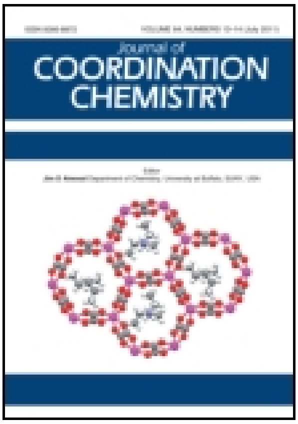

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Synthesis and physico-chemical study of complexation of glyoxylic acid aroylhydrazones with Cu(II) in solution and solid phase

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Synthesis and physico-chemical study of complexation of glyoxylic acid aroylhydrazones with Cu(II) in solution and solid phase

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A series of copper(II) binuclear metallochelates with glyoxylic acid aroylhydrazones have been synthesized. The composition and structure were established with infrared, UV-Vis, ^{1}H NMR, extended X-ray adsorption fine structure spectroscopy as well as magnetochemical studies and potentiometry. The proton-donor and proton-acceptor features of the ligand systems play a key role in the formation of the complexes.

Keywords: Coordination compounds; Hydrazones; Magnetochemistry; Exchange interaction; EXAFS

1. Introduction

Glyoxalic acid and its derivatives play important roles in natural processes, participating in the glyoxylate cycle which functions in plants and in some microorganisms [1]. The presence of aldehyde in the glyoxylic acid allows numerous acyclic derivatives containing C=N bond – azomethines and hydrazones. Interest in hydrazone derivatives is caused by their biological activity [2–7], as well as complexation ability [8–12]. Hydrazones also have valuable analytical [13, 14], photochemical [15–17], and electrochemical properties [18–21]. Structural data on metallocomplexes of glyoxylic acid acylhydrazones [22–35] and thiosemicarbazones [36–54] are available in the literature. However, almost all complexes exhibit mononuclear structures; examples of binuclear are very few [55]. The aim of this work is to synthesize and study a series of principally binuclear transition metal complexes based on glyoxylic acid substituted acylhydrazones.

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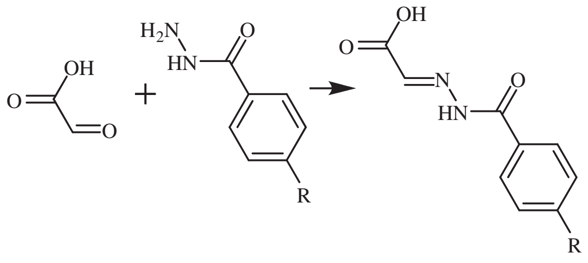


1a-d

R = Br (**1a**)

R = OCH_3 (**1b**)

R = NO_2 (**1c**)

R = $N(CH_3)_2$ (**1d**)

Scheme 1. Synthesis of **1a-d**.

2. Experimental

2.1. *Materials and methods*

All chemicals used for preparative work were reagent grade. The solvents were dried and distilled before use according to standard procedures. The benzoylhydrazine para-substituted derivatives and glyoxylic acid were purchased from Aldrich and used without purification. Copper(II) acetate $Cu(CH_3COO)_2 \cdot H_2O$ was used for synthesis.

2.2. *Ligand synthesis*

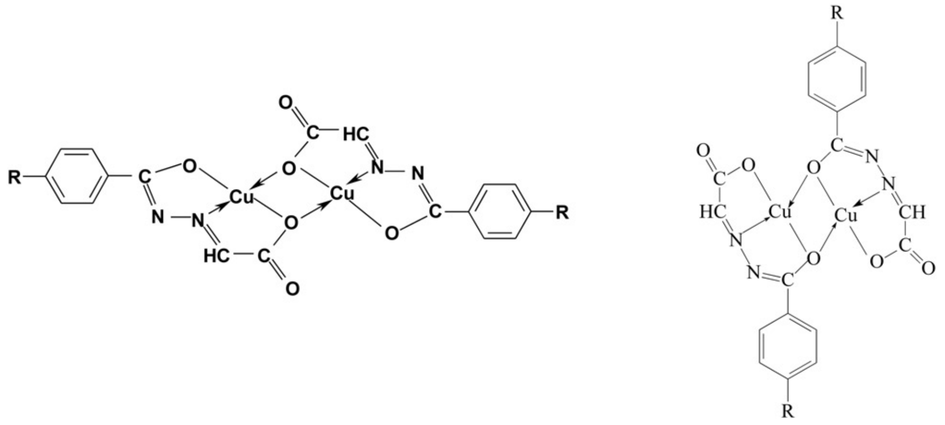
The ligand systems of type **1** have been synthesized by the condensation reaction of glyoxylic acid with benzoylhydrazine para-substituted derivatives as follows (scheme 1).

To a hot solution of corresponding hydrazide (5 mmol) in 5 mL of ethanol a hot solution of glyoxylic acid (5 mmol) in 2 mL of ethanol was added. The solution was refluxed for 3.5 h. Upon cooling a precipitate formed, was filtered off and recrystallized from a mixture of DMFA: ethanol (1 : 4 v/v ratio, when $R = NO_2$, Br) or from ethanol ($R = OCH_3$, $N(CH_3)_2$).

2.3. *Synthesis of complexes*

The type **2** complexes (figure 1) have been synthesized as follows. To a hot solution of hydrazone (1 mmol) in 5 mL of methanol a hot solution of copper(II) acetate (1.1 mmol) in 5 mL of methanol was added. The precipitate immediately formed was boiled for 10–15 min, filtered off, washed with hot methanol, and dried in vacuum.

The melting points, color, and yield as well as elemental analyses are listed in table 1. Conductivity measurements of 0.001 mol L^{-1} DMF solutions of complexes show their non-electrolyte nature.



