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Composition, Stability, and Structure of Cu(II), Ni(II), and Co(II) Complexes with Adipic Acid Dihydrazide in Aqueous and Aqueous–Ethanol Solutions

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Abstract — Solvation and complexation of Cu(II), Ni(II), and Co(II) with adipic acid dihydrazide (L) in aqueous and aqueous–ethanol solutions (ethanol mole fraction 0.07–0.68) were studied by spectrophotometry. The formation constants of the species $M(LH)^{3+}$, ML^{2+}, M_2L^{4+} (μ = Cu^{2+}, Ni^{2+}, Co^{2+}), and also $M_2L_2^{4+}$ and ML_2^{2+} (μ = Cu^{2+}, Ni^{2+}) were determined. With Cu(II), the complexes $Cu(LH)_2^{4+}$, $CuL(LH)^{3+}$, and $Cu_2L(LH)^{5+}$ were also detected and characterized. Evidence is given for the hydrazide coordination mode: tridentate in ML^{2+}, bidentate in $M(LH)^{3+}$ and ML_2^{2+}, and tetradentate in M_2L^{4+} and $M_2L_2^{4+}$. The ligand exchange reactions involving CuL^{2+}, $Cu(LH)^{3+}$, $Cu(LH)_2^{4+}$, $CuL(LH)^{3+}$, CuL_2^{2+}, and $Cu_2L(LH)^{5+}$ in aqueous solutions of Cu(II) were revealed and kinetically characterized by nuclear magnetic relaxation. The heretofore unknown rate constants of formation of these complexes were calculated from the thermodynamic and kinetic parameters. Factors controlling the rate constants of the complex formation and chemical exchange are discussed.
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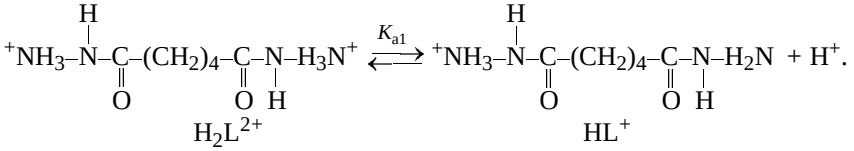
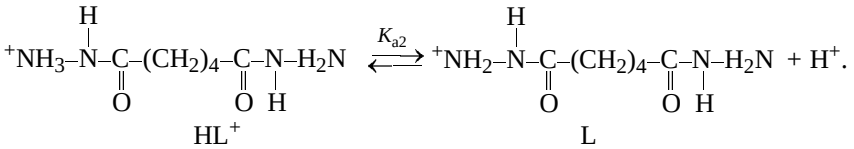
Complexation and acid dissociation processes in aqueous–organic solvents attract steady researchers' attention. These processes may occur with the direct participation of the organic component. As a continuation of studies concerning the effect of an organic solvent on the complexation of aromatic acid hydrazides [1–4], we examined in this study the acid–base and complexing properties of adipic acid dihydrazide (L) in aqueous and aqueous–ethanol solutions.

The main goals of this study were describing the complexation equilibria of Cu(II), Ni(II), and Co(II) with L and revealing the effects of the central metal ion, second hydrazide group in the ligand, and solvent composition on the composition and stability of the complexes. Also we intended to study the ligand exchange in the Cu(II) complexes by nuclear magnetic relaxation. It should be noted that, with adipic acid dihydrazide, it becomes principally possible to study the ligand exchange with the protonated ligand form, which is kinetically inactive in monohydrazides.

Protolytic equilibria. First we determined pH-metrically the acid dissociation constants of the protonated ligand species in aqueous–ethanol solutions under the preset experimental conditions. The dissociation of the protonated species of adipic acid dihydrazide can be described by Eqs. (1) and (2):



(1)



(2)

Table 1. Dissociation constants of protonated forms of adipic acid dihydrazide (L) in aqueous and aqueous–ethanol solutions (298 K)

Ethanol mole fraction	pK_{a1}	pK_{a2}	Ethanol mole fraction	pK_{a1}	pK_{a2}
0	2.93 ± 0.01	3.61 ± 0.03	0.30	1.90 ± 0.08	2.90 ± 0.02
0.07	2.22 ± 0.02	3.31 ± 0.01	0.39	2.15 ± 0.03	3.06 ± 0.01
0.11	1.74 ± 0.06	3.22 ± 0.01	0.50	2.22 ± 0.05	3.06 ± 0.03
0.16	1.86 ± 0.03	3.18 ± 0.01	0.68	2.39 ± 0.02	3.19 ± 0.01
0.22	1.83 ± 0.03	3.09 ± 0.01			

The acid dissociation constants that we determined for HL^+ and H_2L^{2+} are listed in Table 1. It is seen that both deprotonation constants as functions of the ethanol mole fraction pass through a maximum. Similar trends were observed previously for the double-charged cationic form of isonicotinic acid hydrazide [5]. These facts are attributable to the increased donor power (basicity) of aqueous ethanol at an ethanol volume fraction of 30–40 vol % corresponding to maximal stabilization of the solvent structure.

The dissociation constants of the protonated species of the dihydrazide were further used for calculating the stability constants of the complexes.

