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Dedicated to the 90th Anniversary of Corresponding Member of the Russian Academy of Sciences A.N. Pudovik

Complexation and Ligand Exchange in Aqueous of Cu(II) and Ni(II) with Hydrazides of Some Aromatic Acids

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Abstract—Solvation and complexation of Cu(II) and Ni(II) with benzoic (L'), *p*-methoxybenzoic (L''), and isonicotinic (L) acid hydrazides in aqueous-ethanol solutions (ethanol mole fraction 0.07–0.68) were studied by pH-metry, spectrophotometry, and nuclear magnetic relaxation. The formation constants of the species $M(L')^{2+}$, $M(L')_2^{2+}$, $M(L'')^{2+}$, $M(L'')_2^{2+}$, $M(LH)^{3+}$, $M(L)^{2+}$, $M(L)(LH)^{3+}$, and $M(L)_2^{2+}$, where M = Cu^{2+} and Ni^{2+}, were determined. With isonicotinic acid hydrazide, a change in the coordination mode was observed in an isomer of $Cu(L)_2^{2+}$, with one of the ligands coordinating in the bidentate fashion, and the other, in the monodentate fashion via the pyridine nitrogen atom. The suggested structures were confirmed by analysis of the parameters of the ESR and electronic absorption spectra of the complexes. The rate constants of ligand exchange and formation of the complexes $Cu(L')^{2+}$, $Cu(L')_2^{2+}$, $Cu(L'')^{2+}$, and $Cu(L'')_2^{2+}$ in aqueous solutions were determined from nuclear magnetic relaxation measurements; the reactions occur by the associative mechanism. A cyclic process of reduction of Cu(II) to colloidal copper in the presence of L'' and atmospheric oxygen is described.

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An urgent problem in the coordination chemistry of *d* metals in aqueous-organic solvents is elucidation of the influence exerted by the nature and relative content of the organic component on the composition and stability of the complexes. In this paper, which continues our previous studies [1–3], we consider the complexation of Cu(II) with benzoic (L'), *p*-methoxybenzoic (L''), and isonicotinic (L) acid hydrazides in aqueous-ethanol solutions (ethanol mole fraction 0–0.68), and also the complexation of Ni(II) with isonicotinic acid hydrazide in the same media (supplementing our previous data [4]). Our goal was to compare the stability of the Cu(II) and Ni(II) complexes and to assess the role of electronic and solvation factors in the thermodynamics of formation of hydrazide complexes in aqueous-organic media. One more goal of this study was to examine the kinetics of ligand exchange in aqueous solutions of Cu(II) complexes with hydrazides of benzoic and *p*-methoxybenzoic acids by nuclear magnetic relaxation, as we did previously for the system Cu(II)–isonicotinic acid hydrazide [5]. It is important that combined evaluation of the stability constants and ligand exchange rates offers a unique opportunity to estimate the rate constants of complex formation.

Complexation equilibria. For all the systems under consideration, we recorded the absorption spectra of solutions containing constant concentrations of Cu(II) or Ni(II) ions and acid hydrazides in aqueous-ethanol solutions with ethanol mole fractions of 0.07, 0.11, 0.16, 0.22, 0.30, 0.39, 0.50, and 0.68. Figures 1 and 2

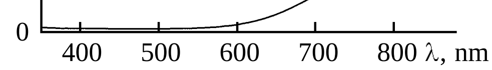


Fig. 1. Electronic absorption spectra of solutions in the system Cu(II)–isonicotinic acid hydrazide (L)–water–ethanol (mole fraction 0.22): (*1*) $c_{Cu(II)}$ 4.9 × 10^{-3}; (*2*) $c_{Cu(II)}$ 4.9 × 10^{-3}, c_L 5.5 × 10^{-3}; and (*3*) $c_{Cu(II)}$ 4.9 × 10^{-3}, c_L 1.08 × 10^{-2} M; pH ~4. *l* 1 cm, *T* 293 K (*A* is optical density).

Table 1. Dissociation constants (pK_a) of the protonated forms of benzoic (L'), *p*-methoxybenzoic (L''), and isonicotinic (L) acid hydrazides in aqueous-ethanol solutions (298 K)

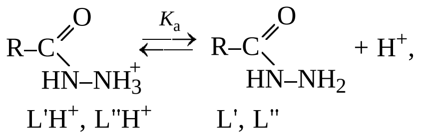
Hydrazide	Ethanol mole fraction								
	0	0.07	0.11	0.16	0.22	0.30	0.39	0.50	0.68
L'	3.27	2.97	2.91	2.85	2.82	2.79	2.75	2.75	2.70
L''	3.37	3.17	3.14	3.09	2.88	2.84	2.77	2.76	2.82
L[a]	1.91	1.73	1.59	1.41	1.17	1.21	1.33	1.28	2.11
	3.56	3.40	3.21	2.94	2.72	2.61	2.46	2.47	2.60

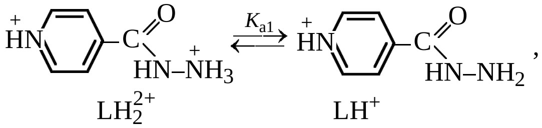
[a] Upper quantities, pK_{a1}; lower quantities, pK_{a2}.

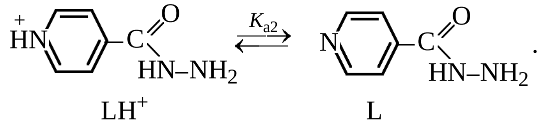
show as examples the electronic absorption spectra and pH dependences of the extinction coefficient of aqueous-ethanol solutions of Cu(II) complexes with L at various metal : ligand ratios. From these dependences, we calculated the complexation patterns and equilibrium constants by computer simulation using the CPESSP program [6].

The acid dissociation constants of the protonated hydrazide species [equilibria (1)–(3)] in aqueous and aqueous-ethanol solutions, required for calculating the complexation parameters, were taken from our previous papers [7, 8] and are given in Table 1.

