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EPR investigation of Cu(II)-complexes with nitrogen derivatives of dialdehyde starch

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ABSTRACT

Dialdehyde starch obtained by periodate oxidation from potato starch was converted into its disemicarbazone (DSC), dithiosemicarbazone (DTSC), dihydrazone (DHZ) and dioxime (DOX). The Cu(II) complexes of these compounds were prepared and characterized by Raman and EPR spectra, as well as by the measurements of magnetic susceptibility. EPR investigations showed that two types of complexes with different surroundings of copper centres existed in each starch derivative. Besides nitrogen atoms of the C=N moiety and sulphur atoms of the C=S moiety, also oxygen atoms from starch hydroxyl groups and/or water molecule were proposed as the coordination sites for the central copper ions.

1. Introduction

A wide range of potential biological activity of semicarbazones, thiosemicarbazones, hydrazones and oximes stimulates considerable interest in this group of compounds. Such kind of activity is met chiefly among derivatives of aromatic and heteroaromatic aldehydes. These nitrogen derivatives of aromatic and heteroaromatic aldehydes exhibit cancerostatic (Blanz & French, 1968), antiviral (Logan, Fox, Morgan, Makohon, & Pfau, 1975), bactericidal (Dobek, Klayman, Dickson, Scovill, & Tramont, 1980) and antimalarial (Klayman, Bartosevich, Griffin, Mason, & Scovill, 1979) properties. Biochemical activity of these compounds may be enhanced by coordination with some metal ions (Hall, Chen, Rajendran, & West, 1996; West & Liberta, 1993). For instance, complexes of dithiosemicarbazone (DTSC) with Cu(II), Co(II) and Ni(II) manifest interesting tuberculostatic activity in in vitro tests (Para, Klisiewicz-Pańszczyk, & Jurek, 2001). On the other hand, nitrogen derivatives of dialdehyde starch and their metal complexes show potential non-pharmacological applications. DTSC and dihydrazone (DHZ), due to their low aqueous solubility, can be utilized for a temporary immobilization of heavy metal ions in soil. Therefore, beneficial soil micro-organisms, such as entomopathogenic nematodes and fungus *Paecilomyces farinosus*, sensitive to heavy metal ions, may be protected from their toxic influence in the period of their seasonal activity (Ropek & Para, 2003), improving yield of crop production. The nitrogen derivatives of dialdehyde starch can be applied also as traps of metal ions from industrial and municipal sewage. Biodegradation of such traps would be ecologically friendly.

Biological activity of these compounds can strongly depend on their structure. Metal complexes with semicarbazones and thiosemicarbazones of aldehydes as the ligands were the objects of many studies (Battaglia, Ferrari, & Boggia, 1994; Kumar & Chandra, 1993; Patel & Agarwala, 1996; Souza et al., 1991), whereas the structure of metal complexes with large ligands, such as starch derivatives, have not yet been investigated in details.

In this work the studies of copper complexes with starch derivatives such as disemicarbazone (DSC), dithiosemicarbazone (DTSC), dihydrazone (DHZ) and dioxime (DOX) have been undertaken. The presence of paramagnetic Cu(II) ions allows using EPR technique to have insight into the molecular structure of such complexes. The measurements of magnetic susceptibility and Raman spectra have been applied as a source of complementary data.

2. Experimental

2.1. Materials

Dialdehyde starch was obtained from potato starch (PPZ Trzemeszno Potato Enterprise, Poland) by oxidation with sodium iodate (analytical grade, Chemical Reagent Enterprise, Lublin, Poland). Semicarbazide hydrochloride (analytical grade, Fluka), thiosemicarbazide hydrochloride (99%, Aldrich), hydroxylamine hydrochloride (99%, Aldrich) and hydrazine sulphate (reagent

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Table 1
Raman data and magnetic moments of nitrogen derivatives of dialdehyde starch – DSC – disemicarbazone, DTSC – dithiosemicarbazone, DHZ – dihydrazone, DOX – dioxime and their complexes with copper(II) ions. Magnetic moments of nitrogen derivatives of dialdehyde starch copper complexes and the content of copper.

Compound	Raman data		Magnetic moment	Copper content
	$\upsilon_{(CN)}$[a] (cm^{-1})	$\delta_{(NH)}$[b] (cm^{-1})	(B.M.)	(mg/1 g sample)
DTSC	1632	1525		
DTSC-Cu(II)	1599	1533	1.51	44.05
DSC	1628	1531		
DSC-Cu(II)	1601	1538	1.70	8.90
DHZ	1587	1557		
DHZ-Cu(II)	1583	1561	1.13	43.15
DOX	1651	–		
DOX-Cu(II)	1643	–	1.82	11.75

[a] C=N stretching vibrations.
[b] NH_2 deformation vibrations.

grade, POCh, Gliwice, Poland) were used for preparation of nitrogen dialdehyde starch derivatives. Copper (II) complexes were obtained using sulphate(VI) pentahydrate (analytical grade) from POCh, Gliwice, Poland.

2.2. Preparation of complexes

Dialdehyde starch (DAS) oxidized with 30% yield was prepared from potato starch in the periodate-oxidation with electrochemical recovery of the oxidant (Para, Karolczyk-Kostuch, Hajdon, & Tomasik, 2000; Pfeifer et al., 1960). Degree of oxidation was determined using the oxime method (Krajcinović, 1948; Veelaert, Polling, & de Wit, 1994).

Nitrogen derivatives of DAS (disemicarbazone, DSC; ditiosemicarbazone, DTSC; dihydrazone, DHZ; dioxime, DOX) were obtained in reaction of dialdehyde starch with NH_2–X type compounds (semicarbazide, tiosemicarbazide, hydrazine and hydroxylamine salts) and used as ligands in reaction with Cu(II) ions.

The Cu(II)-complexes (Cu-DSC, Cu-DTSC, Cu-DHZ, Cu-DOX) were prepared by the following procedure. Water suspension of nitrogen derivatives (2 g/10 cm^3) was added to 0.5 M copper salt solution (10 cm^3). Suspension was agitated gently at room temperature for 2 h, then filtered under reduced pressure and washed with distilled water (3 × 20 cm^3). The samples were dried at 313 K then at 393 K until constant weight. The detailed description of the preparation methods is given in previous papers (Para, 2004; Para, Karolczyk-Kostuch, & Fiedorowicz, 2004; Para & Karolczyk-Kostuch, 2002a, 2002b).