2 a–d **2' a–d**

Figure 1. Proposed structures of binuclear Cu(II) complexes R = Br (**a**), OCH_3 (**b**), NO_2 (**c**), $N(CH_3)_2$ (**d**).

Table 1. Yield, analytical data, color, and m.p. for ligands and complexes.

Compound	Empirical formula	Color (yield %)	m.p. (°)	Found (Calcd) (%) C	H	N	M
1a	$C_9H_7N_2O_3Br$	White (70)	230	39.88/40.0	2.60/2.51	10.33/10.4	–
1b	$C_{10}H_{10}N_2O_4$	White (75)	205	54.05/54.1	4.54/4.5	12.61/12.6	–
1c	$C_9H_7N_3O_5$	White (72)	230	45.58/45.66	2.98/2.86	17.72/17.8	–
1d	$C_{11}H_{13}N_3O_3$	Yellow (78)	180	56.16/56.24	5.57/5.43	17.86/18.0	–
2a	$C_9H_5N_2O_3BrCu$	Dark-green (58)	>250	32.5/32.58	1.52/1.5	8.42/8.36	19.11/19.2
2b	$C_{10}H_8N_2O_4Cu$	Dark-green (56.5)	>250	42.33/42.45	2.84/2.76	9.87/9.94	22.4/22.55
2c	$C_9H_5N_3O_5Cu$	Green (55.8)	>250	36.19/36.07	1.68/1.82	14.07/14.0	21.27/21.11
2d	$C_{11}H_{11}N_3O_3Cu$	Light-green (59.3)	>250	44.52/44.63	3.74/3.6	14.16/14.08	21.41/21.3

2.4. *Analysis and physical measurements*

Microanalyses (C, H, and N) were performed on a Perkin-Elmer 240 C Analyzer. Infrared (IR) spectra were recorded on a Varian Scimitar 1000 IR spectrophotometer from 4000 to 400 cm^{-1}. ^1H NMR spectra were recorded on a Varian "Unity-300" spectrometer using TMS as internal standard and DMSO-d_6 as solvent. UV-Vis spectra were recorded on a Varian Cary 5000 spectrophotometer. Three series of type **1a** ligand solutions according to three ionization constants have been prepared with the following pH values:

The first – 1.09; 1.40; 2.07; 2.50; 3.15; 3.46.
The second – 3.99; 4.15; 4.48; 5.15; 5.51; 6.24.
The third – 10.70; 11.02; 11.37; 11.72; 12.04.

The potentiometric titrations were carried out on an "Ekotest-2000-pH/ATS" pH meter.

The Harvey–Manning spectrophotometric method has been used for the determination of the composition of coordination compounds in accord with the conditions of applicability and taking into consideration the excess of one reagent.

The magnetic susceptibility of powder samples of the complexes was measured from 300 to 77.4 K using a Faraday magnetometer employing magnetic field strength 0.9 T. Corrections were made for diamagnetic contributions of the samples according to Pascal's constants [56]. The values of $2J$ exchange parameters were calculated in the HDVV model [57].

Cu K-edge X-ray adsorption spectra of **2a** (R=Br) and **2b** (R=OCH_3) were recorded in the transmission mode on an extended X-ray adsorption fine structure (EXAFS) spectrometer, based on X-ray powder diffractometer DRON-3 [58]. X-ray beam was generated by BCW-21-Mo X-ray tube ($U = 17$ kV, $I = 32$ mA). Quartz crystal (1340) was used as monochromator.

Powder samples of complexes were thoroughly mixed with apiezon and placed between thin lavsan films. The thickness of the samples was chosen such that the intensity of the transmitted X-ray beam decreases 2.5–3 times.

After standard procedures of background removal, K-edge-step normalization and atomic adsorption μ_0 extraction [59], the experimental EXAFS (χ)-spectra were obtained. The structural parameters, including interatomic distances (R), coordination numbers (CNs), and the distance mean-square deviation Debye–Waller factors (σ^2), were found by non-linear fit of theoretical spectra in equation (1) to experimental:

$$\chi(k) = \sum_j \frac{N_j S_0^2}{kR_j^2} |f_j(k,\pi)| \exp\left(\frac{-2R_j}{\lambda(k)}\right) \exp\left(-2\sigma_j^2 k^2\right) \sin\left(2kR_j + \delta_j(k)\right), \tag{1}$$

where R_j is the radius of coordination sphere number j; N_j is the CN of coordination sphere number j; S_0^2 is the amplitude reduction factor; $|f_j(k,\pi)|$ is the absolute back scattering amplitude of atom number j for electron with wavevector k; $\delta_j(k)$ are phase shifts of electrons moving in the potential of the absorbing atom; $\lambda(k)$ is mean free path of the photoelectron; σ^2 is mean square root deviation of interatomic distance from its mean value (Debye–Waller factor).

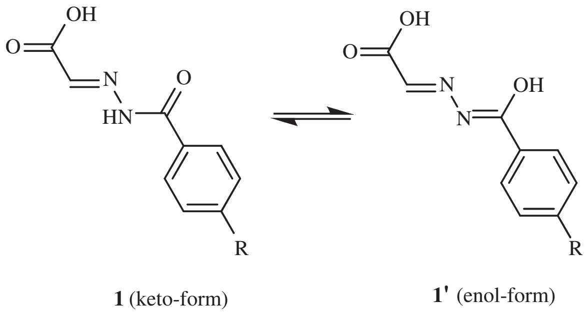
The threshold energy E_0 was chosen as the first peak of the first derivative of K-edge μ(E) and was further varied in fitting procedure as well as the amplitude reduction factor, S_0^2.