For isonicotinic acid hydrazide, in addition to the data reported in [4], we determined pH-metrically the acid dissociation constants at ethanol mole fractions of 0.30, 0.39, 0.50, and 0.68. For this purpose, we titrated 25-ml portions of 0.08 M aqueous-ethanol solutions of the hydrazide with a 0.505 M aqueous-ethanol solution of HCl. The acid dissociation constants of L were calculated from the titration data using the CPESSP program. Data in Table 1 deserve special consideration, but here we mainly use them for discussing the complexation.


(1)


(2)


(3)

The constants of the related equilibria in solutions of L with 1 : 1 and 2 : 1 metal : ligand ratios virtually coincide, which indicates that no binuclear complexes with the dibasic ligand are formed.

The speciation diagram (Fig. 3) shows that the

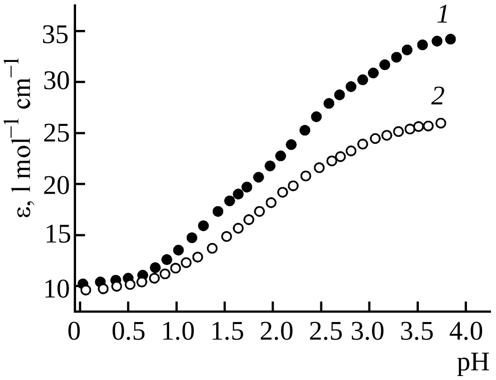


Fig. 2. pH dependence of the extinction coefficient ε in the system Cu(II)–isonicotinic acid hydrazide (L)–water–ethanol (mole fraction 0.22): (*1*) $c_{Cu(II)}$ 8.18 × 10^{-3}, c_L 8.38 × 10^{-3}; (*2*) $c_{Cu(II)}$ 8.18 × 10^{-3}, c_L 1.68 × 10^{-2} M. λ 700 nm, *T* 298 K.

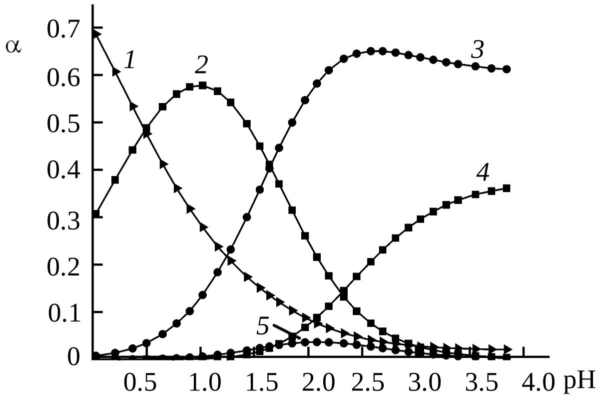


Fig. 3. Speciation diagram (α is relative content, mole fraction scale) of complex species in the system Cu(II)–isonicotinic acid hydrazide (L)–water–ethanol (mole fraction 0.22); $c_{Cu(II)}$ 8.18 × 10^{-3}, c_L 1.7 × 10^{-2} M; *T* 298 K. (*1*) Cu^{2+}, (*2*) $Cu(LH)^{3+}$, (*3*) $Cu(L)^{2+}$, (*4*) $Cu(L)_2^{2+}$, and (*5*) $Cu(LH)L^{3+}$.

Table 2. Formation constants ($\log\beta \pm 0.10$) of Cu(II) complexes with benzoic (L'), *p*-methoxybenzoic (L"), and isonicotinic (L) acid hydrazides in aqueous-ethanol solutions (298 K)

Equilibrium	Ethanol mole fraction								
	0	0.07	0.11	0.16	0.22	0.30	0.39	0.50	0.68
$Cu^{2+} + L' \rightleftarrows Cu(L')^{2+}$	3.67	3.67	3.68	3.63	3.64	3.70	3.77	3.82	3.96
$Cu^{2+} + 2L' \rightleftarrows Cu(L')_2^{2+}$	6.10	6.08	6.28	6.32	6.40	6.45	6.49	6.57	6.98
$Cu^{2+} + L'' \rightleftarrows Cu(L'')^{2+}$	3.95	3.96	4.03	4.03	4.01	4.02	4.05	4.03	–
$Cu^{2+} + 2L'' \rightleftarrows Cu(L'')_2^{2+}$	6.56	6.67	6.94	6.94	6.97	6.95	6.95	7.06	–
$Cu^{2+} + LH^+ \rightleftarrows Cu(LH)^{3+}$	1.75	1.92	2.06	2.40	2.67	2.76	2.88	3.07	–
$Cu^{2+} + L \rightleftarrows Cu(L)^{2+}$	3.63	3.58	3.53	3.60	3.74	3.82	4.05	4.25	–
$Cu^{2+} + LH^+ + L \rightleftarrows Cu(L)(LH)^{3+}$	4.27	(4.15)	(4.55)	(4.60)	(4.76)	(4.83)	(4.95)	(5.04)	–
$Cu^{2+} + 2L \rightleftarrows Cu(L)_2^{2+}$	5.39	5.37	5.63	5.68	5.78	6.14	6.40	6.60	–

Table 3. Formation constants ($\log\beta \pm 0.10$) of Ni(II) complexes with benzoic (L'), *p*-methoxybenzoic (L"), and isonicotinic (L) acid hydrazides in aqueous-ethanol solutions (298 K)