Complexation equilibria. For all the systems we recorded the absorption spectra of solutions in which the concentrations of metal ions and L were fixed and the pH and ethanol mole fraction were varied. The ethanol mole fraction was 0, 0.07, 0.11, 0.16, 0.22, 0.30, 0.39, and 0.50.

Figure 1 shows as example the absorption spectra

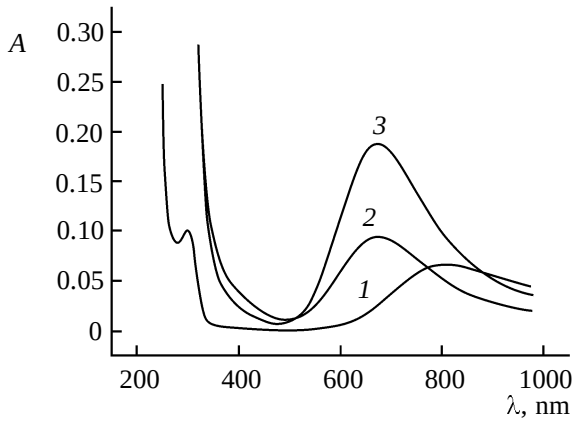


Fig. 1. Absorption spectra of aqueous solutions containing Cu(II) ions and adipic acid dihydrazide L: (*1*) $c_{Cu(II)}$ 4.47×10^{-3} M; (*2*) c_L 5×10^{-3}, $c_{Cu(II)}$ 2.2×10^{-3} M; and (*3*) c_L 5×10^{-3}, $c_{Cu(II)}$ 4.47×10^{-3} M. (*A*) Optical density.

of aqueous solutions of Cu(II) containing adipic acid dihydrazide. Addition of L to solutions of all the three metals increases the optical density and shifts the absorption maximum toward shorter wavelengths, which is indicative of the formation of complexes. Similar changes were observed in the spectra of the aqueous–ethanol solutions.

The following concentration ratios of M and L in each aqueous–organic solvent were set: 1 : 1, 1 : 2, and 2 : 1 for Cu(II) and Ni(II), and 1 : 1 and 1 : 2 for Co(II).

The following analytical wavelengths λ (nm) were chosen: 700 for Cu(II) at all M : L ratios; 610, 600, and 630 for Ni(II) at M : L 1 : 1, 1 : 2, and 2 : 1, respectively; and 500 for Co(II) at M : L 1 : 1 and 1 : 2. At these wavelengths, we measured the optical densities of the solutions at different pH in aqueous–organic solvents of various compositions. Figure 2 shows as example the pH dependences of the extinction coefficients of Ni(II) solutions in the presence of L. From these dependences, taking into account the dissociation constants of the protonated dihydrazide species and using the CPESSP program [6], we calculated the compositions and formation constants of the complexes.

In aqueous solution at M : L 1 : 1, 1 : 2, and 2 : 1, five complexes are formed: $M(LH)^{3+}$, ML^{2+}, M_2L^{4+}, $M_2L_2^{4+}$, and ML_2^{2+}; however, with Co(II) the latter two species are minor, and their formation constants β cannot be determined with reasonable accuracy. Also, in aqueous solutions of Cu(II) at M : L 2 : 1 we detected the binuclear complex $Cu_2L(LH)^{5+}$ ($\log\beta$ 10.47 ± 0.15), but it did not accumulate in appreciable amounts under other conditions. Finally, in Cu(II) solutions at M : L 1 : 4 we detected and characterized the complexes $Cu(LH)_2^{4+}$ ($\log\beta$ 6.60 ± 0.08) and $CuL(LH)^{3+}$ ($\log\beta$ 7.78 ± 0.10). The speciation diagram for Cu(II) is shown as example in Fig. 3.

The calculated formation constants of the complexes of all the three metals in aqueous solution are

Table 2. Formation constants ($\log\beta$) of Cu(II), Ni(II), and Co(II) complexes with adipic acid dihydrazide (L) in aqueous solution (298 K)

Equilibrium	Cu(II)	Ni(II)	Ci(II)
$M^{2+} + LH^2 \rightleftarrows M(LH)^{3+}$	3.63 ± 0.06	3.13 ± 0.03	2.63 ± 0.10
$M^{2+} + L \rightleftarrows ML^{2+}$	4.74 ± 0.04	4.00 ± 0.03	2.79 ± 0.06
$2M^{2+} + L \rightleftarrows M_2L^{4+}$	7.67 ± 0.04	6.34 ± 0.02	4.73 ± 0.14
$2M^{2+} + 2L \rightleftarrows M_2L_2^{4+}$	12.08 ± 0.02	10.22 ± 0.08	–
$M^{2+} + 2L \rightleftarrows ML_2^{2+}$	8.08 ± 0.21	7.08 ± 0.07	–

compared in Table 2. It is seen that the $\log\beta$ values for the complexes of similar composition decrease in the order Cu > Ni > Co, corresponding to the Irving–Williams series.