Experimental EXAFS (χ)-spectra were Fourier transformed in the range of wavevector k from 3.0 to 12 Å^{-1} with weighting function k^2 to give the radial pair distribution around Cu. The position of the peaks on Fourier transform (FT) (r, Å) are determined by coordination spheres radius (R, Å) according to the formula $r = R - \alpha$, where α is the value of the linear phase shift (typical values 0.3–0.5 Å).

Non-linear fitting was performed in R-space with the window of Kaizer–Bessel type with the help of computer program IFFEFIT-1.2.11 [60]. Phases $\delta_j(k)$ and backscattering amplitudes $f_j(k,\pi)$ of the photoelectron wave required for the simulation of theoretical EXAFS spectra were calculated by FEFF7 computer program [61]. As model compounds, copper complexes with similar atomic structure determined by X-ray single-crystal diffraction were used [62].

The quality of the fits was estimated using a least-squares fitting parameter Q, calculated according to equation (2):

$$Q(\%) = \frac{\sum\left[k\chi_{\text{exp}}(k) - k\chi_{\text{th}}(k)\right]^2}{\sum\left[k\chi_{\text{exp}}(k)\right]^2} \cdot 100\%. \tag{2}$$



Scheme 2. Tautomeric forms of **1**.

3. Results and discussion

The well-known keto–enol tautomeric equilibrium for acylhydrazone solutions [63] indicates that type **1** compounds can act as tridentate mono-basic and di-basic ligands (scheme 2).

The ambient coordination of type **1** ligands implies the possibility of the formation of mononuclear as well as binuclear metallochelates. The latter complexes have been obtained with the metal salt-to-ligand ratio being 1 : 1. The composition and structure of both ligands and complexes have been established by elemental analysis (table 1), IR (table 2), UV-Vis, ^{1}H NMR spectroscopy, EXAFS spectroscopy (table 3), and magnetic measurements (table 4).

3.1. *^{1}H NMR spectroscopy*

The aromatic protons of all type **1** hydrazones with para-substituents have been registered as two doublets, each corresponding to two protons at 6.4–8.4 ppm with spin coupling of 7.8–9.0 Hz. Aromatic protons of the unsubstituted hydrazone are complicated multiplets corresponding to five protons at 7.5–7.9 ppm. The azomethine proton HC=N are one proton singlets at 7.69–7.77 ppm. The protons of carboxylic group as well as NH are singlets at 11.80–12.38 ppm; the former has reduced intensity due to chemical exchange with the water in DMSO. The hydrazones under discussion exist predominantly in DMSO as the *trans*-isomer. The influence of the electronic nature of the substituent can be illustrated by the introduction of acceptor substituent ($–NO_2$) in the para-position leading to downfield shift (≈12.38 ppm) of acidic OH + NH proton signals, while introduction of donor substituent ($–N(CH_3)_2$) – shifts upfield (≈11.80 ppm).

3.2. *Potentiometric titration of ligands*

The protolytic equilibria in solutions of di-basic glyoxylic acid aroylhydrazones possessing azomethine nitrogen capable of protonation are quantitatively characterized by K_{a1}, K_{a2}, and K_{a3} ionization constants:

$$H_3R^+ \rightleftarrows H_2R + H^+ \quad K_1 = \frac{[H_2R][H^+]}{[H_3R^+]},$$

Table 2. IR data of **1** and **2**.

Type of compound	R	M	ν(OH) (cm^{-1})	ν(C=O)$_{\text{carboxyl}}$ (cm^{-1})	ν(C=O)$_{\text{hydrazone}}$ (cm^{-1})	ν(C=N) (cm^{-1})
1a	Br	–	3447	1705	1670	1590
1b	OCH_3	–	3440	1695	1660	1607
1c	NO_2	–	3418	1695	1671	1602
1d	$N(CH_3)_2$	–	3447	1706	1640	1605
2a	Br	Cu	–	1660	–	1588
2b	OCH_3	Cu	–	1670	–	1604
2c	NO_2	Cu	–	1657	–	1598
2d	$N(CH_3)_2$	Cu	–	1665	–	1590

Table 3. Structural parameters of the nearest environment of copper ions in **2a** and **2b** metallochelates from best fit EXAFS data analysis.

Compound	N[a]	R[b] (Å)	σ^{2}[c] (Å^2)	Atom	Q[d] (%)
2a	4	1.90	0.0035	O/N	0.5
	2	2.49	0.0035	C/N	
	1	2.70	0.0042	Cu	
2b	4	1.92	0.0034	O/N	2.5
	2	2.53	0.0047	C/N	
	1	2.79	0.0055	Cu	

[a] N – coordination number.
[b] R – interatomic distances.
[c] σ^2 – Debye–Waller factors.
[d] Q – goodness-of-fit.

Table 4. Magnetic properties of **2**.

Type of compound	R	T (K)	μ_{eff} (B.M.)[a]	$2J$[b] (cm^{-1})
2a	Br	294	1.75	−62
		77.4	1.47	
2b	OCH_3	293	1.67	−60
		77.4	1.41	
2c	NO_2	295	1.76	−53
		77.4	1.53	
2d	$N(CH_3)_2$	295	1.67	−50
		77.4	1.47	

[a] The values of μ_{eff} were calculated per one metal ion.
[b] $2J$ – the value of exchange parameter.

$$H_2R \rightleftarrows HR^- + H^+ \quad K_2 = \frac{[HR^-][H^+]}{[H_2R]},$$

$$HR- \rightleftarrows R^{2-} + H^+ \quad K_3 = \frac{[R^{2-}][H^+]}{[HR^-]}.$$

Apparently, the azomethine nitrogen is protonated first in acidic medium due to its most negative effective charge and electron pair density. Most likely, ligand ionization