Equilibrium	Ethanol mole fraction							
	0	0.07	0.11	0.16	0.22	0.30	0.39	0.50
$Ni^{2+} + L' \rightleftarrows Ni(L')^{2+}$	3.00	2.84	3.13	3.20	3.33	3.38	3.54	3.63
$Ni^{2+} + 2L' \rightleftarrows Ni(L')_2^{2+}$	5.23	4.87	5.27	5.39	5.58	5.65	6.12	6.23
$Ni^{2+} + L'' \rightleftarrows Ni(L'')^{2+}$	3.09	2.87	3.25	3.36	3.37	3.40	3.57	3.71
$Ni^{2+} + 2L'' \rightleftarrows Ni(L'')_2^{2+}$	5.40	4.88	5.43	5.62	5.72	5.83	6.17	6.42
$Ni^{2+} + LH^+ \rightleftarrows Ni(LH)^{3+}$	1.54	1.36	1.80	1.94	2.04	2.13	2.27	2.69
$Ni^{2+} + L \rightleftarrows Ni(L)^{2+}$	3.02	3.10	3.37	3.43	3.50	3.75	3.99	4.13
$Ni^{2+} + LH^+ + L \rightleftarrows Ni(L)(LH)^{3+}$	4.75	4.58	4.92	4.84	4.86	–	–	–
$Ni^{2+} + 2L \rightleftarrows Ni(L)_2^{2+}$	5.40	5.41	5.43	5.70	5.88	6.13	6.30	6.48

three complexes with isonicotinic acid hydrazide are accumulated to a significant extent, whereas the maximal relative content α of the protonated species $Cu(L)(LH)^{3+}$ is as low as 0.05; therefore, the formation constants for this complex are determined with a poor accuracy and are hereinafter given in parentheses (Table 2). The formation constants of the complex $Ni(L)(LH)^{3+}$ are determined with a better accuracy, and only at high ethanol concentrations (mole fraction 0.30 – 0.50) their relative content is below the detection limit (dashes in Table 3). The set of complex species formed in aqueous and aqueous-ethanol solutions in the examined concentration range is similar for Cu(II) and Ni(II).

As seen from Tables 2 and 3, with benzoic and *p*-methoxybenzoic acid hydrazides only 1 : 1 and 1 : 2 complexes with the molecular form of the ligand are formed. With isonicotinic acid hydrazide, along with these complexes, also 1 : 1 and 1 : 2 complexes with the protonated form of the ligand (LH^+) were detected.

In Ni(II) solutions at high ethanol concentrations (mole fraction 0.68), the complexation cannot be monitored because of precipitate formation. Copper(II) complexes with *p*-methoxybenzoic and isonicotinic acid hydrazides at high ethanol concentrations show a noticeable tendency to redox transformations with the precipitation of copper metal (see below).

The formation constants (β) of the complexes of similar composition tend to decrease in going from Cu(II) to Ni(II), in agreement with the Irving–Williams series. The 1 : 1 and 1 : 2 complexes of both metals with *p*-methoxybenzhydrazide are appreciably more stable than the related complexes with benzhydrazide, in agreement with the electron-donor properties of the *p*-CH_3O group.

The complexes of Cu(II) and Ni(II) with the protonated form of isonicotinic acid hydrazide are considerably less stable than those with the deprotonated form, because of enhancement of the electron-withdrawing power of the pyridyl substituent upon protonation of

Table 4. Formation constants ($\log \beta'$) and step stability constants of Cu(II) complexes with benzoic (L'), *p*-methoxybenzoic (L''), and isonicotinic (L) acid hydrazides in aqueous-methanol solutions (298 K)

Ligand	Constant	Ethanol mole fraction								
		0	0.07	0.11	0.16	0.22	0.30	0.39	0.50	0.68
L'	$\log \beta'_{\mathrm{Cu(L')}}$	7.15	7.01	6.90	6.71	6.58	6.46	6.33	6.08	5.68
	$\log K_{\mathrm{Cu(L')}}$	3.67	3.67	3.68	3.63	3.64	3.70	3.77	3.82	3.96
	$\log K_{\mathrm{Cu(L').}}$	2.43	2.41	2.60	2.69	2.76	2.75	2.72	2.75	3.02
	$\log (K_{\mathrm{Cu(L')}}/K_{\mathrm{Cu(L')_2}})$	1.24	1.26	1.08	0.94	0.88	0.95	1.05	1.07	0.94
	$\log \beta'_{\mathrm{Cu(L').}}$	13.06	12.72	12.72	12.48	12.28	11.97	11.61	11.06	10.42
L''	$\log \beta'_{\mathrm{Cu(L'')}}$	7.43	7.28	7.25	7.11	6.95	6.78	6.61	6.29	–
	$\log K_{\mathrm{Cu(L'')}}$	3.95	3.96	4.03	4.03	4.01	4.02	4.05	4.03	–
	$\log K_{\mathrm{Cu(L'')_2}}$	2.61	2.71	2.91	2.91	2.96	2.93	2.90	3.03	–
	$\log (K_{\mathrm{Cu(L'')}}/K_{\mathrm{Cu(L'')_2}})$	1.34	1.25	1.12	1.12	1.05	1.09	1.15	1.00	–
	$\log \beta'_{\mathrm{Cu(L'')_2}}$	13.52	13.31	13.38	13.10	12.85	12.47	12.07	11.55	–
L	$\log \beta'_{\mathrm{Cu(LH)}}$	5.23	5.24	5.28	5.48	5.61	5.52	5.44	5.33	–
	$\log \beta'_{\mathrm{Cu(L)}}$	7.11	6.90	6.75	6.68	6.68	6.58	6.61	6.51	–
	$\log K_{\mathrm{Cu(L)}}$	3.63	3.58	3.53	3.60	3.74	3.82	4.05	4.25	–
	$\log \beta_{\mathrm{Cu(L)_2}}$	1.76	1.79	2.10	2.08	2.04	2.32	2.35	2.35	–
	$\log (K_{\mathrm{Cu(L)}}/K_{\mathrm{Cu(L)_2}})$	1.87	1.79	1.43	1.52	1.70	1.50	1.70	1.90	–
	$\log \beta'_{\mathrm{Cu(L)_2}}$	12.35	12.01	12.07	11.84	11.66	11.66	11.52	11.12	–

the heterocyclic N atom, which leads to weakening of the donor power of the hydrazide N atom.