The constants of the complexation equilibria in solutions of Ni(II) with adipic acid hydrazide, benzhydrazide [4], and *p*-methoxybenzhydrazide [4] are compared in Table 3. It is seen that the set of complex species in the solution containing L differs from that observed with L' and L". L' and L" form 1 : 1 and 1 : 2 complexes only in the molecular form, whereas in solutions containing L, owing to the bifunctional structure of adipic acid dihydrazide, binuclear (M_2L^{4+}, $M_2L_2^{4+}$) and protonated [$M(LH)^{3+}$; with Cu, also $\mu(LH)_2^{4+}$ and $ML(LH)^{3+}$] complex species are additionally formed. The assumed (in a rough approximation) structures of the main complex species with L, optimized by the method of molecular mechanics (MM+ program), are shown in Fig. 4.

Table 3 shows that the complex with the monoprotonated form of adipic acid dihydrazide, $Ni(LH)^{3+}$, is appreciably less stable than that with the deprotonated species, NiL^{2+}. This may be due not only to the lower basicity of the first hydrazide fragment, but also to possible coordination of the N^2 atom of the second hydrazide fragment to the metal [Fig. 4, structure

Table 3. Formation constants ($\log\beta$) and ratio of the equilibrium constants of the first and second complexation steps [$\log(K_1/K_2)$] for Ni(II) complexes with adipic acid dihydrazide L, benzhydrazide L' [4], and *p*-methoxybenzhydrazide L'' [4] in aqueous solution (298 K)

Equilibrium	$\log\beta$	$\log(k_1/K_2)$
$Ni^{2+} + LH^+ \rightleftarrows Ni(LH)^{3+}$	3.13	–
$Ni^{2+} + L \rightleftarrows NiL^{2+}$	4.00	–
$2Ni^{2+} + L \rightleftarrows Ni_2L^{4+}$	6.34	–
$Ni^{2+} + 2L \rightleftarrows NiL_2^{2+}$	7.08	0.92
$Ni^{2+} + L' \rightleftarrows Ni(L')^{2+}$	3.00	–
$Ni^{2+} + 2L' \rightleftarrows Ni(L')_2^{2+}$	5.23	0.77
$Ni^{2+} + L'' \rightleftarrows Ni(L'')^{2+}$	3.09	–
$Ni^{2+} + 2L'' \rightleftarrows Ni(L'')_2^{2+}$	5.40	0.78

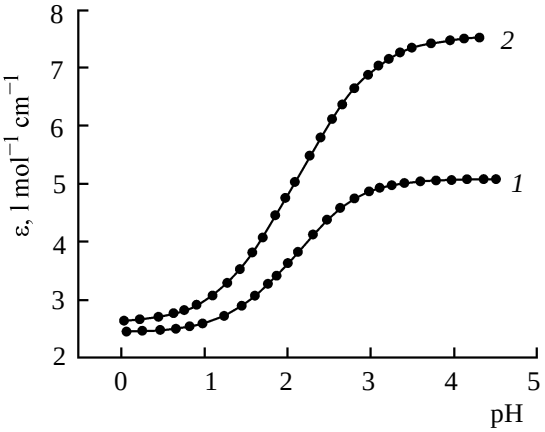


Fig. 2. pH dependence of the extinction coefficient ε of aqueous Ni(II) solutions containing adipic acid dihydrazide (L) at 298 K: (*1*) c_{Ni} 5.42×10^{-3}, c_L 6.00×10^{-3} M; (*2*) c_{Ni} 2.7×10^{-3}, c_L 6.00×10^{-3} M.

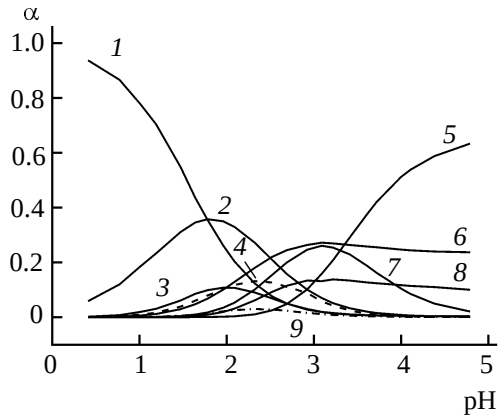
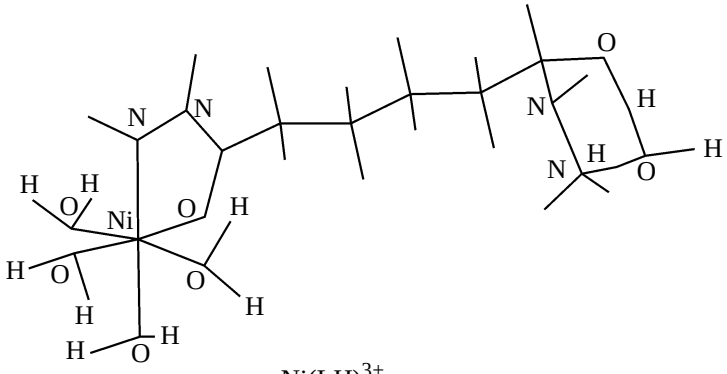
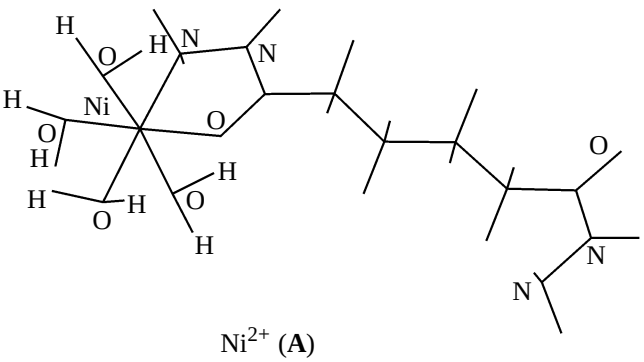


