

## SOLID-STATE STRUCTURE OF COPPER COMPLEXES OF *N*-(2-CARBOXYETHYL)CHITOSAN

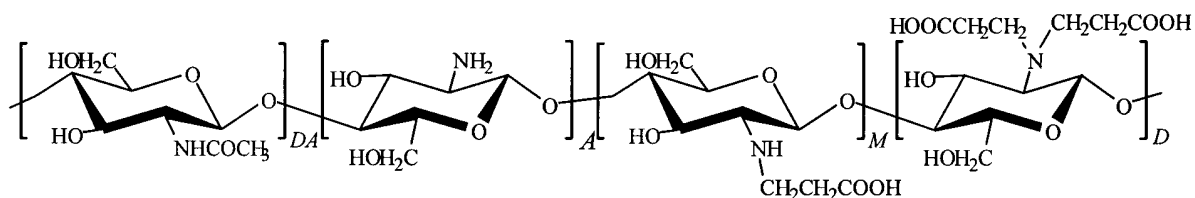
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The sorptivity for ions of the Irving-Williams series ( $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ) was estimated for the chelate sorbent *N*-(2-carboxyethyl)chitosan cross-linked by nanosecond electron-beam irradiation. The maximum capacity reaches 3.7 mmol/g using a mixture of the appropriate sulfates at pH 4.5. The selectivity of copper sorption is 80%. The structure of the coordination sphere of the copper complexes with *N*-(2-carboxyethyl)chitosan was investigated by ESR spectroscopy.

Key words: *N*-(2-carboxyethyl)chitosan, copper complexes, spectroscopy, electron spin resonance.

**Introduction.** Chitosan (poly- $\beta$ -*D*-2-deoxy-2-aminoglucose) is a highly reactive aminopolymer that, in contrast with its structural analog cellulose, can be more effectively functionalized in order to improve and adjust the sorption properties of the products [1–4]. A method for preparing *N*-(2-carboxyethyl)chitosan (CEC) from chitosan and acrylic acid in a gel was previously developed [5]. According to the established structure, CEC is a statistical copolymer of  $\beta$ -*D*-2-deoxy-2-aminoglucose and its *N*-derivatives:



The sorbent produced by cross-linking CEC with lower dialdehydes possesses high sorption capacity for ions of the Irving-Williams series and is highly selective for copper(II) absorption [6]. Using electron beams for cross-linking has an obvious advantage over any cross-linking by chemical reagents because in this instance the specific mass of the matrix ascribed to a single chelate group does not increase [7]. The structure of the coordination sphere of CEC complexes cannot be directly investigated by x-ray diffraction analysis because it is a polymeric substrate. Models of such complexes for the free polymer have been proposed [8]. The dependence of the sorption properties of the material on the structure of the resulting metal complexes must be understood in order to optimize its structure. These data have not been reported for CEC. Herein an attempt is made to describe the structure of the copper complexes formed by sorption of copper in CEC cross-linked using an electron beam. The structure of the linking agent functional groups has no effect because no linking agent is used.

**Experimental.** CEC with various degrees of substitution (DS) was used as the sodium salt and was cross-linked beforehand by nanosecond electron-beam irradiation (80 kGy). An aqueous solution of a mixture of Co(II), Ni(II), Cu(II), and Zn(II) sulfates had the same concentration of each salt (0.025 M) and pH 4.5. The experiment was

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TABLE 1. Sorption of Irving–Williams Series Ions at pH 4.5 by *N*-(2-Carboxyethyl)chitosan Cross-Linked by Nanosecond Electron-Beam Irradiation (80 kGy)

DS	DS(m)	DS(d)	DS(m)/DS(d)	Number of functional groups, mmol/g		Number of sorbed metals, mmol/g (% of $\Sigma$ )				
				$N_{\text{tot}}$	COOH	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	$\Sigma$
0.96	0.71	0.12	6	4.44	3.57	0.08	0.20	1.65 (79)	0.15	2.08
1.06	0.39	0.33	1.18	4.32	3.84	0.33	0.44	1.64 (54)	0.60	3.01
1.25	0.75	0.25	3	4.10	4.35	0.28	0.55	1.94 (52)	0.93	3.70
1.32	0.45	0.44	1	4.02	4.53	0.10	0.25	1.56 (78)	0.08	1.99
1.54	0.46	0.54	0.85	3.82	4.99	0.29	0.45	1.73 (58)	0.52	2.99

Note: DS, total degree of substitution,  $DS = DS(m) + 2DS(d)$ ; DS(m), fraction of N-monosubstituted glucosamine units in the total number of glucosamine units; DS(d), fraction of N,N-disubstituted glucosamine units in the total number of glucosamine units.

carried out under static conditions for 24 h. The amount of sorbed metal ions was determined from the difference in the concentrations of the starting and final solutions. The concentration was determined using atomic-emission analysis on an Optima 4300 DV spectrometer.