2.3. Raman spectra

FT Raman spectra were registered using a Bio-Rad FT Raman spectrometer (Cambridge, USA) with diode Spectra-Physics Nd:YAG laser (1064 nm line).

2.4. Magnetic susceptibility

The magnetic susceptibility measurements were carried out using a commercial Quantum Design SQUID magnetometer (San Diego, USA) in the magnetic field of 2*T* and in temperature range from 10 to 300 K. The polymeric character of the obtained compounds made it impossible to determine the molecular weight of the copper complexes, therefore the magnetic susceptibilities were calculated for 1 g of the samples, in which the copper contents (Table 1) were found with inductively coupled plasma-atomic emission spectrometer ICP-AES, JY 238 ULTRACE JOBIN-YVON (Longjumeau, France). Effective magnetic moments of Cu(II) were estimated from the slope of the inversed susceptibility, after taking diamagnetic background into account.

2.5. EPR spectra

EPR measurements were performed using an X-band Bruker ELEXSYS 500 spectrometer (Karlsruhe, Germany) with 100 kHz field modulation. The spectra of copper complexes were recorded at 293 K and 77 K with modulation amplitude of 0.5 mT. EPR parameters: *g* factor value, hyperfine splitting constant *A*, peak-to-peak line width ΔB_{pp} were found by a simulation procedure using the modified program SIM 14, which included the optimization by Nelder–Mead simplex method (Lozos & Hoffman, 1974). The program calculated the energy levels of the spins to the second order and the transition probabilities to the first order. The obtained theoretical spectrum was the sum of all contributing signals originating from assumed models of paramagnetic centres. The accuracy of determination of EPR parameters was ±0.005 for *g* values and ±0.1 mT for hyperfine splitting constant *A*.

3. Results and discussion

The native potato starch contains neither carbonyl nor carboxyl groups. During oxidation with periodate, 30% of glucose units were transformed into dialdehyde derivatives. The reaction with periodate is specific and only OH groups at carbon atoms C(2) and C(3) of glucose are oxidized to aldehyde groups without formation of carboxyl groups (Para et al., 2000; Pfeifer et al., 1960).

Table 1 presents Raman data and magnetic moments of nitrogen derivatives of dialdehyde starch and their complexes with Cu(II) ions, as well as copper contents in the analyzed samples.

IR spectra of the dialdehyde starch and its derivatives show the intensive band at 1637 cm^{-1} assigned to water H–O–H bending mode. It masks the ν(C=N) stretching vibrations in nitrogen derivatives of dialdehyde starch. Therefore, the Raman spectra in the region of 4000–200 cm^{-1} were recorded instead.

The Raman spectrum of dialdehyde starch exhibits an intense band at 1732 cm^{-1} assigned to the ν(C=O) stretching vibration in the aldehyde carbonyl group. This band vanishes in the spectra of nitrogen derivatives of DAS, indicating that upon reaction all aldehyde groups are converted into nitrogen derivatives. Formation of a carbon–nitrogen bond is confirmed by the appearance of a band assignable to the ν(C=N) stretching mode (Table 1). This band is fairly sensitive to coordination of metal ions. In the spectra of the Cu(II) complexes it moves to lower frequency as a result of reduced electron density at the nitrogen atom caused by coordination to the metal cation (Nawar & Hosny, 2000).

The magnetic susceptibilities of the Cu(II) complexes at different temperatures fit the Curie–Weiss law. The effective magnetic moment expected for the Cu(II) complexes with one unpaired spin localized at cooper ion is equal to 1.73 M.B. and indicates non-degenerated B_{1g} ground state of Cu(II) (Jayaramudu & Reddy, 1999).

The values of magnetic moments for magnetically diluted Cu(II) complexes are generally in the range of 1.7–2.2 B.M., whereas those below this range indicate antiferromagnetic coupling, taking place through X bridges in CuXCu moieties (Cotton, Wilkinson, Murillo, & Bochmann, 1999). Such interactions are probably formed in TSC and, especially, in HZ complexes of copper (Table 1).

All copper complexes exhibit anisotropic EPR spectra characteristic of copper (II) centres with well resolved four hyperfine lines around $g_{//}$. The high field parts of the spectra are not resolved. Only in the case of dithiosemicarbazones, the perpendicular *g* tensor component is slightly split into five super-hyperfine lines. All spectra consist of two overlapping signals indicating the presence of two paramagnetic centres. The simulation procedure of the

Table 2
EPR data of copper complexes with dialdehyde starch nitrogen derivatives (DTSC - dithiosemicarbazone, DSC – disemicarbazone DHZ – dihydrazone, DOX – dioxime).

Compound	Signal	$g_{//}$	$g_{\perp}$	$A_{//}(\times 10^{-4}\,\mathrm{cm}^{-1})$	G	$f = g_{//}/A_{//}$ (cm)	α^2
DTSC	I	2.144	2.030	173	5.11	124	0.67
	II	2.255	2.066	162	3.97	138	0.77
DSC	I	2.303	2.051	132	6.17	174	0.73
	II	2.350	2.075	140	4.78	168	0.81
DHZ	I	2.211	2.059	110	3.68	200	0.58
	II	2.340	2.075	127	4.64	184	0.76
DOX	I	2.168	2.037	111	4.80	195	0.53
	II	2.303	2.068	140	4.58	164	0.76

spectra allows separating particular signals and determination of their parameters.