The stability constants of the 1 : 1 complex species $\mathrm{Cu(L')^{2+}}$ and $\mathrm{Cu(L'')^{2+}}$ only weakly vary with the addition of ethanol up to mole fraction of 0.50 (Table 2). The stability constants of the related Ni(II) complexes increase more significantly. At the same time, with both metals the formation constants of the species $\mathrm{M(L)^{2+}}$ and $\mathrm{M(LH)^{3+}}$ tend to increase with an increase in the ethanol content, which is attributable to the dehydration of the aqua ion in the course of reaction (4):

$$[\mathrm{M(H_2O)_6}]^{2+}_{\mathrm{sol}} + \mathrm{L_{sol}}$$

$$\xrightleftharpoons{\beta'} [\mathrm{M(H_2O)}_{6-m}\mathrm{(L)}]^{2+}_{\mathrm{sol}} + m\mathrm{H_2O}, \tag{4}$$

$$\log \beta \mathrm{M(L)} = \log \mu_{\mathrm{M(L)}} + m \log [\mathrm{H_2O}]. \tag{5}$$

Indeed, Tables 4 and 5 show that the quantities $\log \beta'_{\mathrm{M(L)}}$ and $\log \beta'_{\mathrm{M(LH)}}$ calculated by Eq. (5) taking into account the bidentate coordination of the ligand ($m = 2$) remain essentially constant throughout the examined composition range of the aqueous-organic solvent. This is consistent with the fact that the previously determined free energies of transfer of L and $\mathrm{LH^+}$ from water to aqueous-ethanol solvents only weakly depend on the solvent composition up to ethanol mole fraction of 0.50 [7, 9].

At the same time, the variation of the formation constants of the 1 : 1 and 1 : 2 complexes with benzoic and *p*-methoxybenzoic acid hydrazides and of the 1 : 2 complexes with isonicotinic acid hydrazide, taking place with an increase in the ethanol content, cannot be attributed solely to dehydration of the metal ion by reaction (4). The $\log \beta'$ values calculated for these complexes (at different m, in particular, at $m = 2$ for 1 : 1 and $m = 4$ for 1 : 2 complexes, Tables 4, 5) are not constant, owing both to solvation of the ligands and possible coordination of ethanol molecules to the metal (at its high concentration).

Table 4 shows that the logarithm of the ratio of the step stability constants of the Cu(II) 1 : 1 and 1 : 2 complexes $[\log (K_{\mathrm{Cu(L)}}/K_{\mathrm{Cu(L)_2}})]$ with benzoic and *p*-methoxybenzoic acid hydrazides is essentially independent of the solvent composition and close to the statistically expected value for the coordination of bidentate ligands (1.2 [10, 11]). For the Ni(II) complexes with the same hydrazides, $\log (K_{\mathrm{Ni(L)}}/K_{\mathrm{Ni(L)_2}})$ slightly exceeds the statistically expected value (0.68 [12]) starting from the ethanol mole fraction of 0.11 (Table 5). With isonicotinic acid hydrazide, $\log (K_{\mathrm{M(L)}}/K_{\mathrm{M(L)_2}})$ exceeds the statistically expected value at high ethanol concentrations with M = Ni and at all ethanol concentrations with M = Cu. This somewhat unexpected result can be accounted for by a change in the coordination mode of L, namely, by formation of an appreciable amount of the isomeric complex $\mathrm{M(L)_2^{2+}}$ in which the second ligand is coordi-

Table 5. Formation constants ($\log \beta'$) and step stability constants of Ni(II) complexes with benzoic (L'), *p*-methoxybenzoic (L"), and isonicotinic (L) acid hydrazides in aqueous-ethanol solutions (298 K)

Ligand	Constant	Ethanol mole fraction							
		0	0.07	0.11	0.16	0.22	0.30	0.39	0.50
L'	$\log \beta'_{Ni(L')}$	6.49	6.15	6.34	6.29	6.28	6.15	6.09	5.88
	$\log K_{Ni(L')}$	3.00	2.84	3.13	3.20	3.33	3.38	3.54	3.63
	$\log K_{Ni(L')_2}$	2.23	2.03	2.14	2.19	2.25	2.27	2.58	2.60
	$\log (K_{Ni(L')}/K_{Ni(L')_2})$	0.77	0.81	0.99	1.01	1.08	1.11	0.96	1.03
	$\log \beta'_{Ni(L')_2}$	12.21	11.49	11.69	11.57	11.47	11.18	11.22	10.73
L"	$\log \beta'_{Ni(L'')}$	6.58	6.18	6.46	6.45	6.32	6.17	6.14	5.96
	$\log K_{Ni(L'')}$	3.09	2.87	3.25	3.36	3.37	3.40	3.59	3.71
	$\log K_{Ni(L'')_2}$	2.31	2.01	2.18	2.26	2.35	2.43	2.58	2.71
	$\log (K_{Ni(L'')}/K_{Ni(L'')_2})$	0.78	0.86	1.07	1.10	1.02	0.97	1.01	1.00
	$\log \beta'_{Ni(L'')}$	12.38	11.50	11.85	11.80	11.61	11.36	11.27	10.92
L	$\log \beta'_{Ni(LH)}$	5.02	5.03	5.02	5.03	4.98	4.89	4.82	4.94
	$\log \beta'_{Ni(L)}$	6.50	6.41	6.58	6.52	6.45	6.52	6.54	6.38
	$\log K_{Ni(L)}$	3.02	3.10	3.37	3.43	3.50	3.75	3.99	4.13
	$\log \beta_{Ni(L)_2}$	2.38	2.31	2.06	2.27	2.38	2.38	2.37	2.35
	$\log (K_{Ni(L)}/K_{Ni(L)_2})$	0.64	0.79	1.31	1.16	1.12	1.37	1.62	1.78
	$\log \beta'_{Ni(L)_2}$	12.36	12.03	11.85	11.75	11.76	11.66	11.40	10.98

nated with the metal in the monodentate fashion via the pyridine N atom, as assumed previously for M = Cu [5].