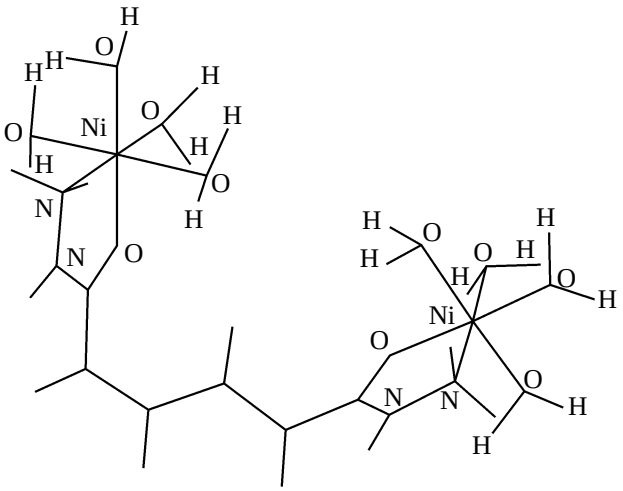
Fig. 3. Distribution of Cu(II) complex species in aqueous solution at c_{Cu} 2.40×10^{-3}, c_L 5.24×10^{-3} M, *T* 298 K: (*1*) Cu^{2+}, (*2*) $Cu(LH)^{3+}$, (*3*) Cu_2L^{4+}, (*4*) $Cu(LH)_2^{4+}$, (*5*) CuL_2^{2+}, (*6*) CuL^{2+}, (*7*) $CuL(LH)^{3+}$, (*8*) $Cu_2L_2^{4+}$, and (*9*) $Cu_2L(LH)^{5+}$.



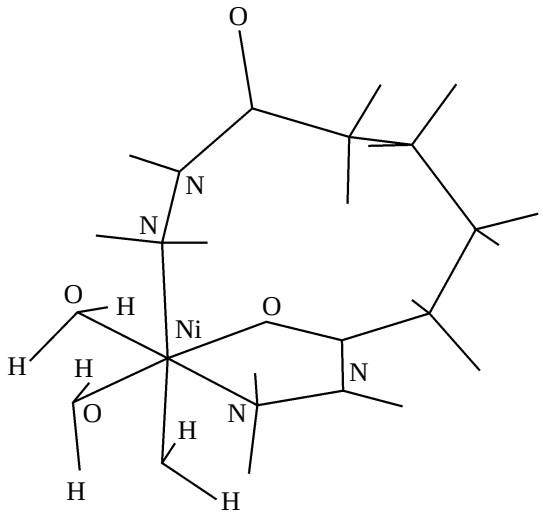
$Ni(LH)^{3+}$



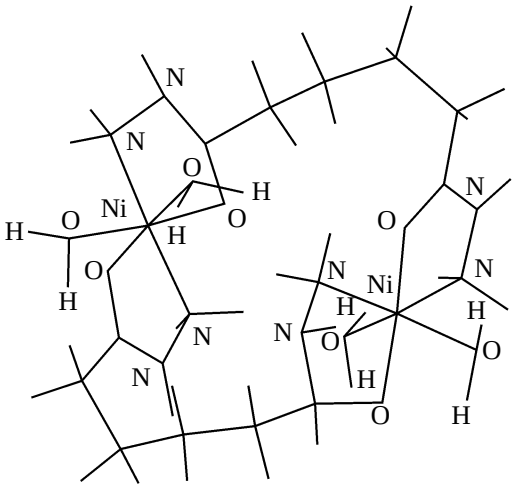
Ni^{2+} (**A**)



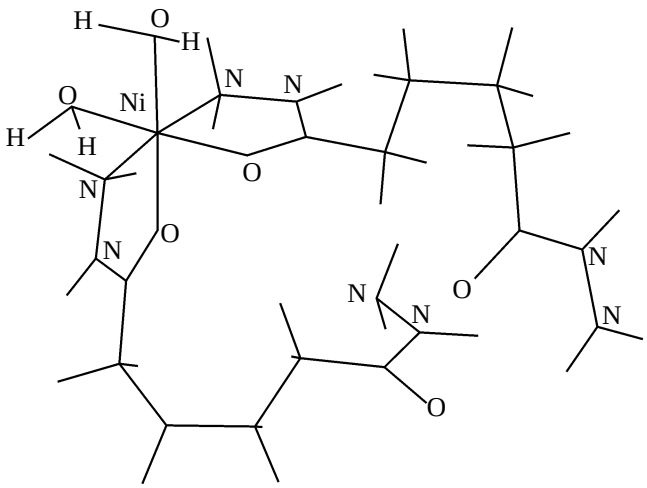
Ni_2L^{4+}



NiL^{2+} (**C**)



$Ni_2L_2^{4+}$



NiL_2^{2+}

Fig. 4. Assumed structures of Ni(II) complexes with adipic acid dihydrazide (L), optimized by the MM+ method. The carbon atoms are not denoted; only the H atoms of water molecules are denoted.