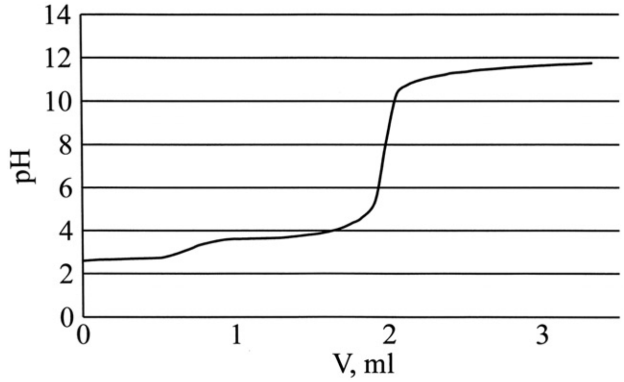


Figure 2. The curve of **1b** ($2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$) potentiometric titration.

starts with the elimination of carboxyl proton and, as a result, monodeprotonated ligand is generated. Then the elimination of enol proton of hydrazide occurs. The first two stages of ionization have constants of acidic–basic titration rather close. Elimination of the hydrazine proton is possible in strong basic medium.

Potentiometric curves for all ligand systems are similar; we show a curve of titration for glyoxylic acid para-methoxybenzoylhydrazone (**1b**) (figure 2). The ionization constant calculation was carried out using formula (3) obtained by the joint solution of the equations of material balance and electroneutrality [64]:

$$pK_{ai} = p\mathrm{H} + \lg\frac{(i-a)C_R - [\mathrm{H}^+] + [\mathrm{OH}^-]}{(a-i+1)C_R + [\mathrm{H}^+] + [\mathrm{OH}^-]}, \tag{3}$$

where K_{ai} is the i-th constant of ionization, a is a degree of neutralization, and C_R is ligand concentration. The acid–base equilibrium constants obtained from potentiometric titration are listed in table 5. The pK_{a3} values should be considered as rough estimates due to the restrictions of potentiometric method of pH determination at pH > 11.

3.3. *UV-Vis spectra*

Glyoxalic acid *p*-bromo-benzoylhydrazone (**1a**) absorption spectra have been studied at pH 1.09–12.04. Using the experimental data (figure 3) the ionization constants have been determined with equation (4) (negative for first and third series of solutions, positive for second series of solutions):

$$pK_{ai} = p\mathrm{H} \pm \lg\frac{(A_{\max} - A_i)}{(A_i - A_{\min})}. \tag{4}$$

The wavelengths, values of absorption maxima, and calculated pK_a values for all (**1a**) forms are listed in table 6. These pK_a values match well to similar values obtained by the potentiometric method (table 5).

Table 5. The values of hydrazone (**1a–d**) ionization constants obtained by potentiometric method.

Compound	pK_{a1}	pK_{a2}	pK_{a3}
1a	1.95 ± 0.10	3.91 ± 0.08	11.92 ± 0.04
1b	2.20 ± 0.11	4.08 ± 0.07	11.54 ± 0.12
1c	1.91 ± 0.10	3.85 ± 0.15	10.84 ± 0.22
1d	2.00 ± 0.04	4.10 ± 0.03	10.65 ± 0.26

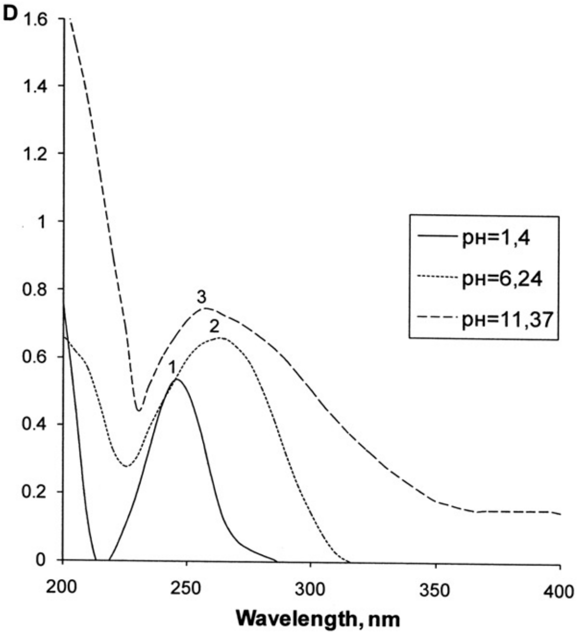


Figure 3. Electronic absorption spectra of 0.001% ethanolic solution of **1a** at pH = 1.4 (1, solid line, $\lambda_{max} = 245$ nm), pH = 6.24 (2, short dash, $\lambda_{max} = 265$ nm), and pH = 11.37 (3, long dash, $\lambda_{max} = 255$ nm).

Table 6. UV-Vis data and calculated values of protonation constant for **1a**.

λ_{max}, nm (A_{max}; A_{min})					
Mono-cation[a]	Neutral form[b]	Mono-anion[c]	pK_{a1}	pK_{a2}	pK_{a3}
245 (0.546; 0.471)	265 (0.658; 0.481)	255 (0.828; 0.644)	2.01	4.01	11.95

[a] First series.
[b] Second series.
[c] Third series (see Section 2).

3.4. *IR spectra*

The $\nu_{C=O}$ (COOH) and $\nu_{C=O}$ (hydrazide) are 1695–1671 and 1640–1671 cm^{-1} for **1a–d** (table 2). The bond stretch of middle intensity attributed to ν_{OH} of carboxylic group is 3418–3447 cm^{-1}. The $\nu_{C=N}$ (middle intensity) was at 1590–1607 cm^{-1}. Disappearance of

ν_{OH} and $\nu_{C=O}$ (hydrazide) was observed upon complexation with copper (type **2** complexes); the bands attributed to $\nu_{C=N}$ and $\nu_{C=O}$ (COOH) shift to low frequencies by 25–45 and 2–15 cm^{-1} (table 2), supporting the idea that ligands coordinate through the deprotonated oxygen of carboxylate, oxygen of hydrazide carbonyl, and azomethine nitrogen.