Our conclusions are confirmed by analysis of the parameters of the electronic absorption and ESR spectra of the Cu(II) complexes detected. Examples of the computer-resolved electronic spectra of particular species are shown in Fig. 4, and some ESR spectra (experimental spectra and computer-resolved spectra of particular species), in Fig. 5.

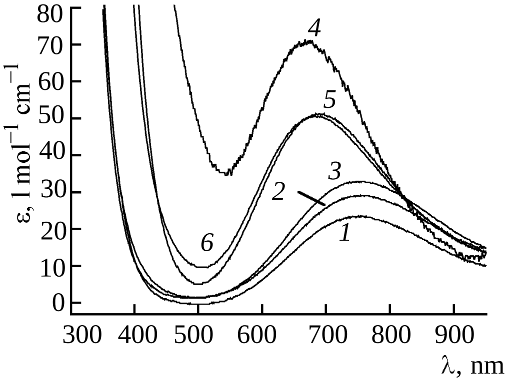


Fig. 4. Computer-resolved electronic absorption spectra of particular complex species in aqueous and aqueous-ethanol solutions of Cu(II) with isonicotinic acid hydrazide (L) at 293 K: (*1*) $Cu(L)^{2+}$ in H_2O, (*2*) $Cu(L)^{2+}$ in H_2O–EtOH (50 vol %), (*3*) $Cu(L)^{2+}$ in H_2O–EtOH (80 vol %), (*4*) $Cu(L)_2^{2+}$ in H_2O, (*5*) $Cu(L)_2^{2+}$ in H_2O–EtOH (50 vol %), and (*6*) $Cu(L)_2^{2+}$ in H_2O–EtOH (80 vol %).

The spectral parameters are listed in Table 6. It is seen that an increase in the ethanol content results in an appreciable increase in the extinction coefficients of the monoligand complexes, which suggests equatorial coordination of ethanol molecules. At the same time, additions of ethanol only weakly affect the extinction coefficients of the 1 : 2 complexes with benzoic and *p*-methoxybenzoic acid hydrazides, which is consistent with the bidentate coordination of both ligands, leaving no space for the equatorial coordination of ethanol with Cu(II). However, the 1 : 2 complxes with isonicotinic acid hydrazides behave differently. They exhibit abnormal electronic absorption spectra and considerably increased *g*-factor, which, according to [13], suggests the coordination of a weaker field ligand, pyridine nitrogen atom, which was assumed above on the basis of thermodynamic data.

Ligand exchange. Information on the chemical exchange in solutions of Cu(II) with benzoic and *p*-methoxybenzoic acid hydrazides was obtained by nuclear magnetic relaxation measurements from the pH dependence of the molar spin–spin relaxation coefficient of water protons $(c_M T_{2p})^{-1}$ under conditions of ligand excess (Fig. 6). An increase in $(c_M T_{2p})^{-1}$ with pH suggests acceleration of the chemical exchange by the second-order mechanism under the action of the accumulating free ligand [5].

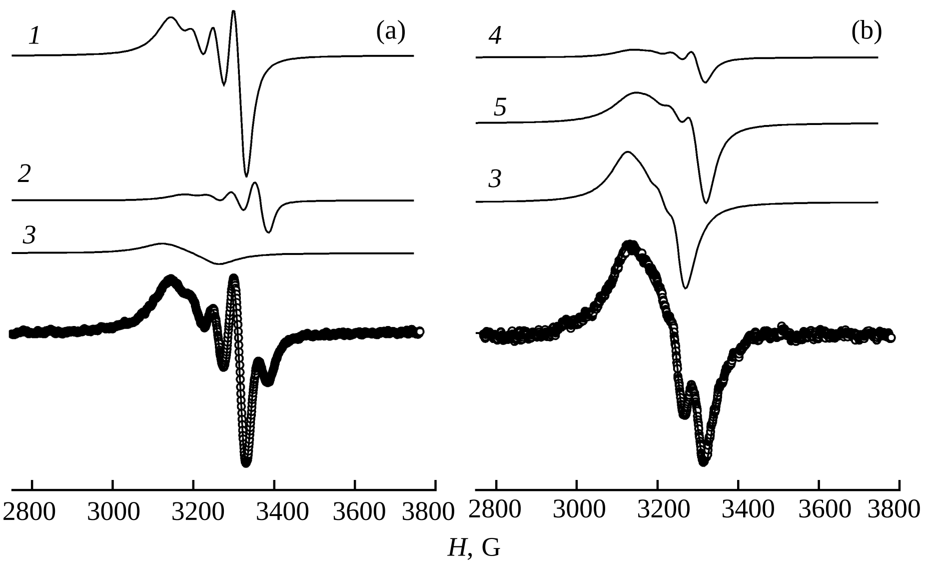


Fig. 5. ESR spectra (circles, experimental; lines, computer-resolved) of the systems (a) Cu(II)–*p*-methoxybenzhydrazide (L'')–water at pH 2.43 and (b) Cu(II)–isonicotinic acid hydrazide (L)–water–ethanol (80 mol %) at pH 0.66. $c_{Cu(II)}$ 4.91 × 10^{-3}, $c_{L''}$ 1.00 × 10^{-2}, c_L 1.04 × 10^{-2} M; *T* 293 K. Components: (*1*) $Cu(L'')^{2+}$ (A_0 49.1 × 10^{-4} cm^{-1}, g_0 2.162), (*2*) $Cu(L'')_2^{2+}$ (A_0 52.5 × 10^{-4} cm^{-1}, g_0 2.130), (*3*) $Cu_{aq}{}^{2+}$, (*4*) $Cu(L)^{2+}$ (A_0 46.1 × 10^{-4} cm^{-1}, g_0 2.162), and (*5*) $Cu(LH)^{3+}$ (A_0 45.6 × 10^{-4} cm^{-1}, g_0 2.171).

