Sorption of copper(II) on resins was determined by contacting amount of the resin containing 0.05 mmol of ligand with 10 ml of 1×10^{-4} N Cu(II) solution in 0.2 M acetate buffer for 48 h. After that time, the solution was filtered and the metal ion concentration measured using atomic absorption spectroscopy on a Perkin-Elmer AAnalyst 100 spectrophotometer with wavelength set at 324.8 nm.

The EPR spectra were recorded on a Bruker ESP 300 E spectrometer operating at X-band (9.1–9.9 GHz) and equipped with the Bruker NMR gaussmeter ER 035M and the Hewlett-Packard microwave frequency counter HP at 77 K. The spectra were analysed by computer simulation programme [13] based on resonance fields calculated according to method of Sakaguchi et al. [14] The EPR measurements were performed on resins swollen in 10 ml of aqueous solutions of 1×10^{-4} M $CuCl_2$, separated by filtration and air dried. The EPR spectra were recorded after 2 days of pH adjustment of the resin with HCl and/or NaOH at constant ionic strength ($I = 0.5$ M).

Table 1
Capacity of the ligands for Cu(II)

Resin	pH			
	3.7	5	3.7	5
	mg Cu/g		log D[a]	
bis-EDA	0.28	1.85	2.02	3.81
mono-EDA	0.20	0.72	1.84	2.57
bis-DETA	1.10	> 1.5	3.49	–[b]
mono-DETA	1.10	1.85	3.04	4.49
bis-2AMP	0.70	1.23	2.44	3.06
mono-2AMP	0.42	0.98	1.65	2.76
bis-3AMI	1.69	> 1.56	5.18	–[b]
mono-3AMI	0.56	1.01	2.58	3.01

[a] Distribution coefficient D is calculated as mg of Cu(II) complexed by 1 g of resin/mg of Cu(II) in 1 ml of solution after contact with polymer.

[b] Entire amount of Cu(II) complexed under experimental conditions.

3. Results and discussion

Metal uptake studies of the solutions being in equilibrium with solid polymers appears to be insufficient to obtain information about the coordination processes between metal ions and polymer functional groups. Hence the type of the complexes formed and complex stability remain unknown. Recently, we have been engaged in applying EPR spectroscopy to detect the formation of the Cu(II) complexes directly in the resin phase [15–17]. The main indication of Cu(II) complex formation is based on the distinct difference between the EPR spectra of Cu(II) aqua ions ($g_{II} = 2.24$, $A_{II} = 125 \times 10^{-4}\ \mathrm{cm}^{-1}$) and Cu(II) immobilised due to the coordination by donor atoms of the functional groups. It has been shown empirically by Peisach and Blumberg [18] and commented to some extend theoretically by Pilbrow [19] that between A_{II} and g_{II} parameters there are relations, which are specific and characteristic for complexes with similar donor sets (4O, 3O1N, 2O2N, 1O3N or 4N) around Cu(II) in the *xy* plane. The parameters for Cu(II) complexes with a particular set of donor atoms are additionally affected by the total charge of the complexes and aromaticity of the chelate rings. Hence, the analysis of the change in the EPR parameters appeared to be specially useful evidence of the coordination mode of polyfunctional ligands providing different donor atoms able to bind Cu(II) depending on pH and Cu/ligand ratio.

3.1. Coordination ability of EDA and DETA ligands

Table 1 presents significantly lower Cu(II) capacity of EDA than DETA ligands, which is the usual trend due to the bidentate character of each ethylenediamine group. A much stronger increase in Cu(II) binding upon pH increase is observed for bis-DETA than for bis-EDA which additionally suggests that the ability to form a chelate ring with Cu(II) in the case of bis-DETA predominates an appearance of deprotonated nitrogen donors which is similar for both types of the resins. The change of the EPR parameters with an increase of pH for bis-DETA compared to mono-DETA implies that at lower pH (about 4 and at 3.11, respectively)