3.5. *Determination of copper(II) complex composition by the method of inclination ratio of Harvey–Manning*

The coordination activity of ligands has been confirmed with the study of complex formation in methanol solution by the method of inclination ratio of Harvey–Manning [65]. This method allows the determination of the ligand-to-metal ratio in polynuclear complex formation:

$$m\text{M} + n\text{R} = \text{M}_m\text{R}_n$$

applicable when stepwise complex formation does not occur.

Two series of measurements were carried out. The first one was performed when metal concentration is much higher than ligand: $C_\text{M} \gg C_\text{R}$, $C_\text{M} = \text{const}$. The stoichiometric coefficient n has been determined from equation (5) using the UV-Vis absorption data of solutions with constant copper(II) concentration and variable concentration of ligands,

$$A = \varepsilon \cdot l \cdot [\text{M}_m\text{R}_n] = \varepsilon \cdot l \cdot \left(\frac{C_\text{R}}{n}\right), \tag{5}$$

where l is the thickness of absorption layer in cm, ε is the extinction coefficient in $\text{L}(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$, and C_R is the total ligand concentration in mol L^{-1}.

Data for the determination of stoichiometric coefficient n for Cu^{2+} with **1b** ($\text{R} = \text{OCH}_3$) and **1a** ($\text{R} = \text{Br}$) in methanol are presented in table 7. The "b" value, where $b = \epsilon \cdot l/n$, was obtained by least-squares using the data of $D = \text{f}\ (C_\text{R})$ dependence. The second series of measurements was carried out in conditions when $C_\text{R} \gg C_\text{M}$, $C_\text{R} = \text{const}$. The stoichiometric coefficient m has been determined from equation (6) using data for the absorption of solutions with constant ligand concentration and variable copper(II) concentration,

$$A = \varepsilon \cdot l \cdot [M_m R_n] = \varepsilon \cdot l \cdot \left(\frac{C_\text{M}}{m}\right), \tag{6}$$

where C_M is the total concentration of copper(II). Data for the determination of m for Cu^{2+} with **1b** and **1a** in methanol are listed in table 8. The "a" value, where $a = \boldsymbol{\varepsilon} \cdot l/m$, was obtained by least-squares using the data of $D = f\ (C_\text{M})$.

Thus, having calculated the ratio for the complexes under study and using $a/b = n/m$ one can conclude that compounds with 1 : 2 (metal : ligand) composition are formed in solutions. The obtained results support the idea that type 1 ligands exist predominantly in keto-form in water–methanol solutions at equilibrium pH values.

Table 7. Determination of stoichiometric coefficient ***n*** for Cu^{2+} with **1a** (R = Br) and **1b** ($R = OCH_3$) by the Harvey–Manning method, $C_{Cu} = 4.0 \times 10^{-5}\,mol\,L^{-1}$ ($l = 1$ cm).

1a		**1b**	
C_R ($mol\,L^{-1}$)	*D*	C_R ($mol\,L^{-1}$)	*D*
1.0×10^{-5}	0.110	1.0×10^{-5}	0.134
1.2×10^{-5}	0.145	1.4×10^{-5}	0.185
1.6×10^{-5}	0.185	1.6×10^{-5}	0.214
1.8×10^{-5}	0.210	1.8×10^{-5}	0.240
2.0×10^{-5}	0.195	2.0×10^{-5}	0.270
	$b = 11{,}013$		$b = 13{,}381$

Table 8. Determination of stoichiometric coefficient ***m*** for $Cu^{2+}$with **1a** and **1b** by the Harvey–Manning method $C_R = 4.0 \times 10^{-5}$ ($l = 1$ cm).

1a		**1b**	
C_{Cu} ($mol\,L^{-1}$)	*D*	C_{Cu} ($mol\,L^{-1}$)	*D*
1.0×10^{-5}	0.24	1.0×10^{-5}	0.31
1.4×10^{-5}	0.29	1.4×10^{-5}	0.35
1.6×10^{-5}	0.33	1.6×10^{-5}	0.43
1.8×10^{-5}	0.38	1.8×10^{-5}	0.48
2.0×10^{-5}	0.44	2.0×10^{-5}	0.50
	$a = 21{,}505$		$a = 26{,}085$

3.6. *EXAFS of copper complexes*

It is reasonable to suppose that in binuclear metallocomplexes, type **1** ligands are tridentate with deprotonated oxygens of carboxylate and hydrazide and the nitrogen of hydrazone =C=N–N= as donors. Two isomeric structures type **2** and **2′** (figure 1) are possible in this case.

The local structure of copper in **2a** and **2b** was probed with EXAFS spectroscopy. In figure 4, phase shift uncorrected Fourier transforms (FTs) of EXAFS Cu-K-edge adsorption spectra of **2a** and **2b** are shown. Both samples are similar with the most intense peak at $r \approx 1.50$ Å and two peaks of lower amplitude at $r \approx 2.00$ and $r \approx 2.40$ Å. The first peak is formed due to photoelectronic wave scattering on the nearest-neighbor coordinated nitrogen and oxygen. First coordination sphere parameters determined by non-linear fitting are shown in table 3. The best fit parameters with minimal *Q* value correspond to the first coordination sphere with radius $R = 1.90$–1.92 Å, which includes four oxygens and nitrogens, common for the studied copper complexes. The second peak on FTs of the complexes can be attributed to the scattering on the light atoms (C/N) of the chelate cycles. The third peak on FTs can be attributed to $Cu \cdots Cu$ scattering; its position ($r = 2.4$ Å) is typical for dimeric copper complexes with oxygen bridging atoms. Further evidence that the third peak is due to copper–copper scattering can be obtained by varying the integration limits of χ-spectra when performing Fourier transformation of EXAFS data. Increasing the lower integration limit during Fourier