Taking into account the calculated relative contents (α) of all the species present in each system, including the aqua ion (α_0), 1 : 1 complex (α_1), and 1 : 2 complex (α_2), and also the equilibrium concentrations of the ligands ([L]), we calculated from the dependences shown in Fig. 6, using the Origin program, the rate constants of the chemical exchange by the following expression (cf. [5, 14, 15]):

$$(c_M T_{2p})^{-1} = \alpha_0 K_0 + \sum_i \alpha_i \left(K_{A(i)} + \frac{P'_{(i)}}{(k_{1(i)} + k_{L(i)}[L])^{-1} + T_{2M(i)}} \right), \qquad (6)$$

where K_0 is the molar coefficient of spin–spin relaxation of the Cu^{2+} aqua ion; K_A, contribution to the relaxation from the coordinated water molecules (taken equal to 400 l mol^{-1} s^{-1} for the 1 : 1 and 1 : 2 complexes according to [16]); k_1, rate constant of spontaneous dissociation of the ligand (first-order pathway); k_L, rate constant of the second-order ligand exchange activated with the free ligand L; $P' = P_M/c_M$, where P_M is the mole fraction of equatorially coordinated protons of the hydrazide NH_2 group; and T_{2M}, spin–spin relaxation time of these protons.

The evaluated rate constants correspond to the following reactions (L stands for any of the three hydrazides under consideration):

$$Cu(L)^{2+} \underset{k_{f(1)}}{\overset{k_{1(1)}}{\rightleftarrows}} Cu^{2+} + L, \qquad (7)$$

$$Cu(L)^{2+} + {}^*L \overset{k_{L(1)}}{\rightleftarrows} Cu({}^*L)^{2+} + L, \qquad (8)$$

$$Cu(L)_2^{2+} \underset{k_{f(2)}}{\overset{k_{1(2)}}{\rightleftarrows}} Cu(L)^{2+} + L, \qquad (9)$$

$$Cu(L)_2^{2+} + {}^*L \overset{k_{L(2)}}{\rightleftarrows} Cu(L)({}^*L)^{2+} + L. \qquad (10)$$

The first-order reaction rate constants $k_{1(i)}$ correspond to the dissociation of the complexes $Cu(L)^{2+}$ or $Cu(L)_2^{2+}$ and are related to the rate constants of formation of these complexes ($k_{f(i)}$) by

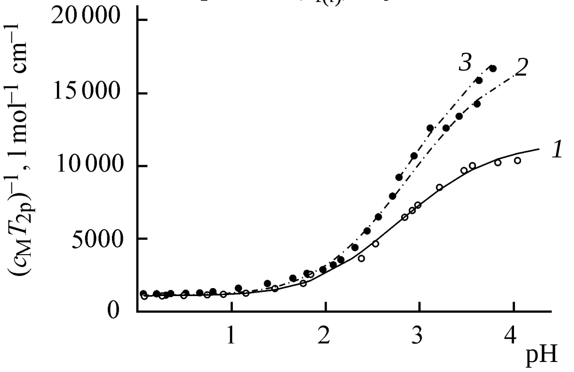


Fig. 6. pH dependences of the molar spin–spin relaxation coefficient of water protons [$(c_M T_{2p})^{-1}$] (circles, experimental; lines, calculated) in the systems (*1*) Cu(II)–benzhydrazide (L')–water and (*2*, *3*) Cu(II)–*p*-methoxybenzhydrazide (L'')–water. (*1*) $c_{Cu(II)}$ 2.246 × 10^{-3}, (*2*) $c_{Cu(II)}$ 2.499 × 10^{-3}, and (*3*) $c_{Cu(II)}$ 1.270 × 10^{-3}; $c_{L'} = c_{L''}$ = 1.25 × 10^{-2} M, *T* 298 K.

Table 6. Parameters of the electronic absorption spectra and isotropic ESR spectra of complexes in aqueous and aqueous-ethanol solutions of Cu(II) with hydrazides of benzoic (L'), *p*-methoxybenzoic (L"), and isonicotinic (L) acids at 293 K

Complex	Solvent	$\lambda_{max} \pm 5$, nm	ε_{max}, mol l^{-1} cm^{-1}	$g_0 \pm 0.01$	$A_0 \times 10^4$, cm^{-1}
$Cu(L')^{2+}$	H_2O	780	26.1	2.164	48.7
$Cu(L')^{2+}$	H_2O–EtOH (50 vol%)	776	33.0		
$Cu(L')^{2+}$	H_2O–EtOH (80 vol%)	795	38.6	2.161	47.8
$Cu(L')_2^{2+}$	H_2O	687	67.4	2.134	50.5
$Cu(L')_2^{2+}$	H_2O–EtOH (50 vol%)	684	58.3		
$Cu(L')_2^{2+}$	H_2O–EtOH (80 vol%)	680	63.4	2.133	50.5
$Cu(L'')^{2+}$	H_2O	773	29.5	2.162	49.1
$Cu(L'')^{2+}$	H_2O–EtOH (50 vol%)	785	39.0		
$Cu(L'')^{2+}$	H_2O–EtOH (80 vol%)	785	40.6	2.158	46.1
$Cu(L'')_2^{2+}$	H_2O	671	68.4	2.130	52.2
$Cu(L'')_2^{2+}$	H_2O–EtOH (50 vol%)	673	63.4	2.130	52.6
$Cu(LH)^{3+}$	H_2O–EtOH (80 vol%)			2.171	45.6
$Cu(L)^{2+}$	H_2O	751	23.6	2.167	46.1
$Cu(L)^{2+}$	H_2O–EtOH (50 vol%)	754	29.1		
$Cu(L)^{2+}$	H_2O–EtOH (80 vol%)	754	32.9	2.164	46.1
$Cu(L)_2^{2+}$	H_2O	667	71.3	2.139	48.8
$Cu(L)_2^{2+}$	H_2O–EtOH (50 vol%)	689	51.3		
$Cu(L)_2^{2+}$	H_2O–EtOH (80 vol%)	683	50.6	2.143	48.9

$$k_{f(i)} = k_{1(i)}K_i, \qquad (11)$$

where K_i is the step stability constant of the complex $Cu(L)^{2+}$ (i = 1) or $Cu(L)_2^{2+}$ (i = 2) (Table 4).