ESR spectra were recorded using a PS 100.X ESR spectrometer (Adani, Belarus) at 298 K. Samples for ESR studies were prepared by storing for 4 days a weighed portion of CEC in a solution of the appropriate copper salt (acetate or nitrate) with subsequent filtration and drying at 70°C. The copper content in the sample was determined as above.

**Discussion.** Table 1 lists the results for sorption of ions of the Irving–Williams series by cross-linked CEC with a high DS and various ratios of mono- and disubstituted glucosamine units. It can be seen that the capacity increased significantly initially with increasing DS whereas the selectivity for Cu(II) sorption decreased. This was easily explained within the framework of known sorption rules. The sorption capacity decreased at first and then increased with a further increase of the DS. The selectivity changed in the opposite direction. It increased at first and then decreased. It should be noted that the number of absorbed ions exceeded the number of ion-binding carboxylate groups. This indicated that some of the sulfate ions were absorbed in addition to the cations.

The molar amount of absorbed metal ions did not exceed the molar content of N in the sorbent. Acetamide groups coordinate weakly as a result of the poor donor properties of the amide N. However, balance calculations confirmed that some of the amino groups were not involved in complex formation, i.e., they were sterically unavailable. The use of sulfate solutions, which is advantageous from a practical viewpoint, introduced definite complications for the sorption study. In contrast with the corresponding salts of monobasic acids, chitosan sulfate cross-linked by the doubly charged anion was insoluble in water and swelled poorly. The possibility of the same CEC cross-linking with its larger basicity, which increased with increasing DS, complicated the process even further. It should also be considered that the nature of the cross-linking by acetamide, amine, and mono- and disubstituted units of the polymeric chain due to electron-beam irradiation cannot be entirely the same. The complicated interplay of these factors did not allow prevailing tendencies to be revealed. Nevertheless, it is certain that lower capacity always correlated with maximum selectivity; higher capacity, with minimum selectivity.

Solutions of copper nitrate were used in order to avoid the effect of ionic cross-linking during the investigation of the complex structure. Solutions of copper acetate were used to account for the possibility of complex formation by low-molecular-weight ligands because the stability of copper sulfate complexes is about the same as that of the acetate complexes.

Copper complexes of CEC were studied using ESR spectroscopy in order to establish the structure of the compounds formed upon sorption. The corresponding complexes with chitosan and carboxymethylchitosan (CMC) were studied for comparison. The results indicated that polymers were formed even in relatively acidic media (pH 3.1–4.3) by N-containing copper complexes despite the fact that the  $pK_a$  of the amino group in the starting chitosan was 5.6 [9]; in CEC ( $DS = 1$ ),  $pK_a = 6.42$  [10]. This was in complete agreement with an analogous phenomenon that was observed earlier for cross-linked polymeric complexants with aliphatic amino or aminoacetate ligands [11, 12].

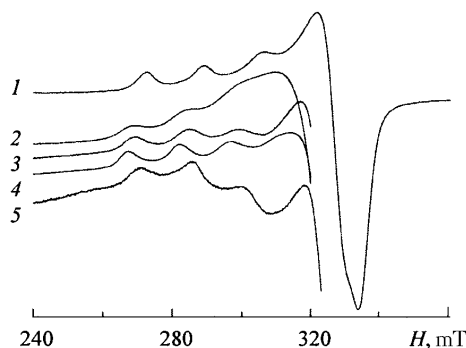


Fig. 1. ESR spectrum of  $\text{Cu}^{2+}$  in samples at 293 K at 9.3 GHz: carboxymethylchitosan, 1.0 ( $\text{Na}^+$ ) (1), *N*-(2-carboxyethyl)chitosan, 1.0 ( $\text{H}^+$ ,  $\text{Na}^+$ ) (2), *N*-(2-carboxyethyl)chitosan, 0.31 ( $\text{H}^+$ ) (3), *N*-(2-carboxyethyl)chitosan, 1.0 ( $\text{Na}^+$ ) (4), chitosan (5).