Table 4. Formation constants ($\log\beta$)[a] of Cu(II), Ni(II), and Co(II) complexes with adipic acid dihydrazide (L) 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
$Cu^{2+} + LH+ \rightleftarrows Cu(LH)^{3+}$	3.63	3.56	3.96	4.01	4.04	4.25	4.65	4.79
$Cu^{2+} + L \rightleftarrows CuL^{2+}$	4.74	5.08	5.21	5.45	5.55	6.08	6.31	6.88
$2Cu^{2+} + L \rightleftarrows Cu_2L^{4+}$	7.67	8.07	8.07	8.25	8.52	8.53 ± 0.26	9.34	9.77
$2Cu^{2+} + 2L \rightleftarrows Cu_2L_2^{4+}$	12.08	–	–	–	–	–	–	–
$Cu^{2+} + 2L \rightleftarrows CuL_2^{2+}$	8.08 ± 0.21	–	–	–	–	–	–	10.82 ± 0.17
$Ni^{2+} + LH+ \rightleftarrows Ni(LH)^{3+}$	3.13	3.00	3.24	3.30	3.37	3.50	3.78	4.05
$Ni^{2+} + L \rightleftarrows NiL^{2+}$	4.00	4.01	4.16	4.24	4.42	4.80	5.11	5.60
$2Ni^{2+} + L \rightleftarrows Ni_2L^{4+}$	6.34	6.73	6.81	6.94	7.12	7.40	7.81	8.28
$2Ni^{2+} + 2L \rightleftarrows Ni_2L_2^{4+}$	10.22	10.56	10.68	10.88	–	–	–	–
$Ni^{2+} + 2L \rightleftarrows NiL_2^{2+}$	7.08	–	7.82	–	8.00	–	–	–
$Co^{2+} + LH+ \rightleftarrows Co(LH)^{3+}$	2.63	2.87	3.18	3.25	3.33	3.42	3.55	3.62
$Co^{2+} + L \rightleftarrows CoL^{2+}$	2.79	3.45	3.56	3.84	3.98	4.11	4.21	4.66
$2Co^{2+} + L \rightleftarrows Co_2L^{4+}$	4.73	–	–	–	–	–	–	7.04 ± 0.22

[a] Error ±0.10, unless otherwise indicated.

NiL^{2+} (B)]. The latter assumption is supported by the higher stability constant of the complex NiL^{2+} ($\log\beta$ 4.00) compared to $Ni(L')^{2+}$ ($\log\beta$ 3.00) and $Ni(L'')^{2+}$ ($\log\beta$ 3.09). Similar relationships between the constants are also observed for the complexes of Cu(II) with the same ligands. The coordination of the second hydrazide N atom of L in ML^{2+} is also suggested by the considerably higher extinction coefficient of ML^{2+} compared to $M(LH)^{2+}$.

However, the bischelate (tetradentate) coordination of L is sterically impossible; therefore, $\log\beta$ of NiL^{2+} is appreciably lower than $\log\beta$ for the bis-complexes with benzhydrazide and p-methoxybenzhydrazide, $Ni(L')_2^{2+}$ and $Ni(L'')_2^{2+}$ (Table 3). On the other hand, addition of M^{2+} to ML^{2+} with the formation of the binuclear complexes M_2L^{4+}, in which the dihydrazide is coordinated in the tetradentate fashion (Fig. 4), is very favorable ($\log K$ 2–3, Table 2).

Let us consider the equilibrium constants of particular steps of Ni(II) complexation with acid hydrazides. Table 3 shows that the ratio of the equilibrium constants of the first and second steps of Ni(II) complexation with L' and L'' is close to the statistical value for bidentate coordination of the ligands: $\log(K_1/K_2)$ 0.70 [7]. With adipic acid dihydrazide, $\log(K_1/K_2)$ is somewhat larger (0.92), which is consistent with the assumption that the first ligand is coordinated in the tridentate fashion and one of the N atoms should be displaced upon addition of the second ligand to NiL^{2+}; in NiL_2^{2+}, both ligands are apparently bidentate (Fig. 4). The tridentate coordination of both ligands in NiL_2^{2+} is sterically impossible. The same reasoning is valid for Cu(II) dihydrazide complexes, for which the relationships between the equilibrium constants of the complexation steps are similar.

Let us analyze how the stability constants of the Cu(II), Ni(II), and Co(II) complexes depend on the solvent composition (Table 4). The stability constants of the complexes $M(LH)^{3+}$ of all the three metals with the protonated ligand species as functions of the ethanol mole fraction show an inflection and correlate with pK_{a1} (Table 1), reflecting changes in the basicity of the medium. The stability constants of the complexes with the neutral form of the ligand increase more monotonically with an increase in the ethanol mole fraction from 0.11 to 0.50. This trend is attributable to the dehydration of the metal aqua ions:

$$m[M(H_2O)_6]^{2+}_{sol} + nL_{sol} \overset{\beta'}{\longleftrightarrow} [M_m(H_2O)_k(L)_n]^{2+}_{sol} + hH_2O, \quad (3)$$

$$\log\beta'(M_nL_n^{2+}) - \log\beta(M_nL_n^{2+}) + h\log[H_2O]. \quad (4)$$

Indeed, the constants $\log\beta'$ calculated by Eq. (4) vary insignificantly with an increase in the ethanol mole fraction up to 0.50 [h 2 for $M(LH)^{3+}$, 3 for ML^{2+}, and 4 for M_2L^{4+} and ML_2^{2+}, Table 5]. This fact is a strong argument in favor of the tridentate coordination of L in ML^{2+}, bidentate coordination in $M(LH)^{3+}$ and $ML2^{2+}$, and tetradentate coordination in M_2L^{4+}, supporting the above assumptions.