All signals show the dependence $g_{//} > g_{\perp} > g_e$ suggesting that the copper complexes have approximate axial symmetry D_{4h} (square planar, or octahedral with tetragonal distortion) with $|B_{1g}\rangle$ as the ground state of Cu (II), which is in accordance with measurements of magnetic susceptibility. The unpaired electron is localized on the b_{1g} antibonding molecular orbital, which is the linear combination of $\left|d_{x2-y2}\right\rangle$ orbital of copper and $|\Phi_L\rangle$ ligand orbitals of adequate symmetry (Abragam & Bleaney, 1986; Kivelson & Neiman, 1961; McGarvey, 1967):

$$b_{1g} = \alpha \left|d_{x^2-y^2}\right\rangle - \alpha' \left|\Phi_L\right\rangle$$

where α and α' are the metal d-orbital and the ligand group orbitals bonding coefficients, respectively. The effective spin Hamiltonian describing spectra of the copper complexes for axial symmetry D_{4h} is following:

$$H = \beta[g_{//}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + A_{//}S_zI_z + A_{\perp}(S_xI_x + S_yI_y)$$

with terms having usual meanings. Resolution of the axial spin Hamiltonian with $S = 1/2$ and nuclear spin $I = 3/2$ gives the parameters presented in Table 2.

The character of the copper complexes can be estimated from the values of $g_{//}$ which are sensitive to the bond covalency (Kivelson & Neiman, 1961). The centres giving $g_{//} \geq 2.3$ are ionic in their nature and characteristic for copper in distorted octahedral or planar oxygen surroundings, whereas those with $g_{//} < 2.3$ have the dominant covalent character. The values of $g_{//}$ between 2.2 and 2.3 correspond to copper centres bonded to nitrogen or those with mixed system of copper–nitrogen and copper–oxygen bonds. The lowering of $g_{//}$ value below 2.2 is typical for copper–sulphur bonds. A better information about the degree of localization of an unpaired electron on the copper $d_{x^2-y^2}$ orbital can be obtained from the approximate equation (Kivelson & Neiman, 1961):

$$\alpha^2 = \frac{-A_{//}}{P} + (g_{//} - g_e) + \frac{3}{7}(g_{\perp} - g_e) + 0.04$$

where $A_{//}$, assumed to be negative, is the value of parallel component of the hyperfine tensor and P is a direct dipolar term, equal

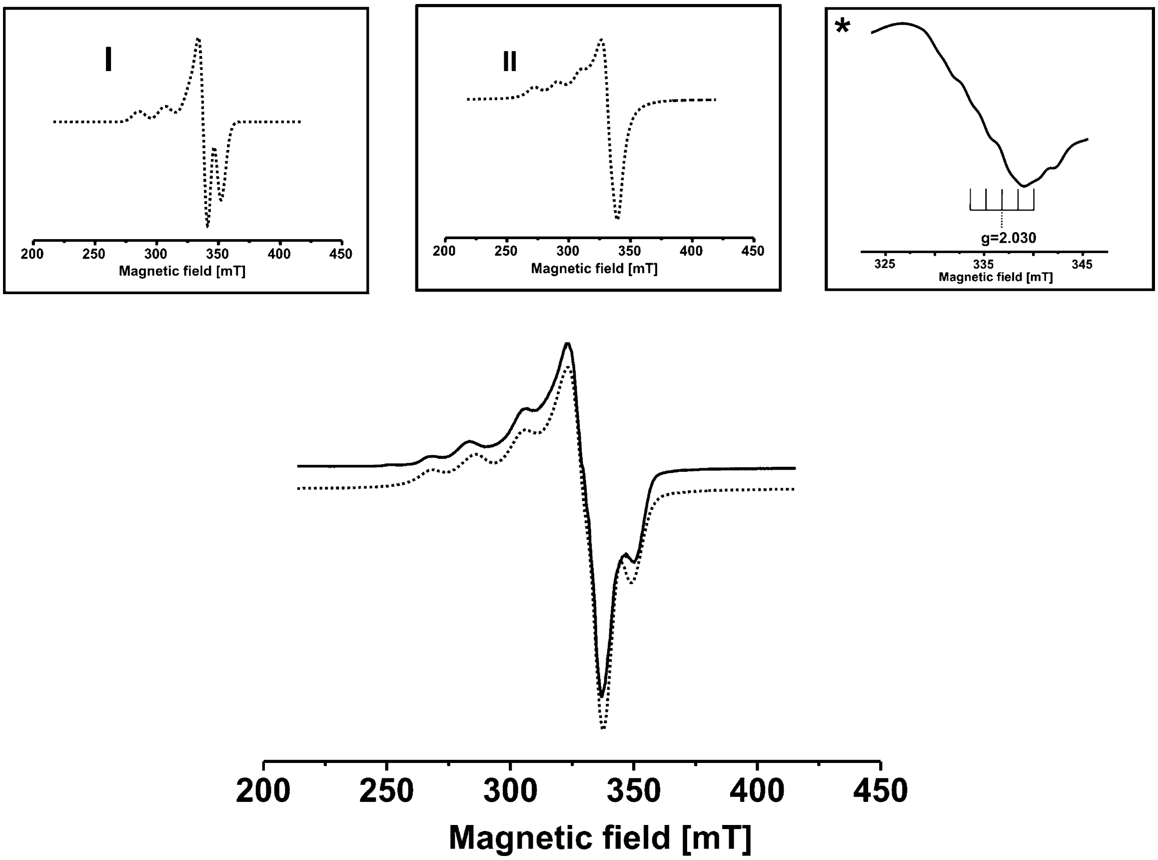

Fig. 1. Experimental and simulated EPR spectrum (registered at 77 K) of Cu-DTSC complex and signal components (I, II) and the perpendicular component of the spectrum registered in the range of 30 mT (*).

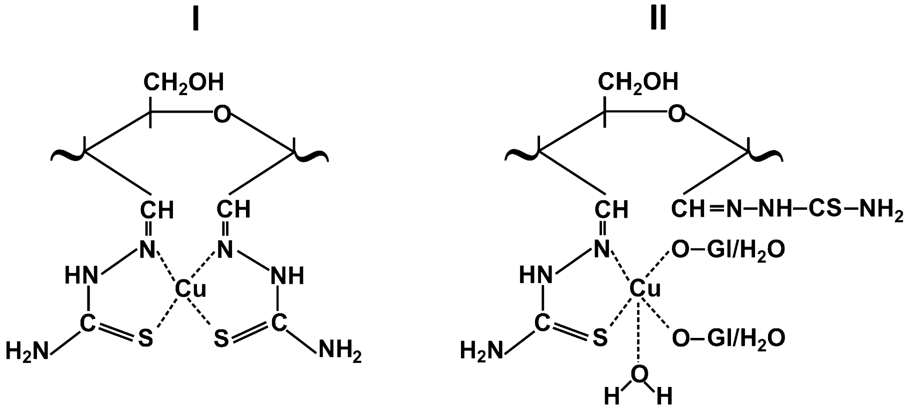

Fig. 2. Scheme of structure of copper centres in Cu-DTSC complex.