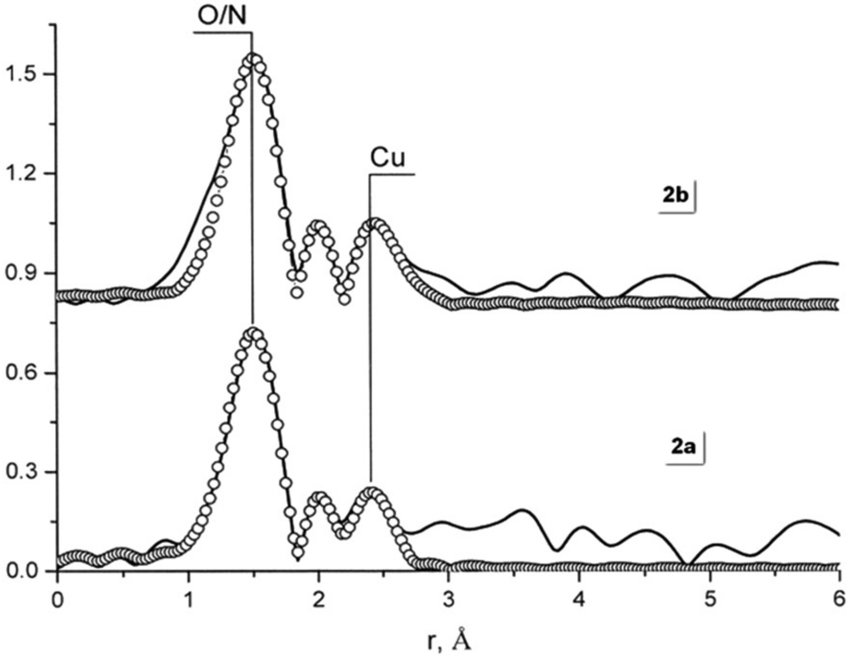
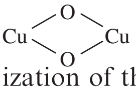


Figure 4. Phase shift uncorrected FTs of the CuK-edge EXAFS spectra for **2a** and **2b**: experiment (solid lines) and best-fits (open circles).

transformation results in the increase in the contribution of heavier (copper) atoms scattering paths and decrease in the contribution of light atoms (nitrogen, oxygen) scattering paths, because of the differences in amplitude-scattering function of these atoms. When Fourier transformation of χ – spectra is performed in the wavevector k range of 5.0–12 Å^{-1}, amplitude of the third peak increases relative to other peaks for both complexes, demonstrating that it is due to copper scattering, not light atoms. The interatomic distances $\text{Cu}\cdots\text{Cu}$ obtained by fitting procedure $R = 2.70$ Å (**2a**) and 2.79 Å (**2b**) support the dimeric structure of the complexes with the formation of the four-membered exchange fragment with bridging oxygen.

3.7. *Magnetic properties*

The binuclear structure of type **2** complexes has been confirmed by magnetic measurements. The type **2** complexes are characterized by antiferromagnetic exchange interaction with values of $2J$ exchange parameters calculated from HDVV theory in the range of -50 to $-62\,\text{cm}^{-1}$ (table 4). The peculiarities of ligand structure imply binuclear complexes through bridging oxygens of carboxylate (type **2**) or through oxygens of hydrazide (type **2′**).

Irrespective of the way dimerization occurs the antiferromagnetic exchange interaction will not be strongly changed due to the bending of the exchange fragment  along the bridging oxygens. The latter takes place because of sp^3-hybridization of these atoms [66]. Indeed all type **2** copper(II) complexes exhibit rather small values of $2J$ (table 4). The substituents of "R" have insignificant influence on the magnetic properties of the complexes. This is an indirect confirmation of dimerization through the bridging carboxylate since bridging through oxygen of hydrazide (type **2′**) should have more pronounced influence of these substituents on the magnetic properties.

4. Conclusion

The aim of this work was to synthesize and study a series of binuclear exchange-coupled copper(II) complexes based on glyoxylic acid substituted acylhydrazones. The results obtained represent rather unique examples of utilization of both typically analytical and physical chemical research methods. The data of IR, EXAFS spectroscopy, and magnetochemical measurements indicate binuclear complex in the solid state. The magnetochemical data were interpreted in terms of the theoretical model elaborated by our research group. In solution the aroylhydrazone ligands exhibit different coordination activity due to keto–enol tautomerism and proton-donor and proton-acceptor features of the ligand systems themselves. The acid–base equilibrium constants obtained by potentiometric method match well to the similar values deduced from absorption spectra of the ligands. The results for the coordination of ligands have been confirmed with the study of copper(II) complex formation in methanol solution by the method of inclination ratio of Harvey–Manning. The obtained results support type **1** ligand systems existing predominantly in keto-form in water–methanol solutions in the absence of added acid or alkali.

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References

[1] V.L. Kretovitch. *Plant Biochemistry*, Vysshaya Shkola, Moscow (1980).
[2] S.N. Pandeya, J.R. Dimmock. *Pharmazie*, **48**, 659 (1993).
[3] P. Vicini, M. Incerti, I.A. Doytchinova, P. La Colla, B. Busonera, R. Loddo. *Eur. J. Med. Chem.*, **41**, 624 (2006).
[4] Z.Y. Yang, R.D. Yang, L.F. Wang, X.P. Xang. *Bull. Soc. Chim. Belg.*, **3**, 104 (1995).
[5] J. Patole, V. Sandbhor, S. Padhye, D.N. Deobagkar, C.E. Anson, A. Powel. *Bioorg. Med. Chem. Lett.*, **13**, 51 (2003).
[6] P. Genova, T. Varadinova, A.I. Matesanz, D. Marinova, P. Souza. *Toxicol. Appl. Pharmacol.*, **197**, 107 (2004).
[7] J.C. Messender, L.W. Tinoco, J.D. Figueroa-Villar. *Bioorg. Med. Chem. Lett.*, **5**, 3079 (1995).
[8] L.D. Popov, A.N. Morozov, I.N. Shcherbakov, Yu.P. Tupolova, V.V. Lukov, V.A. Kogan. *Russ. Chem. Rev.*, **78**, 643 (2009).
[9] S. Padhye, G.B. Kauffman. *Coord. Chem. Rev.*, **63**, 127 (1985).