Table 5. Calculated values of $\log\beta'$ for Cu(II), Ni(II), and Co(II) complexes with adipic acid dihydrazide L in aqueous and aqueous–ethanol solutions

Parameter	Ethanol mole fraction							
	0	0.07	0.11	0.16	0.22	0.30	0.39	0.50
$\log\beta'_{Cu(LH)}$ (h 2)	7.12	6.87	7.17	7.10	6.99	7.02	7.20	7.04
$\log\beta'_{CuL}$ (h 3)	9.97	10.05	10.03	10.08	9.97	10.23	10.14	10.26
$\log\beta'_{Cu_2L}$ (h 4)	14.65	14.69	14.49	14.43	14.41	14.06	14.44	14.27
$\log\beta'_{CuL_2}$ (h 4)	15.06	–	–	–	–	–	–	15.32
$\log\beta'_{Ni(LH)}$ (h 2)	6.62	6.31	6.45	6.39	6.32	6.27	6.33	6.30
$\log\beta'_{NiL}$ (h 3)	9.23	8.98	8.98	8.87	8.83	8.95	8.94	8.98
$\log\beta'_{Ni_2L}$ (h 4)	13.32	13.35	13.23	13.12	13.01	12.93	12.91	12.78
$\log\beta'_{NiL_2}$ (h 4)	14.06	–	–	–	–	–	–	14.62
$\log\beta'_{Co(LH)}$ (h 2)	6.11	6.18	6.39	6.34	6.28	6.19	6.10	5.87
$\log\beta'_{CoL}$ (h 3)	8.02	8.42	8.38	8.47	8.40	8.26	8.04	8.04
$\log\beta'_{Co_2L}$ (h 4)	11.71	–	–	–	–	–	–	11.54

The constancy of $\log\beta'$ is consistent with the assumption that the free energies of transfer of LH^+ and L from water to aqueous ethanol only weakly depend on the solvent composition up to the ethanol mole fraction of 0.50, as it was shown previously for benzoic, *p*-methoxybenzoic, and isonicotinic acid hydrazides [4].

Note that certain deviations from the general trend toward an increase in the formation constants of the complexes at small ethanol additions (ethanol mole fraction 0.07) are attributable to a decrease in pK_{a2} in this range (see above) and hence to an increase in the basicity of the medium. On the other hand, the calculated values of $\log\beta'$ for the complexes Ni_2L^{4+} at the ethanol mole fraction of 0.50 are somewhat lower than the values estimated assuming only the occurrence of dehydration (3). This may be due to the resolvation, i.e., to possible coordination of not only water but also ethanol to the metal.

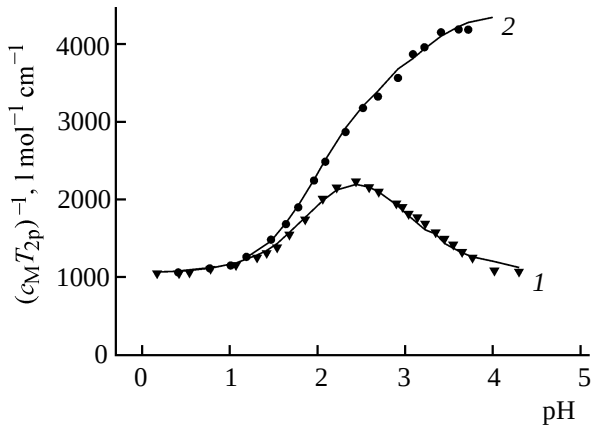


Fig. 5. pH dependence of $(c_MT_{2p})^{-1}$ in the system Cu(II)–adipic acid dihydrazide (L)–H_2O (c_L 5.24 × 10^{-3} M, ™ 298 K). $c_{Cu(II)}$, M: (*1*) 4.82 × 10^{-3} and (*2*) 2.40 × 10^{-3}. Points are experimental, and lines are calculated.

Chemical exchange. Let us consider the information on the chemical exchange in the Cu(II)–adipic acid dihydrazide system, furnished by nuclear magnetic relaxation measurements. The pH dependence of the spin–spin relaxation coefficient of water protons $(c_MT_{2p})^{-1}$ at M : L 1 : 1 passes through a maximum, and its values for M : L 1 : 2 are higher than those for the 1 : 1 ratio in the entire pH range. According to the previous data for the Cu(II)–isonicotinic acid hydrazide system [8], this fact suggests the occurrence of chemical exchange with LH^+ or L as a second-order reaction, since the calculated equilibrium concentrations of these species are higher at an excess of the ligand.