to $360 \times 10^{-4}\,\mathrm{cm}^{-1}$. Values of α^2 approaching 1 indicate a strongly ionic bond, while the opposite points to the increasing bond covalency. The calculated values of α^2 are given in Table 2 and show that investigated complexes differ in the degree of bond covalency. The "in plane" (β_1) and "out of plane" (β) π bonding coefficients for d_{xy} and $d_{xz,yz}$ orbitals, respectively, can be found from the relations (Chikate, Belapure, Padhye, & West, 2005):

$$\alpha^2\beta_1^2 = \frac{[(g_{//} - g_e)E_1]}{8\lambda}$$

$$\alpha^2\beta^2 = \frac{[(g_\perp - g_e)E_2]}{2\lambda}$$

where g_e is a free electron g value, λ is the spin-orbit coupling for Cu (II) equal to $-821\,\mathrm{cm}^{-1}$ and E_1 and E_2 are the energies attributed to the optical transitions $b_1(d_{x^2-y^2}) \rightarrow b_{2g}(d_{xy})$ and $b_1(d_{x^2-y^2}) \rightarrow e_g(d_{xz},d_{yz})$, respectively.

Information about the symmetry of copper centres can be drawn from the values of $g_{//}$ and $g_\perp$, which are greatly influenced by the ligand type and by the coordination geometry. Generally, two types of axial copper centres can be distinguished (Hathaway & Billing, 1970). The centres exhibiting the lowest g value (in the present case $g_\perp$) higher than 2.03, with all principal axes aligned parallel and geometry corresponding to elongated tetragonal octahedron or planar square belong to the first type. If g values of such signals fulfil the relation:

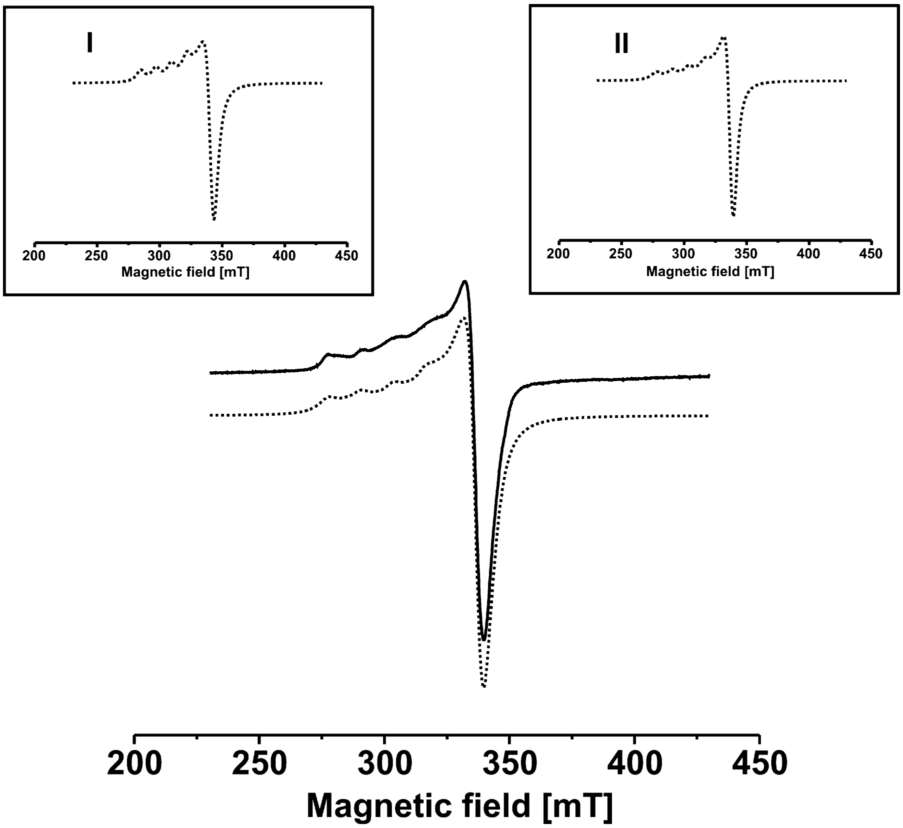

Fig. 3. Experimental and simulated EPR spectrum (registered at 77 K) of Cu-DSC complex and signal components.

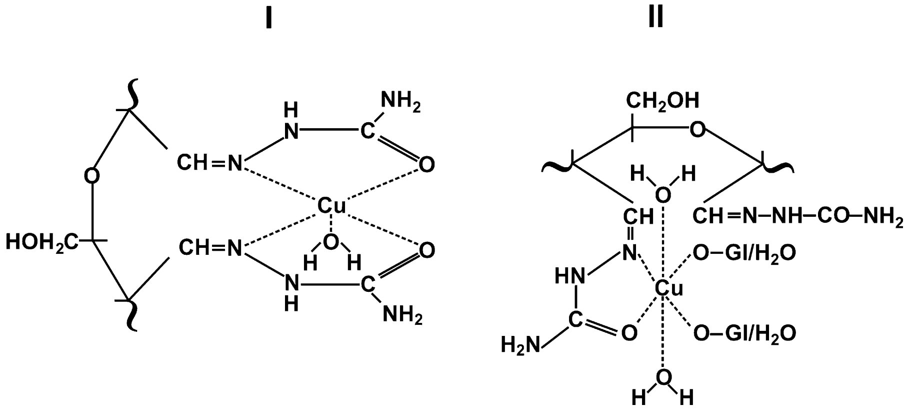

Fig. 4. Scheme of structure of copper centres in Cu-DSC complex.

$$G = \frac{(g_{//}-g_e)}{(g_{\perp}-g_e)} = 3.92 - 7.45$$

the local tetragonal axes are aligned parallel or only slightly misaligned. If G is lower than 4.0 a significant exchange coupling exists. With decreasing coordination of copper centre a decrease of g values is observed.