The results of the kinetic calculations are listed in Table 7 together with the previous data for the corresponding complexes with isonicotinic acid hydrazide [5]. It should be primarily noted that the rate constants $k_{L(1)}$ and $k_{f(2)}$ are close for each of the ligands L' and L" ($k_{L(1)} = 6.7 \times 10^7$ l mol^{-1} s^{-1} = $k_{f(2)}$ for L' and $k_{L(1)} = 1.3 \times 10^8$ l mol^{-1} $s^{-1} \approx 1.5 \times 10^8$ l mol^{-1} s^{-1} = $k_{f(2)}$ for L"). This fact means that the 1 : 2 complex $Cu(L)_2^{2+}$ formed by reverse reaction (9) (cf. [5]) is, indeed, an intermediate in ligand exchange (8). Table 7 shows that for both 1 : 1 and 1 : 2 complexes the constants $k_{L(i)}$ and $k_{f(2)}$ increase in the order L–L'–L". The donor power of the ligands increases in the same order, which is reflected in the corresponding increase in the stability constants of their Cu(II) complexes (Table 2). In agreement with this trend, the quantities $k_{f(1)}$ and $\log K_1$ for L virtually coincide with those for L' (Table 7). An increase in $k_{L(1)}$ and $k_{f(2)}$ with the enhancement of the ligand nucleophilicity in the order L–L'–L" is in full agreement with the associative mechanism of the ligand exchange and formation of Cu(II) complexes [17, 18]. With L' and L", $k_{L(i)}$ and $k_{f(i)}$ decrease by a factor of approximately 3 in going from the 1 : 1 to 1 : 2 complexes. Lower $k_{f(2)}$ values compared to $k_{f(1)}$ are typical of Cu(II) complexes, and this trend is due to three factors: (1) decrease in the charge on the metal ion after addition of the first ligand, leading to a decrease in the formation constant of the outer-sphere complex; (2) elimination of Jahn–Teller distortions in the 1 : 1 complexes; and (3) blocking by the first coordinated ligand of the site for the attack of the second ligand (statistical factor) [18]. The first factor is insignificant for the neutral hydrazide ligands in question. At fast Jahn–Teller distortions in the 1 : 1 complex, the statistical factor is 5/12 [18–20]. Therefore, with L' and L" the ratio $k_{f(2)}/k_{f(1)} \approx 1/3$, close to the statistical factor of 5/12, is indicative of fast Jahn–Teller distortion in their complexes. However, with isonicotinic acid hydrazide L, $k_{f(2)}$ is abnormally low compared to $k_{f(1)}$ (Table 7), which may be due to coordination of the second ligand L to $Cu(L)^{2+}$ via pyridine nitrogen atom whose nucleophilicity (basicity) is lower. The same conclusion follows from the thermodynamic and spectral data.

Thus, the structure of the hydrazide ligand strongly affects the composition, stability, and structure of its complexes and the kinetics of the complexation and ligand substitution.

Reduction of Cu(II). The systems in question show an interesting behavior on alkalization to pH ~5 in air. In the presence of L", the spectra gradually change (Fig. 7) with a continuous decrease in the solution pH (insert in Fig. 7). In the process, the intensity of the absorption band in the near-UV range sharply in-

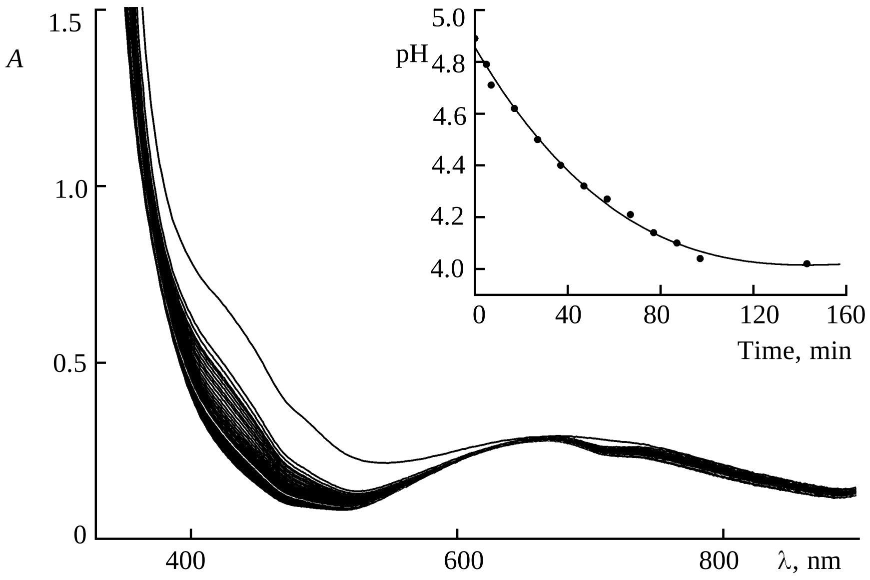


Fig. 7. Evolution of the electronic absorption spectra during the period of 12 h (from the bottom upwards) and the spectrum recorded after storage for 20 h (upper curve). Insert: variation of the pH with time. System Cu(II)–*p*-methoxybenzhydrazide (L'')–water–ethanol (50 vol %) in air. $c_{\mathrm{Cu(II)}}$ 5.00 × 10^{-3}, $c_{\mathrm{L''}}$ 1.09 × 10^{-2} M. *T* 293 K.

creases. Simultaneously, an increase in the relative content of the Cu^{2+} aqua ion is detected by ESR, and in 36 h it becomes the only ESR-detectable species. In the first day of storage, the solution becomes colloidal, and on the second day finely dispersed copper starts to precipitate. After storage for several days, the electronic absorption spectra contain only the band of the Cu(II) aqua ion with a maximum at about 800 nm and a new band with a maximum at 410 nm, imparting the yellow color to the solution. Notably, these transformations do not occur after purging of stock and freshly prepared solutions with argon and their storage in sealed cells; monitoring for several days revealed no changes in the absorption spectra.