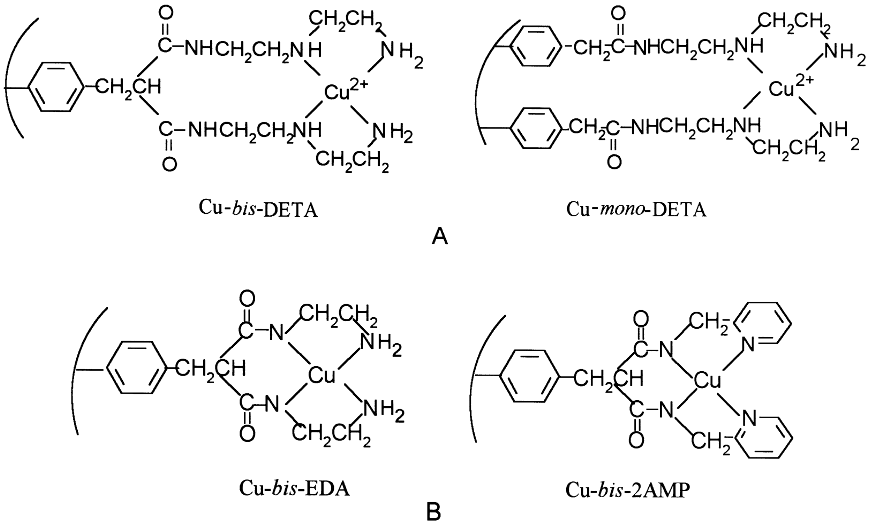

Fig. 2. Cu(II) complexes formed by resins.

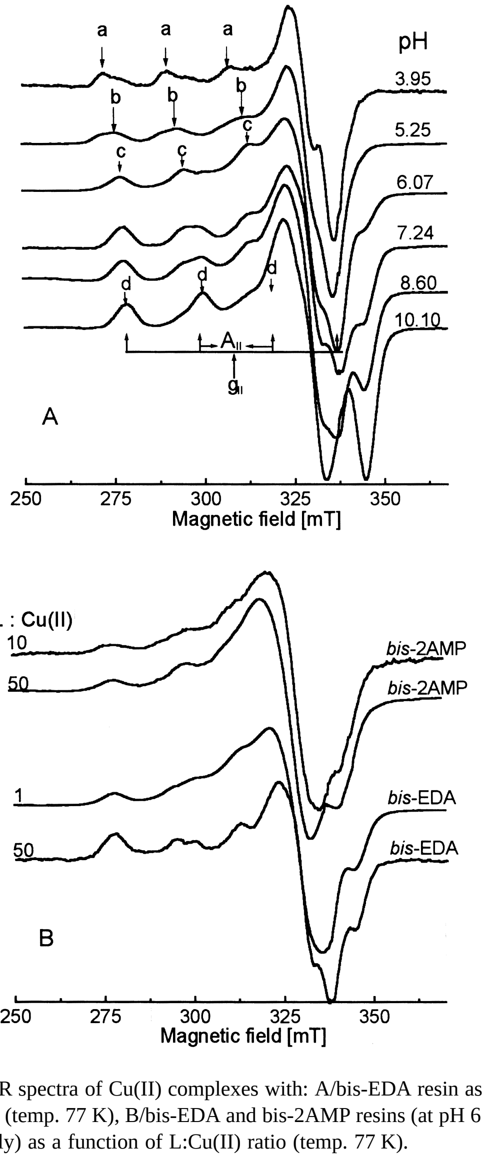

Fig. 3. EPR spectra of Cu(II) complexes with: A/bis-EDA resin as a function of pH (temp. 77 K), B/bis-EDA and bis-2AMP resins (at pH 6 and 10, respectively) as a function of L:Cu(II) ratio (temp. 77 K).

Cu(II) ions are attached to a smaller number of nitrogen atoms. A substantial increase of donors able to coordinate occurs at higher pH. It causes a characteristic increase of A_{II} and decrease of g_{II} parameters. The EPR parameters for bis- and mono-DETA ligands loaded with Cu(II) at pH above 5 are apparently similar, indicating the same structure of the complexes formed. These complexes are formed by four nitrogen atoms from two bidentate L groups supplied by mono- and bis-DETA ligands which should be assigned to the ligand arrangement illustrated in Fig. 2A.

It should be noted that this stable coordination environment is achieved by two L bidentate groups in the case of DETA ligands, while for EDA the higher number of monodentate L groups is necessary to form the stable complex in the mid pH range. These results suggests that close neighbouring of L groups in bis-DETA ligand is a major factor determining its higher efficiency towards Cu(II) than that observed for mono-reference.

3.2. Coordination ability of EDA and 2AMP

The greater value of g_{II} at pH about 4 for EDA than for 2AMP indicates a lower symmetry of the complex formed or/and a smaller number of nitrogen donors coordinated to Cu(II). Both these effects should lead to lower stability of the complex. The EPR parameters are indicative of two or less nitrogen donors of EDA bound to Cu(II). The structural differences suggested by EPR data are in a good agreement with more efficient Cu(II) uptake by 2AMP than that for EDA at pH 3.7 (see Table 1).