The second type of copper centres in axial symmetry, represented by compressed tetragonal octahedron or trigonal bipyramid, is characterized by the lowest g value lower than 2.03.

The degree of tetrahedral distortion, occurring frequently for square planar copper complexes, is reflected by the ratio of $g_{//}/A_{//} = f$ and can be considered as a measure of distortion and the deviation from perfect geometry depending on the nature of coordinated ligands (Addison, 1983; West, Padhye, & Sonawane, 1991). The f value in the range of 110–120 cm is characteristic for signals of copper complex with planar geometry, whereas its increase to 150 cm indicates a slight or moderate distortion of planar symmetry and further rise to the values 180–250 cm suggests a strong deviation from square planar geometry.

The best resolved EPR spectrum was obtained for dithiosemicarbazone copper complex (Fig. 1). This spectrum consists of two axial signals with well resolved hyperfine structure around $g_{//}$, indicating two isolated copper centres (Fig. 1, inserts: I, II). The parameters of centre I are characteristic for square planar copper complexes,

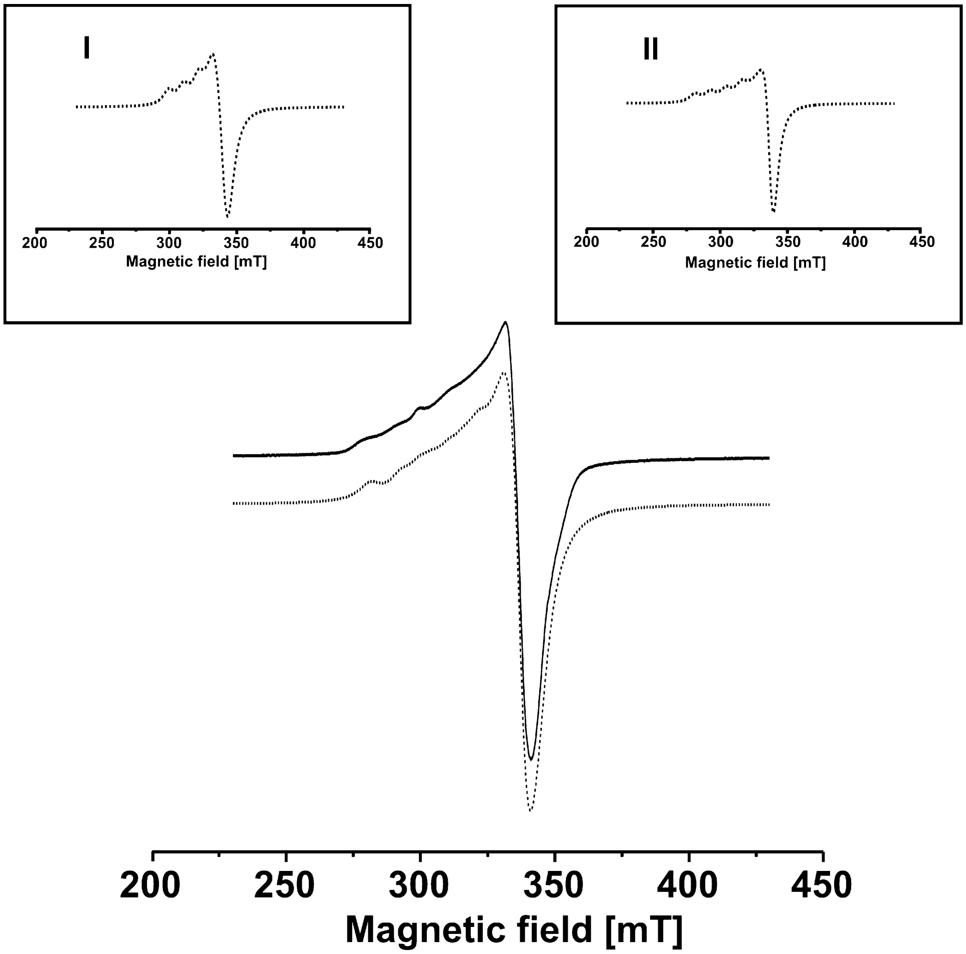

Fig. 5. Experimental and simulated EPR spectrum (registered at 77 K) of Cu-DHZ complex and signal components.

typical for dithiosemicarbazones with ligands acting as chelating agents (Table 2). The low value of $g_{//}$ indicates a considerable covalency of the planar bond resulting from two sulphur donor atoms, as well as by chelating character of thiosemicarbazone ligands and their pseudo-aromatic nature. The calculated α^2 value is typical for planar complex and similar to those found for other dithiosemicarbazone copper complexes (Beraldo & West, 1997; Beraldo, Boyd, & West, 1998; Chandra & Gupta, 2005; Chikate et al., 2005; Diaz et al., 1997; Diaz, Pogni, Cao, & Basoi, 1988; Hassanien, Gabr, Abdel-Rhman, & El-Asmy, 2008; West et al., 1997), confirming a significant covalency of the σ bond. Also the value of parameter f points to the pure square planar geometry of the complex. The five weak lines separated by 1.5 mT, visible in insert (*) in Fig. 1, overlapping with perpendicular g tensor component of the signal, strongly suggest the super-hyperfine interaction with two nitrogen atoms. The lack of the exchange interaction for centre I is confirmed by the value of G (Table 2). The model of the Cu-DTSC centre is presented in Fig. 2.