The observed ESR spectra were characteristic of  $\text{Cu}^{2+}$  ions in an axially symmetric field. They were anisotropic signals with well resolved hyperfine splitting (HFS) in the parallel orientation of the unpaired electron spin and external magnetic field (Fig. 1). This enabled ESR parameters  $g_{\parallel}$  and  $A_{\parallel}$  to be measured. The ESR parameters  $g_{\perp}$  and  $A_{\perp}$  were not determined because the HFS was not resolved for the perpendicular orientation. The ESR parameters for the  $\text{Cu}^{2+}$  complexes of chitosan ( $g_{\parallel} = 2.255$  and  $A_{\parallel} = 15.3$  mT) (spectrum 5) agreed well with those of the complex  $[\text{Cu}(\text{MEA})_2(\text{H}_2\text{O})_2]^{2+}$  in which two N,O rings from bidentate monoethanolamine ligands with protonated alcohol groups are located in the equatorial plane of the copper complex [13]. The ESR parameters did not exclude the possibility that a complex with an elongated octahedron of three N atoms in the Cu(II) coordination sphere and alcohol groups situated along the apical axis was formed in chitosan the same as in some weakly basic anion exchangers [11]. The fourth coordination site in the equatorial plane would probably be occupied by a water molecule. A choice between these two interpretations was impossible based on the ESR data.

The ESR parameters of the  $\text{Cu}^{2+}$  complexes with CMC (spectrum 1) were typical of the formation by Cu ions of *trans*-complexes with two aminoacetate ligands in the equatorial plane. Complexes with analogous compositions and structures were observed in three-dimensional polymeric matrices of styrene and polyacrylate with complex-forming amino- and iminodiacetic and ethanolaminoacetic acids (Table 2).

Various copper complexes were formed with CEC depending on the DS, initial form of the sorbent (Na- or H-form), and copper salt (acetate or nitrate II). Complexes of 1:2 composition with *trans*-location of amino groups of  $\beta$ -alaninate 6-membered rings and ESR parameters  $g_{\parallel} = 2.269$  and  $A_{\parallel} = 15.8$  mT (spectrum 3) were formed with the minimum DS (0.31) where only  $\beta$ -aminopropionic acid groups are found in the polymeric chain. We observed analogous complexes for CEC with DS = 1.0 upon reaction with copper nitrate solution. The ESR parameters changed to  $g_{\parallel} = 2.288$  and  $A_{\parallel} = 14.8$  mT if copper acetate solution was used. This was consistent with a structural change of the copper complex (spectrum 4). Iminodipropionate groups were also formed in the polymer molecules for DS = 1.0. Their involvement in the complexation to form at once two coordinated  $\beta$ -alaninate rings upon reaction with copper ion generated in this instance complexes of 1:1 composition. Apparently the presence of acetate ions, which form copper complexes, stabilized this complex in the polymer by occupying the vacant fourth position in the equatorial plane. This conclusion agreed with those above about the sorption of inorganic anions. The  $\text{Cu}^{2+}$  complex with *N*-(2-hydroxyethyl)iminodipropionic acid (diHe-ala) of 1:1 composition ( $\text{CuL}$ ) has the same ESR parameters (Table 2). Complexes of 1:2 composition ( $\text{CuL}_2$ ) were not observed. The lack of a low-molecular-weight ligand in the solution (replacing acetate by nitrate) made existence of the 1:1 complex energetically unfavorable. In this instance incorporation into the copper coordination sphere of a carboxylate from another iminopropionate group caused rearrangement of the copper complex, involvement in the complexation of the  $\beta$ -alaninate chelate ring of this group, and formation of the 1:2 complex, the structure of which was analogous to that described above for CEC with DS = 0.31.