The coordination power of EDA and 2AMP is reversed upon pH increase. The spectrum of EDA complex at pH about 6, with apparently lower $g_{II} = 2.226$, reflects a more saturated coordination environment due to the involvement of at least three nitrogen atoms in the Cu(II) plane. This corresponds with higher Cu(II) uptake found for EDA.

Table 2
EPR parameters of Cu(II)-loaded resins

Resin	L:Cu(II)	pH	g_{II}	A_{II} (10^{-4} cm^{-1})	
bis-EDA	50	3.95	2.263;(2.226)	177;(182)	a[a]; c[a]
	50	6.0–7.2	2.226;(2.19)	184;(200)	c[a]; d[a]
	50	10	2.180	209	d[a]
	1	5.25	2.263;2.240	176;180	a[a]; b[a]
	1	6.07	2.223	184	c[a]
	1	6.15	2.223;(2.190)	182;(206)	c[a]; d[a]
mono-EDA	45	4.11	2.254	179	b[a]
	45	8.2–9.9	2.228	185	c[a]
bis-DETA	50	3.11	2.229	182	
	50	5.12–9.01	2.210	192	
mono-DETA	40	3.97	2.229	183	
	40	5.10–9.80	2.210	192	
bis-2AMP	40	3.2–4.62	2.245	178	
	40	6.45	2.246; (2.20)	178(195)	
	40	9.52	2.20	195	
	100	10.3	2.190	195	
mono-2AMP	40	2.32–9.60	2.243	180	
bis-3API	200	3.43–6.70	2.262	183	
	50	2.65	2.272	175	
	50	3.70–9.24	2.260	183	
	5	3.03	2.270	175	
	5	4.70–6.25	2.260	185	
mono-3API	200	3.35–9.5	2.262	185	
	50	2.76	2.272	166	
	50	5.54–9.24	2.260	183	
	5	2.90	2.273	178	
	5	4.7–5.5	2.265	182	
		6.6	2.260	186	

Two sets of the EPR parameters are related to the complexes existing in equilibrium; in parentheses are the parameters of the complex giving a smaller contribution to the spectra.

[a] Denotes the spectra indicated in Fig. 3.

The structural parameters of the Cu-2AMP system remain unaffected up to pH ca. 6.

The EPR spectra of both bis-EDA and bis-2AMP ligands loaded with Cu(II) at pH 6 reveal equilibrium between the former complex (e.g. three N atoms in the Cu(II) plane) and new species characterised by extraordinary high A_{II} and low g_{II} parameters (Fig. 3A). The stepwise change in pH from 6 to 10 results in a consequent increase of the new spectrum contribution. Its parameters are typical for specially stable Cu(II) complexes due to tetradentate coordination realised by four nitrogen atoms. These parameters are close to those observed for the Cu(II) ion coordinated in the equatorial plane by four extra strong nitrogen donors provided by porphyrine-like ligands [19]. The change of charge from dipositive in the previous complex to neutral for the complex formed by loss of protons from amide groups produces an additional significant shift in EPR parameters [18] . This specific Cu(II) chelation leads to an apparent increase in the Cu(II) sorption capacity of the polymers at higher pH in comparison to their mono-references. The functional groups of the polymers act as tetracoordinate ligands including amide N atom according to Fig. 2B.

The spectrum assigned to the species presented in Fig. 2B is not observed in the case of Cu(II)-loaded mono-EDA and mono-2AMP references; their functional groups separately attached to the polymer chains are not able to encapsulate one copper(II) ion in a manner similar to that realised by bis-type resins.

The spectra with $A_{II} = 183 \times 10^{-4}$ cm^{-1} and $g_{II} = 2.226$ at the highest pH for mono-EDA and at pH 4–8 for bis-EDA indicate a similar coordination environment of the Cu(II) realised most likely by three ligands in monodentate fashion; according to the above results the bidentate coordination in the complexes with bis-EDA leads to distinctly different spectral properties.