The centre II exhibits signal parameters different from those of centre I. The values of g tensor components are higher than those of signal I, whereas parameter $A_{//}$ is lower (Table 2). The parameter G, equal 4.0, confirms, similarly as for centre I, the lack of exchange interactions. However, the measurements of magnetic susceptibility of the sample give the value of 1.51 B.M. for magnetic moment, which is lower than 1.73 B.M., expected for spin-only magnetic moment (Table 1). The characteristic features of this centre are higher values of both: the parameter α^2, pointing to the increase of the ionicity of the σ bond and the parameter f suggesting a slight tetrahedral distortion of centre's geometry (Table 2). The increase of $g_{//}$ with simultaneous decrease of $A_{//}$ value, together with tetrahedral distortion, may result from influence of electron-donating ability of ligand (Yokoi & Addison, 1977) or/and from the apical coordination of the fifth ligand, for example water molecule. In the latter case the change of copper square planar environment to square pyramid would occur. The observed significant changes in EPR parameters suggest that the substitution of more electronegative ligand for one thiosemicarbazone group, for example oxygen atoms, is a likely possibility. Taking into account the lack of carbonyl groups in nitrogen derivatives, found from Raman spectra, it may be concluded that oxygen atoms originate only from hydroxyl groups of starch or water molecule. Hence, the proposed model of the second centre includes one thiosemicarbazone ligand and two oxygen bonded ligands (glucose units of starch and/or water molecules). However, the presence of the apical oxygen, originating from water molecule, cannot be excluded, considering the lower than 1.73 B.M. value of magnetic moment and the rather high value of $g_{\perp}$ (Tables 1 and 2). The location of oxygen in the apical position would make possible exchange interaction of the Cu centre with another Cu site, via Cu–O–Cu bridge. This, in turn, would explain the observed decrease of the magnetic moment value (Tandon, Thompson, Mike, Manuel, & Bridson, 1994, Thompson, Lee, & Gabe, 1988). The increase of $g_{\perp}$, which has been observed after introduction of the fifth ligand into planar complex structure (Antolini, Menabue, & Saladini, 1985; Dehand et al., 1979) is consistent with above supposition. Hence, signal II is tentatively attributed to copper coordinated to one thiosemicarbazone group, the remaining positions being occupied by oxygens, to give either square planar or square pyramidal environment (Fig. 2).

Similarly as thiosemicarbazones, semicarbazone copper complex exhibits spectrum consisting of two signals with different parameters (Fig. 3 and Table 2). The main feature of these signals is the increase of g tensor component values in comparison with those found for Cu-DTSC complex, resulting from the substitution of more electronegative oxygen atoms for sulphur ones. The effect of such rearrangement of complex geometry is reflected in the increase of α^2 values (Table 2) pointing to the higher ionicity of the in-plane bonds of the complexes. Both centres are monomeric ($G > 4$ and magnetic moment equal to 1.70 B.M.) and reveal larger tetrahedral distortion from the planar geometry, than that exhibited in dithiosemicarbazone and thiosemicarbazone complexes. This is confirmed by the $g_{//}$ values higher than those expected for the pure planar symmetry with two oxygen and two nitrogen atoms (Prushan, 2001). Taking into account the value of the f parameter, lower than 180 cm (Table 2), the signal I can be tentatively assigned to the copper ion surrounded by two oxygen and two nitrogen atoms occupying the tetragonal in-plane positions and one oxygen atom situated at the axial position (Fig. 4). The bonding of the third oxygen atom (originating from water molecule) at axial position pulls the copper ion out of the equatorial plane (Narang, Pandey, & Singh, 1994; Singh, Kushawaha, & Ayyagari, 2001), causing the weakening of equatorial bonds. The increase of axial interaction at the Cu centre is the reason of the higher $g_{//}$ value.

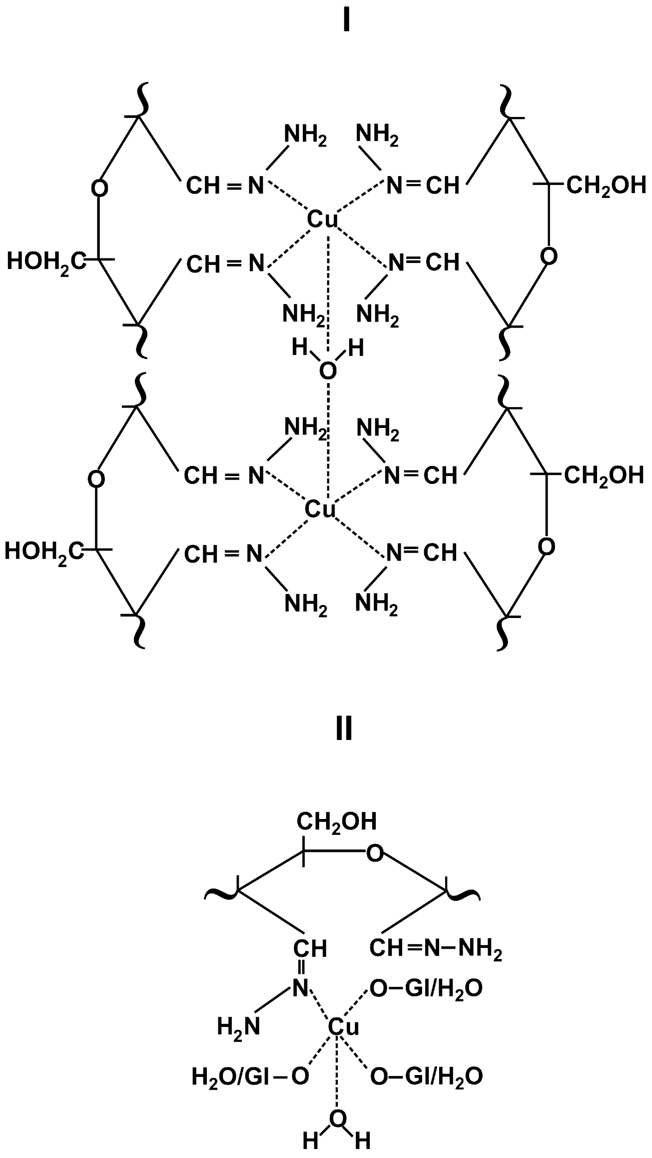

Fig. 6. Scheme of structure of copper centre in Cu-DHZ complex.