[10] J.S. Casas, M.S. Garcia-Tasende, J. Sordo. *Coord. Chem. Rev.*, **209**, 197 (2000).
[11] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbbar, R.G. Yerande. *Coord. Chem. Rev.*, **123**, 49 (1993).
[12] T.S. Lobana, R. Sharma, G. Bawa, S. Khanna. *Coord. Chem. Rev.*, **253**, 977 (2009).
[13] M. Katyal, Y. ag Dutt. *Talanta*, **22**, 151 (1975).
[14] A.A. Schilt, P.C. Quinn, C.L. Johnson. *Talanta*, **26**, 373 (1979).
[15] V.A. Bren, V.I. Minkin, E.W. Shepelenko, A.D. Dubonosov, A.Y. Bushkov. *Mendeleev. Commun.*, **1**, 72 (1991).
[16] J.L. Wang, M.F. Zady. *J. Org. Chem.*, **40**, 2512 (1975).
[17] H. Chai, G. Liu, L. Liu, D. Jia. *Spectrochim. Acta*, **A61**, 2590 (2005).
[18] C. Serbutoviez, C. Bosshard, G. Knopfle, P. Wyss, P. Pretre, P. Günter, K. Schenk, E. Solari, G. Chapuis. *Chem. Mater.*, **7**, 1198 (1995).
[19] I. Liakatas, M.S. Wong, V. Gramlich, P. Günter. *Adv. Mater.*, **10**, 777 (1998).
[20] O.-Pil. Kwon, M. Jazbinsek, H. Yun, J.-I. Seo, E.-M. Kim, Y.-S. Lee, P. Günter. *Cryst. Growth Des.*, **8**, 4021 (2008).
[21] R. Lygaitis, V. Getautis, J.V. Grazulevicius. *Chem. Soc. Rev.*, **37**, 770 (2008).
[22] M. Hong, H.-D. Yin, D.-Q. Wang. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **62**, m1555 (2006).
[23] W.-G. Lu, H.-W. Liu, X.-L. Feng. *Wuji Huaxue Xuebao (Chin.) (Chin. J. Inorg. Chem.)*, **20**, 313 (2004).
[24] S.-Y. He, R. Yang, W.-K. Cao, A.-P. Gu, Q.-Z. Shi, Z.-M. Wang, C.-H. Yan. *Huahue Xuebao (Chin.) (Acta Chim. Sin.)*, **61**, 715 (2003).
[25] P. Domiano, P.L. Messori, C. Pelizzi, G. Predieri. *Inorg. Chim. Acta*, **70**, 21 (1983).
[26] H.-W. Liu, W.-G. Lu, J.-X. Tao, R.-J. Wang. *Wuji Huaxue Xuebao (Chin.) (Chin. J. Inorg. Chem.)*, **19**, 1351 (2003).
[27] W.-K. Cao, S.-Y. He, J.-S. Zhao, R. Yang, Q.-Z. Shi, D.-Q. Wang, J.-M. Dou. *Huahue Xuebao (Chin.) (Acta Chim. Sin.)*, **61**, 1612 (2003).
[28] H.-D. Yin, M. Hong, Q.B. Wang, S.C. Xue, D.Q. Wang. *J. Organomet. Chem.*, **690**, 1669 (2005).
[29] Z.-P. Kong, R.-L. Bao, X.-G. Zhou, Z. Pang, L. Jiang, Z.-X. Chen, B. Yue. *Z. Kristallogr.-New Cryst. Struct.*, **220**, 85 (2005).
[30] Z. Yang, R. Yang, K. Yu. *Polyhedron*, **15**, 3749 (1996).
[31] S.-Y. He, W.-K. Cao, J.-L. Chen, J.-S. Zhao, Q.-Z. Shi, R.-X. Wang, J. Sun. *Gaodeng Xuexiao Huaxue Xuebao (Chin.) (Chem. J. Chin. Univ. (Chinese Edition))*, **23**, 991 (2002).
[32] R.-J. Chen, Y.-Z. Zhou, D.-D. Hu, S.-J. Tu, L.-M. Xiao. *Jiegou Huaxue (Chin.) (Chinese J. Struct. Chem.)*, **25**, 219 (2006).
[33] H.-D. Yin, M. Hong. *Appl. Organomet. Chem.*, **19**, 401 (2005).
[34] R. Yang, S.-Y. He, W.-T. Wu, Z.-Y. Wen, Q.-Z. Shi, D.-Q. Wang. *Huaxue Xuebao (Chin.) (Acta Chim. Sin.)*, **62**, 2040 (2004).
[35] H.-D. Yin, S.W. Chen, L.W. Li, D.Q. Wang. *Inorg. Chim. Acta*, **360**, 2215 (2007).
[36] G.F. Volodina, G.A. Kiosse, N.V. Gerely. *Dokl. Akad. Nauk SSSR (Russ.) (Proc. Natl Acad. Sci. USSR)*, **200**, 1349 (1971).
[37] B. Ya. Antosyak, V.N. Byushkin, N.I. Belichuk. *Koord. Khim. (Russ.) (Coord. Chem.)*, **10**, 269 (1984).
[38] G.G. Taran, N.M. Samus, I.D. Samus, V.E. Zavodnik, V.K. Bel'skii, V.G. Bodyu. *Izv. Akad. Nauk Mold. SSR. Ser. Fiz.-Tek. Mat. Nauk (Russ.) (Bull. Acad. Sci. Moldova, Phys. Eng. Math. Sci.)*, 27 (1984).
[39] Yu.M. Chumakov, V.N. Byushkin, V.G. Bodyu, N.M. Samus. *Koord. Khim. (Russ.) (Coord. Chem.)*, **11**, 551 (1985).
[40] M.D. Timken, S.R. Wilson, D.N. Hendrickson. *Inorg. Chem.*, **24**, 3450 (1985).
[41] I.F. Burshtein, N.V. Gerbeleu, A.Yu. Kon, O.A. Bologa, T.I. Malinovskii. *Zh. Strukt. Khim. (Russ.) (J. Struct. Chem.)*, **28**, 188 (1987).
[42] I.F. Burshtein, N.V. Gerbeleu, O.A. Bologa, A.Yu. Kon, T.I. Malinovskii. *Metalloorg. Khim. (Russ.) (Organomet. Chem. (USSR))*, **3**, 1162 (1990).
[43] I.F. Burshtein, N.V. Gerbeleu, O.A. Bologa, A.V. Verezhan, T.I. Malinovskii. *Dokl. Akad. Nauk SSSR (Russ.) (Proc. Natl Acad. Sci. USSR)*, **295**, 863 (1987).
[44] P. Sonawane, R. Chikate, A. Kumbhar, S. Padhye, R.J. Doedens. *Polyhedron*, **13**, 395 (1994).
[45] M.B. Ferrari, G.G. Fava, P. Tarasconi, C. Pelizzi. *J. Chem. Soc., Dalton Trans.*, 361 (1989).
[46] S. Knoll, F. Tschwatschal, T. Gelbrich, T. Ristau, R. Borsdorf. *Z. Anorg. Allg. Chem.*, **623**, 1959 (1997).
[47] P. Sonawane, A. Kumbhar, S. Padhye, R.J. Butcher. *Transition Met. Chem.*, **19**, 277 (1994).
[48] M.B. Ferrari, G.G. Fava, G. Pelosi, P. Tarasconi. *Polyhedron*, **19**, 1895 (2000).
[49] M.B. Ferrari, G.G. Fava, C. Pelizzi, G. Pelosi, P. Tarasconi. *Inorg. Chim. Acta*, **269**, 297 (1998).
[50] I.F. Burshtein, N.V. Gerbeleu, O.A. Bologa, A.V. Verezhan, T.I. Malinovskii. *Dokl. Akad. Nauk SSSR (Russ.) (Proc. Natl Acad. Sci. USSR)*, **300**, 1382 (1988).
[51] R. Chikate, P. Sonawane, A. Kumbhar, S. Padhye, R.J. Butcher. *Inorg. Chim. Acta*, **205**, 59 (1993).
[52] M.B. Ferrari, G.G. Fava, C. Pelizzi, P. Tarasconi. *J. Chem. Soc., Dalton Trans.*, 2153 (1992).
[53] M.B. Ferrari, G.G. Fava, G. Pelosi, M.C. Rodriguez-Arguelles, P. Tarasconi. *J. Chem. Soc., Dalton Trans.*, 3035 (1995).