3.3. Coordination ability of 2AMP and 3API

It appears that 2AMP possessing a shorter arm between nitrogen donor and =CH carbon than 3API exhibits lower Cu(II) capacity. This effect is observed in spite of the fact that the smaller ring size and ring angles of imidazole compared to pyridine should lower the coordination ability of 3API [12]. The EPR parameters of 3API (both mono- and bis-types) are typical for a highly saturated coordination environment, including three or four monodentate groups of 3API. This assumption is supported by EPR data for monomeric analogues [12,20]. EPR spectral similarity between bis-3API and mono-3API indicate that their functional groups operate as monodentate ligands; their amide nitrogen atoms are not included into coordination. It is noteworthy that the 4N complex for bis-3API appears already at pH about 4, while with mono-3API at pH higher than 5. It is obvious that bis-3API is a more efficient sorbent for Cu(II) than its mono-reference, but higher Cu(II) loading capacity of bis-3API than bis-2AMP and in consequence, much higher distribution coefficients (Table 1) indicate that the complexes with longer pendant groups provided by 3API lead to favourable thermodynamic stability of the complexes on the polymer. A positive influence on Cu(II) coordination ability of 2AMP at higher pH arises from deprotonated amide nitrogen involvement in complexation, as is shown in Fig. 2B.

3.4. The change of L:Cu(II) ratio

The influence of ligand excess on the coordination sphere around Cu(II) in the case of polymer bound functional groups is specific and differs from Cu(II) binding by low molecular ligand analogues. The data shown in Table 2 reveal that the coordination sphere of Cu(II) is rather weakly affected by the significant change in the L:Cu(II) ratio. The influence of a large excess of the ligands (L:Cu(II) ratio about 200) was tested for bis- and mono-3API. The final complex including four nitrogen coordinating group L exists over the entire (2.7–9.5) pH range. By decreasing L excess to 50 and further to 5 this maximum saturation of the coordination environment is reached at higher pH, 3.7 and 4.7, respectively for bis-3API, and at pH 5.5 and 6.6, respectively, for mono-3API. A deficiency of L groups for bis-EDA (for L:Cu(II) ratio equal 1) leads to complexes with a lower participation of nitrogen donors coordinated to Cu(II) up to the $\mathrm{pH} = 5.3$ as indicated by $g_{\mathrm{II}} = 2.240$. The spectrum relevant to this coordination is not observed when a 50-fold excess of the ligand is used; more stable complex with $g_{\mathrm{II}} = 2.223$ is formed at the same pH value as a consequence of increasing involvement of EDA ligands in the Cu(II) plane. The specific effect of increasing Cu(II) concentration on the EPR spectra is illustrated in Fig. 3B. The short distance between Cu(II) ions distributed mainly on the polymer surface leads to a significant broadening of hyperfine splitting lines of parallel orientation due to Cu–Cu exchange interaction and to the appearance of an isotropic line overlapped perpendicular region of the spectrum as a result of Cu–Cu dipole–dipole interaction [10,19].

4. Conclusions

The correlation between EPR spectra parameters and uptake capacity for Cu(II) reveals two main factors influencing the ability of the ligand to coordinate metal ion. The first is the length of the pendant group facilitating their accessibility for Cu(II) ions; the second is the ligand potential to create chelate rings with Cu(II). The latter strongly improves the complex stability. All bis-type ligands are able to be chelating due to the presence of two pendant group attached to one =CH carbon. The mobilisation of some donors to participate in the Cu(II) coordination sphere results also from their deprotonation at higher pH. The stronger fixation of the ligand is stimulated efficiently by increasing the ligand:Cu(II) ratio which makes the functional groups more accessible for metal ions. This may be reached either by changing the pH of the metal ion solution in equilibrium with the polymer or/and by the experimental conditions of the metal ion uptake.

Unusual values of EPR parameters for Cu-bis-EDA and Cu-bis-2AMP systems at $\mathrm{pH} > 6$ indicate that extremely stable Cu(II) complexes are formed. The functional groups of these polymers act as tetracoordinate ligands including deprotonated amide N atoms. This specific Cu(II) chelation leads to a significant increase in Cu(II) sorption capacity of these polymers at higher pH. The functional groups of mono-EDTA and mono-2AMP act at higher pH as bidentate ligands leading to less stable complexes and lower Cu(II) uptake.

EPR spectral properties of Cu(II) complexes with bis-DETA and mono-DETA polymers resemble each other quite closely indicating similar structure of the formed complexes; the same $-\mathrm{NH}-(\mathrm{CH}_2)_2-\mathrm{NH}_2$ group of both ligands participates in Cu(II) coordination. Their amide N atoms are not involved in Cu(II) chelation.

A significant increase in coordination ability is observed for 3API in comparison with 2AMP as a result of greater distance of the former from main polymer chain and thus higher accessibility.

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