Taking into account the calculated relative contents α of all the species present in the system, including the aqua ion (α_0), and the equilibrium concentrations of the ligand species [LH^+] and [L], using the Origin program, we calculated from the pH dependences of $(c_MT_{2p})^{-1}$ (Fig. 5) the rate constants of chemical exchange reactions by Eq. (5) [8–10]:

$$(c_MT_{2p})^{-1} = \alpha_0K_0 + \Sigma\alpha_i\{K_{A(i)} + P'_i(k_{L(i)} + k_{LH(i)}[LH^+] + k_{L(i)}[L]\}. \quad (5)$$

Equation (5) is valid for the case of "slow exchange" [9–11] when $\tau_M >> T_{2M}$ (τ_M is the lifetime and T_{2M}, relaxation time of ligand protons in the first coordination sphere of the metal). Here K_0 is the

Table 6. Rate constants of ligand exchange (k_1, k_{LH}, k_L) and of complex formation (k_f) and equilibrium constants of complexation steps ($\log K$) for Cu(II) complexes with adipic acid dihydrazide, benzhydrazide (L') [13], and *p*-methoxybenzhydrazide (L'') [13] at 298 K [$\log K$ for $Cu_2L(LH)^{5+}$ corresponds to the addition of LH^+ to Cu_2L^{4+}]

Complex	$\log K$	k_1, s^{-1}	k_{LH}, $l\,mol^{-1}\,s^{-1}$	k_L, $l\,mol^{-1}\,s^{-1}$	k_f, $l\,mol^{-1}\,s^{-1}$
$Cu_2L(LH)^{5+}$	2.80	7.3×10^5	8.5×10^7	1.7×10^8	4.6×10^8
$Cu(LH)^{3+}$	3.63	6.1×10^4	1.1×10^8	2.2×10^8	2.6×10^8
$Cu(LH)_2^{4+}$	2.97	1.1×10^5	4.1×10^7	7.5×10^7	1.0×10^8
$CuL(LH)^{3+}$	3.04	7.8×10^4	3.6×10^7	7.5×10^7	8.6×10^7
CuL^{2+}	4.74	1.1×10^4	8.9×10^7	1.6×10^8	6.0×10^8
CuL_2^{2+}	3.34	7.1×10^4	3.3×10^7	4.4×10^7	1.6×10^8
$Cu(L')^{2+}$	3.67	5.0×10^4	–	6.7×10^7	2.3×10^8
$Cu(L')_2^{2+}$	2.43	2.5×10^5	–	2.1×10^7	6.7×10^7
$Cu(L'')^{2+}$	3.95	4.5×10^4	–	1.3×10^8	5.0×10^8
$Cu(L'')_2^{2+}$	2.61	3.6×10^5	–	4.6×10^7	1.5×10^8

molar spin–spin relaxation coefficient of Cu^{2+} aqua ion; K_A, contribution to the relaxation from the coordinated water molecules; k_1, rate constant of spontaneous dissociation of the ligand (first-order reaction); k_{LH} and k_L, rate constants of ligand exchange with activation by LH^+ and L, respectively (second-order reaction); $P' = P_M/c_M$, where P_M is the mole fraction of equatorially coordinated NH_2 protons of the hydrazide. For all the complexes, according to [12], K_A was taken equal to 400 $l\,mol^{-1}\,s^{-1}$, and its variations within ±30% had virtually no effect on the estimated kinetic constants.

The results of calculating the kinetic parameters are given in Table 6. With $Cu(LH)^{3+}$ as example, let us write the reactions to which the above-mentioned rate constants correspond:

$$Cu(LH)^{3+} \underset{k_f}{\overset{k_1}{\rightleftarrows}} Cu^{2+} + H^+, \quad (6)$$

$$Cu(LH)^{3+} + {}^{\cdot}LH^+ \overset{k_{LH}}{\rightleftarrows} Cu(^*LH)^{3+} + LH^+, \quad (7)$$

$$Cu(LH)^{3+} + {}^*L \overset{k_L}{\rightleftarrows} Cu(^*LH)^{3+} + L. \quad (8)$$

It should be emphasized that the first-order rate constant k_1 corresponds to the dissociation of the complex $Cu(LH)^{3+}$ and is related to the rate constant of its formation k_f by

$$k_f = k_1 K, \quad (9)$$

where K is the equilibrium constant of the step of $Cu(LH)^{3+}$ formation (Tables 2, 4). The relationships similar to (9) are also valid for the other Cu(II) complexes. The k_f values found from them are also given in Table 6, together with the previously obtained data [13] for the complexes with benzhydrazide (L') and *p*-methoxybenzhydrazide (L'').