The signal II exhibits values of g tensor components greater than those of signal I and moreover, the value of $g_{//} > 2.3$ points to the presence in coordination sphere of copper of a ligand more electronegative than nitrogen atom. The higher α^2 value (Table 2) indicating a decrease of σ bonds covalency, supports such reasoning. Taking into account simultaneous increase of $g_{//}$ and $g_{\perp}$ values, the signal II can be considered as originating from distorted

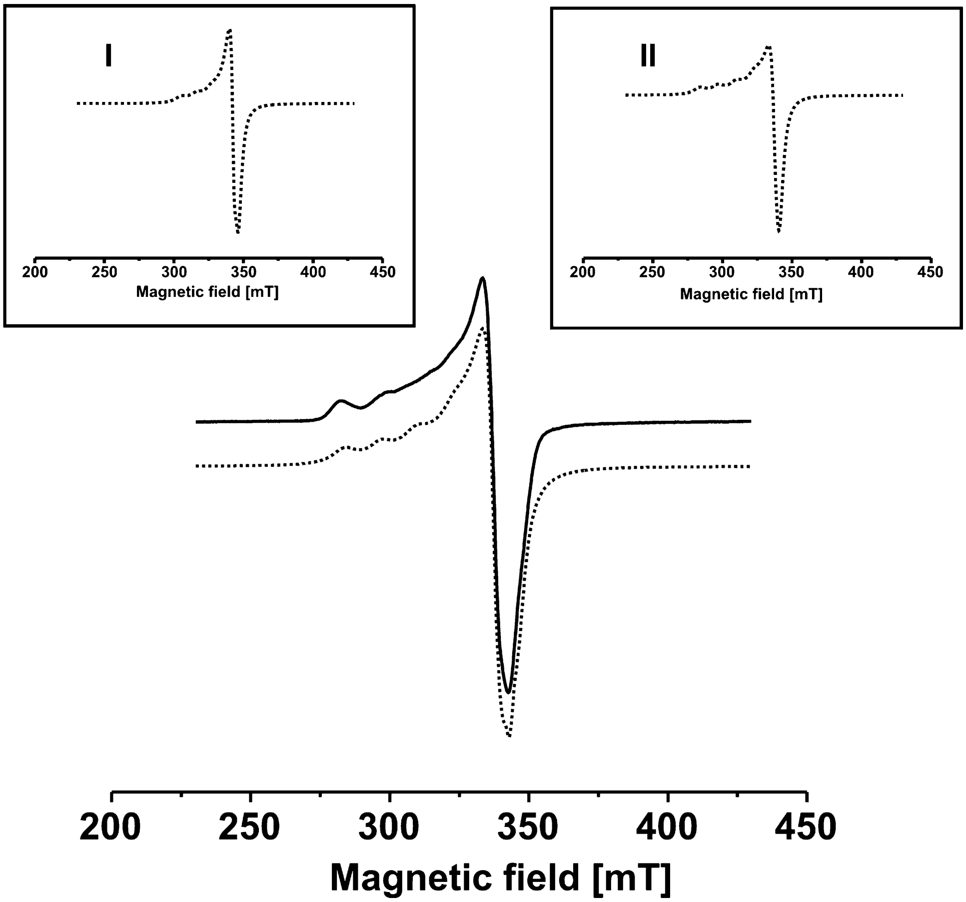

Fig. 7. Experimental and simulated EPR spectrum (registered at 77 K) of Cu-DOX complex and signal components.

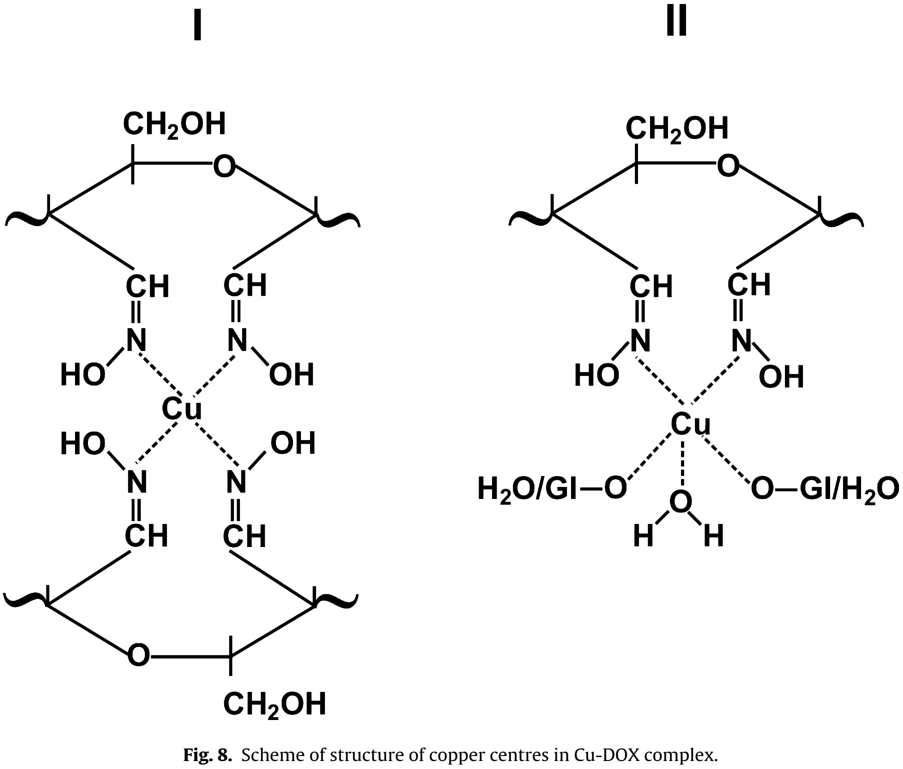

Fig. 8. Scheme of structure of copper centres in Cu-DOX complex.

octahedral or square planar complex of copper, in which only one semicarbazone ligand is bonded to copper ion, whereas remaining coordination positions are occupied by oxygen atoms originating from hydroxyl groups of starch and/or water molecules, similarly as in centre II of thiosemicarbazone complex (Fig. 4).

We suggest that two types of copper complexes with semicarbazone and thiosemicarbazone exist. One of them, which contains only one SC or TSC ligand in coordination sphere of copper, is formed with yield of about 75%, whereas the second, in which two SC or TSC ligands are coordinated to copper ion, is created with much lower efficiency, possibly caused by steric reasons.