[54] N.I. Dodoff, D. Kovala-Demertzi, M. Kubiak, J. Kuduk-Jaworska, A. Kochel, G.A. Gorneva. *Z. Naturf., B: Chem. Sci.*, **61**, 1110 (2006).

[55] M.B. Ferrari, F. Bisceglie, G.G. Fava, G. Pelosi, P. Tarasconi, R. Albertini, S. Pinelli. *J. Inorg. Biochem.*, **89**, 36 (2002).

[56] V.T. Kalinnikov, Yu.V. Rakitin. *Modern Magnetochemistry*, p. 272, Science, St-Petersburg (1994).

[57] B. Bleaney, K.D. Bowers. *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

[58] A.T. Shuvaev, B.Yu. Helmer, T.A. Lyubeznova, V.A. Shuvaeva. *J. Synchrotron Radiat.*, **6**, 158 (1999).

[59] M. Newville. *J. Synchrotron Radiat.*, **8**, 96 (2001).

[60] D.I. Kochubey, Yu.A. Babanov, K.I. Zamaraev, R.V. Vedrinskii, V.L. Kraizman, G.N. Kulipanov, L.N. Mazalov, A.N. Skrinskii, V.K. Fedorov, B.Yu. Kshelmer, A.T. Shuvaev. *X-ray Method of Study of Amorphous Substance's Structure: EXAFS Spectroscopy*, p. 306, Science Publishing, Siberia Dep., Novosibirsk (1988).

[61] S.I. Zabinski, J.J. Rehr, A. Ankudinov, R.C. Alber. *Phys. Rev.*, **B52**, 2995 (1995).

[62] A.R. Oki, J. Sanchez, R.J. Morgan, T.J. Emge. *J. Coord. Chem.*, **36**, 167 (1995).

[63] V.A. Kogan, V.V. Zelentsov, G.M. Larin, V.V. Lukov. *Transition Metal Complexes with Hydrazones*, Nauka, Moscow (1990).

[64] J. Inczédy. *The Application of Complexes in Analytical Chemistry*, Mir Publishing, Moscow (1979).

[65] M.S. Chernov'yantz. *Photometrical Methods of Study and Analysis (School-book guide for the students of the Department of Chemistry)*, Rostov State University Publishing, Rostov-on-Don (1992).

[66] Yu.P. Tupolova, V.A. Kogan, V.V. Lukov, L.D. Popov, I.E. Gevorkyan. *J. Transition Met. Chem.*, **32**, 656 (2007).