Note that, for the binuclear complexes Cu_2L^{4+} and $Cu_2L_2^{4+}$, the constants k_1, k_{LH}, and k_L are too small to be determined reliably, which reflects the low lability of the bridging bischelate ligands L (Fig. 4). On the other hand, in the complex $Cu_2L(LH)^{5+}$ one of the ligands (LH^+) is not bridging and is therefore highly labile (Table 6). Apparently, high extent of mutual correlation of the optimization parameters allows only rough estimation of the errors of their calculation (10–30%). However, the reliability of the calculated rate constants is confirmed by certain quantitative relationships between them. In particular, k_L for CuL^{2+} (1.6×10^8 $l\,mol^{-1}\,s^{-1}$) coincides with k_f of CuL_2^{2+} (1.6×10^8 $l\,mol^{-1}\,s^{-1}$). This fact confirms that the biscomplex CuL_2^{2+} is an intermediate in the exchange between CuL^{2+} and L (cf. [8, 13]). Similarly, coincidence between k_{LH} for CuL^{2+} (8.9×10^7 $l\,mol^{-1}\,s^{-1}$) and k_f of $CuL(LH)^{3+}$ (8.6×10^7 $l\,mol^{-1}\,s^{-1}$) indicates that the second complex is an intermediate in the exchange of CuL^{2+} with LH^+; likewise, in the exchange of $Cu(LH)^{3+}$ with LH^+ (k_{LH} 1.1×10^8 $l\,mol^{-1}\,s^{-1}$), $Cu(LH)_2^{4+}$ (k_f 1.0×10^8 $l\,mol^{-1}\,s^{-1}$) is an intermediate.

Table 6 shows that, in contrast to monohydrazides, not only the deprotonated ligand form (L) but also the monoprotonated species of adipic acid dihydrazide (LH^+) is active in the ligand exchange, because the second nucleophilic center in LH^+ remains available. The kinetic activity of species L containing two nucleophilic centers is higher than that of LH^+ ($k_L \approx 2k_{LH}$), and the proton transfer from the incoming to leaving ligand and vice versa is not, apparently, the limiting step of exchange of the nonequivalent ligand

species [e.g., reaction (8)]. Note that the rate constants k_{LH} and k_L of ligand substitution in the protonated complexes $Cu(LH)^{3+}$ and $Cu(LH)_2^{4+}$ or $CuL(LH)^{3+}$ are somewhat higher than in the related deprotonated species CuL^{2+} and CuL_2^{2+}. This fact is consistent with the lower strength of binding of the leaving protonated ligand LH^+ relative to L, irrespective of the substitution mechanism. The rate constants k_{LH}, k_L, and k_f for the bis-complexes $Cu(LH)_2^{4+}$ and CuL_2^{2+} are approximately three times higher than for the corresponding monoligand species $Cu(LH)^{3+}$ or CuL^{2+}. Similar ratios are observed with benzhydrazide and p-methoxybenzhydrazide (Table 6); they can be accounted for, in terms of the associative substitution mechanism, by blocking of the coordination sites as sites of attack by the incoming ligand [13–15]. For Cu(II), the ratio of k_f of the bis- and monochelate complexes is close to the statistical factor of 5/12 [13].

As seen from Table 6, in the series L'–L"–L the calculated rate constants of formation (k_f) of the mono- and bis-complexes (CuL^{2+}, CuL_2^{2+}) increase, which corresponds to an increase in the nucleophilicity of the ligands (pK_a): L' (3.27)–L" (3.37)–L (3.61). This fact confirms the associative mechanism of the ligand substitution in the Cu(II) complexes [14, 15].

Thus, the kinetic data obtained are well consistent with the thermodynamic data concerning the influence of the structure of the dihydrazide ligand on the composition, stability, and structure of the complexes.

EXPERIMENTAL

The complexation of Co(II), Cu(II), and Ni(II) with adipic acid dihydrazide in aqueous and aqueous–ethanol solutions was studied by pH-metry, spectrophotometry, and nuclear magnetic relaxation. The absorption spectra were recorded on an SF-46 spectrophotometer in 2-, 3-, and 5-cm cells. The optical density of the solutions was measured relative to reference solutions containing the same components as the test solution except the metal ion. All the measurements were performed at 25°C using a thermostat. For each solution, no less than two replicate measurements of the optical density and pH were made, and the averaged results are given in the paper. The optical density of solutions was measured with an accuracy of 0.005 unit.

The pH values of solutions containng ethanol were measured with a pH-673 pH-meter. An ESL-43-07-type glass electrode was calibrated using HCl solutions of known concentration [16]. Reproducible potentials of the glass electrode in aqueous–ethanol solvents were attained within 5–10 min. The spin–spin relaxation time of water protons (T_2) was measured on a pulse coherent NMR spectrometer (15 MHz) with an accuracy of ±2%.

Copper(II), nickel(II), and cobalt(II) nitrates were of chemically pure grade; adipic acid dihydrazide (analytically pure grade) was recrystallized from aqueous alcohol. The pH was adjusted with titrated nitric acid solutions. Solutions of the dihydrazide were prepared gravimetrically. The concentrations of the initial solutions of salts and acids were determined by volumetric titration.

Addition of a supporting electrolyte to aqueous–ethanol solutions of complexes of metal ions with the dihydrazide resulted in salting-out of the ligand. Therefore, in all the systems the ionic strength was created by the system components and varied within 0.02–0.6.

To determine pH-metrically the dissociation constants of the protonated ligand species, solutions of the dihydrazide of a definite concentration (0.006 M, 25 ml) were titrated with aqueous and aqueous–ethanol solutions of HCl (0.03 M). No less than two replicate runs were performed for each test solution. The constant ionic strength (I 0.01) was supported by $NaNO_3$. The dissociation constants of the dihydrazide and stability constants of the complexes were calculated by the CPESSP program [6].

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