The signal I of hydrazone copper complex is characterized by g factor values lower than those observed for disemicarbazone and semicarbazone complexes (Fig. 5 and Table 2), which is the result of substitution of two, less electronegative nitrogen atoms in the coordination sphere of copper, for more electronegative oxygen ones. Such rearrangement leads to a more covalent character of in-plane σ bonds (Table 2). The characteristic features of signal I are the high value of the f parameter ($f = 200$), indicating a significant tetrahedral distortion, and a small value of $A_{//}$ (Table 2). The distortion renders the symmetry of copper centre an intermediate between planar square and flattened tetrahedron. For the latter case the d_{xy} orbital constitutes the ground state. The admixture of the state $4p_z$ to the d_{xy} ground state can occur, leading to a decrease of $A_{//}$ value (Hoffmann & Goslar, 1983). Therefore, the observed diminishing of $A_{//}$ can be considered as a consequence of tetrahedral distortion. Hence, it can be supposed that the planar coordination of two dihydrazone ligands in CuN_4 centre I is strongly disturbed by tetrahedral distortion, which can admix the d_{xy} state to the ($d_{x^2-y^2}$) ground state of copper. From among copper complexes investigated in this study, the dihydrazone complex exhibits the smallest value of the parameter G ($G = 3.68$) and exceptionally low value of magnetic moment (1.13 B.M.), pointing to the presence of exchange interactions between copper ions (Table 2). Such exchange interactions may originate from a Cu–O–Cu bridge (Tandon et al., 1994; Thompson et al., 1988), whose formation is possible by assuming the presence of water in an additional coordination position. This interpretation is confirmed by the observed relatively high value of $g_\perp$, which is consistent with the complex geometry distortion. Fig. 6 illustrates the model of centre I.

The parameters of the EPR signal II, observed in the spectrum (Fig. 5), are similar to those of signal II of semicarbazone copper complex. This suggests that probably only one nitrogen atom of hydrazone group is linked with copper centre. The remaining positions can be occupied by oxygen atoms, like in Cu-SC. The centre II in hydrazone copper complex is formed with higher yield (70%).

The oxime copper complexes can be considered as systems of copper–nitrogen bonds with distorted octahedral or planar symmetry. For such system the values of $g_{//}$ in the range of 2.1–2.3 are expected (Kivelson & Neiman, 1961; Prushan, 2001). Similarly, as in the compounds described above, two signals can be distinguished in the spectrum of oxime copper complex (Fig. 7). Signal I exhibits values of g tensor components lower than those found for signal I in dihydrazone complex (Table 2). The parameter G ($G = 4.8$), as well the value of magnetic moment equal to 1.82 B.M. are typical for monomeric complex (Table 2). The parameter α^2, equal 0.53, points to the almost pure covalent σ bonds and the low value of $g_\perp$ confirms lack of axial interactions (Table 2). On the other hand, the parameter $f = 195$ cm indicates high tetrahedral distortion of the square planar geometry of the complex (Table 2). Similarly as in DHZ complex, low value of $A_{//}$, can be caused by the admixture of d_{xy} state to the ground state of copper. The lowering of $g_{//}$ value for signal I of dioxime complex in comparison with that found for signal I in dihydrazone complex results probably from the influence of oxygen atoms in the outer coordination sphere of copper. Comparing the structures of outer coordination spheres of copper in dihydrazone and dioxime complexes, it should be noticed that substitution of more electronegative oxygen in dioxime complex (–Cu–N–OH) for less electronegative nitrogen atoms in $–Cu–N–NH_2$ fragment of dihydrazone can influence the strength of interaction between central copper ion and ligands of inner coordination sphere (Figs. 6 and 8). The presence of more electronegative atoms in outer coordination sphere leads to stronger interactions and decrease of $g_{//}$. Moreover, the possibility of the formation of short intramolecular H-bonds (–NO–H···O–N–) can be an important factor modifying the structure of dioxime compounds. In view of this, we attribute signal I to the monomeric CuN_4 with strong tetrahedral distortion of planar symmetry (Fig. 8). In such complex two molecules of dioxime ligands are coordinated by copper.

Signal II exhibits parameters close to those found for CuN_2O_3 centre responsible for signal I in the spectrum of disemicarbazone copper complex (Table 2). Assuming similarity of coordination sphere of copper in both compounds, signal II in the spectrum of oxime complex can be attributed to copper ion surrounded by two nitrogen atoms of oxime groups and two oxygen atoms in an equatorial plane, and one oxygen atom occupying the axial position (Fig. 8). Some small differences in EPR parameters result probably from different structures of the outer coordination sphere of both copper centres. The possibility of hydrogen bonds formation between NO–H···O → Cu cannot be excluded. Centre II of oxime complex is formed with 80% yield.

4. Conclusion

The Raman and EPR spectroscopies, as well as the magnetic susceptibility measurements have been applied to investigate the copper complexes with nitrogen derivatives of dialdehyde starch. Among them, EPR spectroscopy appears to be a particularly useful to differentiate various copper complexes. Two types of complexes with different surroundings of copper centres have been found for each starch derivative. In the case of Cu-thiosemicarbazone complexes, the centre with the planar structure of CuN_2S_2 and another with the square pyramidal $CuNSO_3$ geometry, in which apical oxygen atom can interact with the second neighbouring $CuNSO_3$ centre, have been proposed. A similar square pyramidal coordination environment CuN_2O_3, albeit of monomeric character, is formed in Cu-DSC complex. The second type of copper centres in the semicarbazone complex reveals distorted octahedral or square planar arrangement engaging one semicarbazone ligand and oxygen atoms originating from hydroxyl groups of starch and/or water molecules. In the copper complexes with DHZ and DOX two molecules of starch dihydrazone or dioxime, respectively, are coordinated to the copper ions. These centres, containing CuN_4 moiety, exhibit planar geometry with strong tetrahedral distortion. In the case of DHZ complex, Cu–O–Cu coupling is postulated, whereas in DOX complex the Cu centre is monomeric. The second type of copper centres in Cu-DOX complex, referred to as CuN_2O_3, are also monomeric. Two nitrogen atoms from dioxime molecule and two oxygen atoms from hydroxyl groups of starch or water are situated in the equatorial plane, whereas the third oxygen atom from water molecule occupies the axial position. The existence of hydrogen bonds stabilizing the structure of DOX complexes cannot be excluded. In the case of the second type of Cu-hydrazone complex, copper ion coordinates one hydrazone ligand and four oxygen atoms, coming from hydroxyl groups of starch or water molecules.

The space conformation of starch ligands influences the mechanism of the complex formation. Of two kinds of formed complexes, the centres engaging lower number of nitrogen derivatives of dialdehyde starch are preferred.

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