These conclusions were directly confirmed by an ESR study of CEC with DS = 1.0 in the mixed  $\text{H}^+$ ,  $\text{Na}^+$ -form that had absorbed various amounts of  $\text{Cu}^{2+}$  from acetate solution. At first the ESR signal for the 1:1 complex

TABLE 2. ESR Parameters of Various Chelating Polymers

Sample, DS	Form	$g_{\parallel} \pm 0.005$	$A_{\parallel} \pm 0.03, \text{ mT}$
Chitosan	-NH <sub>2</sub> , acetate	2.255	15.3
CEC, 0.31	H <sup>+</sup> , acetate	2.269	15.8
CEC, 1.0	Na <sup>+</sup> , acetate	2.271	15.6
CEC, 1.0	Na <sup>+</sup> , acetate	2.288	14.8
CEC, 1.0	H <sup>+</sup> , Na <sup>+</sup> , acetate	2.293	14.9
		2.273	15.6
CEC, 1.62	Na <sup>+</sup> , acetate	2.291	14.8
	Na <sup>+</sup> , nitrate		
CMC, 1.0	Na <sup>+</sup> , acetate	2.263	16.7
AMP-95 [12]	H <sup>+</sup> , sulfate	2.303	14.9
		2.266	16.5
ANKB-10/35 [12]	H <sup>+</sup> , sulfate	2.303	14.9
		2.265	16.7
ANKB-50 [12]	H <sup>+</sup> , sulfate	2.298	15.3
		2.264	17.2
AMP-15 [12]	H <sup>+</sup> , sulfate	2.316	14.8
		2.301	15.7
diHe-ala [14]	CuL	2.295	15.2
	CuL <sub>2</sub>	2.261	13.4

(at low copper contents) was observed. A signal for the 1:2 complex in addition to that for the 1:1 complex appeared in the ESR spectrum as the amount of absorbed copper increased. The fraction of the 1:2 complex increased rapidly so that the ratio of copper ions bound in the different complexes equaled 1:1 upon reaching 0.8 mmol/g of absorbed copper (spectrum 2). Further increasing the DS of CEC up to the maximum (DS = 1.62) resulted in formation of only the 1:1 copper complexes. The composition of the complexes remained the same regardless of whether the H<sup>+</sup>-form was used or acetate ions were replaced by nitrate in the initial solution. Thus, it was established that 1:1 copper complexes were formed under all conditions with primarily iminodipropionic groups in the CEC. This distinguished the cross-linked polymer from the one-dimensional acid diHe-ala, for which 1:2 complexes formed in addition to the 1:1 complexes [14].

A comparison of our ESR parameters for Cu<sup>2+</sup> with those in the literature [9, 15] showed that fundamentally different conclusions were made about the structure of the copper complexes in modified chitosans from similar ESR spectra. The previous interpretation [9, 15] was based on the hypothesis that Cu<sup>2+</sup> can react with only one amino group of chitosan and only at rather high pH values (pH ≥ 8) where it is expected to be deprotonated. Attempts were not even made to show that the polymeric chain is flexible enough to twist and form di- and even higher amine copper complexes. However, it was proved experimentally [8] that this is possible. ESR investigations of amine, aminoalcohol, and aminocarboxylate polyelectrolytes (including cross-linked) and their monomeric analogs confirmed that diamine (and higher) copper complexes are formed even in acidic media [11–13, 16, 17]. It should be noted that there is a general tendency for the ESR parameters of Cu<sup>2+</sup> complexes of similar structure with aminoacetic groups of polymers to have large  $A_{\parallel}$  values (and in several instances  $g_{\parallel}$  too) compared with Cu<sup>2+</sup> complexes with aminopropionic groups.

A comparison of the results with those in the literature showed that the nature of the polymeric backbone (natural or synthetic polymer) had no effect on the structure of the resulting copper complexes. The structure of the functional group had the main influence. It should be noted that the presence of a low-molecular-weight ligand, even one so simple as acetate, in the solution from which copper is extracted caused formation of mixed complexes.

**Conclusion.** The DS of *N*-(2-carboxyethyl)chitosan corresponding to the highest capacity and selectivity for Cu(II) in Irving–Williams series metals (maximum capacity up to 3.7 mmol/g; selectivity, up to 80%) was found. It was shown that anions of the absorbed solution are involved in the sorption. The structure of copper complexes involving mono- and disubstituted units was studied using ESR spectroscopy. Bis- and monoligand complexes were formed for both fragments. It should also be noted that bisligand complexes were not formed with disubstituted units, in contrast with low-molecular-weight (model) compounds.

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