All these facts are attributable to the occurrence of the following cyclic process. Mild reduction of Cu(II) with an aromatic acid hydrazide $RC(O)NHNH_2$ yields colloidal copper which is oxidized back to Cu(II) with atmospheric oxygen and is returned to the cycle of oxidation of the hydrazide ligand:

$$2Cu^{2+} + RC(O)NHNH_2 + H_2O \longrightarrow 2Cu + RC(O)OH + N_2 + 4H^+, \qquad (12)$$

$$2Cu + O_2 + 4H^+ \longrightarrow 2Cu^{2+} + 2H_2O. \qquad (13)$$

The process continues until the whole amount of the hydrazide transforms into the aromatic acid RC(O)OH. This acid is a weak ligand; therefore, under the experimental conditions, the free Cu^{2+} is virtually the only copper species in solution.

The occurrence of the redox processes under mild conditions and the possibility of their easy control

Table 7. Rate constants of ligand exchange (k_1, k_L) and complex formation (k_f), spin–spin relaxation times (T_{2M}), and step stability constants (log*K*) of Cu(II) complexes with isonicotinic (L), benzoic (L'), and *p*-methoxybenzoic (L'') acid hydrazides at 298 K (data for L were taken from [5])

Complex	log*K*	k_1, s^{-1}	k_L, l mol^{-1} s^{-1}	k_f, l mol^{-1} s^{-1}	T_{2M}
$Cu(L)^{2+}$	3.63	6.0×10^4	1.4×10^7	2.6×10^8	6.0×10^{-7}
$Cu(L_2^{2+}$	1.76	3.6×10^5	1.1×10^7	2.1×10^7	6.0×10^{-7}
$Cu(L')^{2+}$	3.67	$(5.0 \pm 0.5) \times 10^4$	$(6.7 \pm 0.9) \times 10^7$	2.3×10^8	$(6.1 \pm 0.9) \times 10^{-7}$
$Cu(L'^{2+}_2$	2.43	$(2.5 \pm 0.3) \times 10^5$	$(2.1 \pm 0.3) \times 10^7$	6.7×10^7	$(5.8 \pm 0.8) \times 10^{-7}$
$Cu(L'')^{2+}$	3.95	$(5.6 \pm 0.6) \times 10^4$	$(1.3 \pm 0.2) \times 10^8$	5.0×10^8	$(5.8 \pm 0.8) \times 10^{-7}$
$Cu(L''^{2+}_2$	2.61	$(3.6 \pm 0.4) \times 10^5$	$(4.6 \pm 0.4) \times 10^7$	1.5×10^8	$(5.4 \pm 0.7) \times 10^{-7}$

make the systems Cu(II)–aromatic acid hydrazides–ethanol–water attractive for further studies.

EXPERIMENTAL

The complexation of Cu(II) and Ni(II) with acid hydrazides in aqueous-ethanol solutions was studied by pH-metry, spectrophotometry, and ESR [for Cu(II) solutions]. The absorption spectra were taken on an SF-46 spectrophotometer in 2-cm cells and on a Perkin–Elmer Lambda EZ-210 spectrophotometer in a 1-cm cell. The optical density of the solutions was measured relative to the reference solutions containing the same components as the solution under consideration, except for the metal ion. All the measurements were performed at 25°C (temperature control). For any solution we performed no less than two replicate measurements of the optical density and pH; the mean values are reported.

To measure the pH of solutions containing definite amounts of ethanol, we used a pH-673 pH meter. The glass electrode was calibrated with HCl solutions of known concentrations [21]. In the aqueous-ethanol solvents used in the study, the reproducible potential of the glass electrode was attained within 5–15 min.

The ESR spectra were recorded on a Bruker ESR-300 spectrometer (working frequency 9.3 GHz). The signal of diphenylpicrylhydrazyl was used as reference. Solutions for recording the ESR spectra were sealed in special capillaries immediately after the preparation.

The ligand exchange was studied by nuclear magnetic relaxation [22]. The spin–spin relaxation times of water protons (T_2) were measured on a pulse coherent NMR spectrometer (15 MHz) with an accuracy of ±2% under temperature control. The paramagnetic (p) contribution to the spin–spin relaxation rate ($1/T_{2p}$) was calculated as the difference between the relaxation rates in the presence and in the absence of the paramagnetic ion.

Copper(II) nitrate and nickel(II) nitrate were of chemically pure grade; isonicotinic acid hydrazide was of pharmacopoeia grade; benzoic and *p*-methoxybenzoic acid hydrazides were purified by recrystallization from aqueous-alcoholic solutions. The compounds were identified by the elemental analyses and melting points. The required pH was adjusted with titrated HNO_3 solutions. Solutions of hydrazides were prepared from accurately weighed portions. The concentrations of the initial solutions of the salt and acid (HNO_3) were determined by volumetric titration.

The compositions and stability constants of the complexes were calculated by the CPESSP program [6] from the pH dependences of the extinction coefficient of the solutions (ε) at various metal : ligand ratios (examples are shown in Fig. 2).

The electronic absorption spectra of particular complexes were constructed by computer resolution of the experimental spectra using the Origin 6.0 program, taking into account the relative contents of the species calculated from their stability constants. The ESR spectra of particular species were constructred by computer resolution of the experimental spectra using a specially developed program, taking into account the relative content of the species. This program is the modified version of program [24] based on Wilson–Kivelson's approach [25, 26] applied to several simultaneously present complexes with two magnetic isotopes. Using this program, we calculated the isotropic parameters of the spin Hamiltonian (g_0, A_0).

The rate constants of ligand exchange were determined from the pH dependences of the parameter $(c_M T_{2p})^{-1}$, taking into account the relative contents of complex species and equilibrium lihand concentrations (calculated by the CPESSP program) and using the Origin 6.0 program.

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