Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 926–920. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 986–990.
Original Russian Text Copyright © 2001 by Bychkova, Shtyrlin, Sadykova, Zakharov, Popova.

Solvation and Complex Formation of Nickel(II) with Benzoic, *p*-Chlorobenzoic, and *p*-Methoxybenzoic Hydrazides in Aqueous-Dioxane Media

T. I. Bychkova, V. G. Shtyrlin, E. R. Sadykova, A. V. Zakharov, and Yu. I. Popova

Kazan State University, Kazan, Tatarstan, Russia

Received December 14, 1999

Abstract—Solvation and complex formation of nickel(II) with benzoic, *p*-chlorobenzoic, and *p*-methoxybenzoic hydrazides in aqueous-dioxane media were studied. The mean coordination numbers of water and 1,4-dioxane in Ni(II) solvation complexes, the formation constants of mono- and biscomplexes of nickel(II) of the listed hydrazides at dioxane contents of 0–0.65 mole fraction, as well as the free energies of transfer of the ligands from water to aqueous-dioxane solvents were determined. An important role the basicity and solvation of the ligands play in te stability of Ni(II) complexes with benzoic hydrazides was demonstrated.

Proceeding with our studies on complex formation of nickel(II) with *p*-chlorobenzoic and isonicotinic hydrazides in aqueous-DMSO media [1], in the present work we turned to solvation and complex formation of nickel(II) with benzoic (L^1), *p*-chlorobenzoic (L^2), and *p*-methoxybenzoic (L^3) hydrazides in water–1,4-dioxane medium. The comparative study of hydrazides L^1–L^3 was undertaken for assessment of the role of electronic factors in the stability of the resulting complexes, since ligand L^2 has in the *para* position the electron-acceptor chlorine substituent, while ligand L^3, the electron-donor methoxy group. To assess the effect of ligand solvation in the complex formation, by the solubility method we determined the free energies of transfer of ligands L^1 and L^3 from water to aqueous-dioxane solvents.

Resolvation processes. The method for determination of mean coordination numbers in nickel(II) solvation complexes, proposed in [1], is also valid for dioxane media. Actually, the symmetry of the coordination polyhedron NiO_6 in all the complexes remains unchanged and, consequently, the proton spin–spin relaxation time for each solvent (S) in the inner coordination sphere of any solvation complex (T_{2M}^{S}) can be taken constant. Figure 1 shows the dependences of the parameters $(1/c_M T_{2p}^{S})(c_S/c_S^0)$ on the composition of the solvent in the system Ni(II)–H_2O–dioxane (do). From these dependences by the procedure in [1] we estimated by Eq. (1) mean coordination numbers for both components of the solvent ($\bar{n}_S$).

$$\frac{1}{c_M T_{2p}^{S}} = K_0^S + \frac{\bar{n}_S}{c_S}\frac{1}{T_{2M}^{S}} = K_0^S + \frac{\bar{n}_S}{c_S}\,\text{const.} \qquad (1)$$

Here K_0^S is the outer-sphere contribution into the spin-spin relaxation factor and c_S is the concentration of solvent S. Therewith, the contribution $K_0^{do}(c_{do}/c_{do}^0)$ into the factor $(c_M T_{2p}^{do})(c_{do}/c_{do}^0)$ form outer-sphere dioxane molecules for the aqua anion $Ni(H_2O)_6^{2+}$ was set equal to 207 mol^{-1} l s^{-1} ($\bar{n}_{do}$ 0), the factor $(1/c_M T_{2p}^{do})(c_{do}/c_{do}^0)$ for $Ni(do)_6^{2+}$ (in pure dioxane), to 750 mol^{-1} s^{-1} ($\bar{n}_{do}$ 6), and the factors $(1/c_M T_{2p}^{H_2O})\cdot(c_{H_2O}/c_{H_2O}^0)$ for $Ni(H_2O)_6^{2+}$ and $Ni(do)_6^{2+}$ were estimated at 1844 and 0 mol^{-1} l s^{-1}, respectively. The resulting data are listed in Table 1.

Note that throughout the entire range of composition of the binary solvent the sum of the mean coordination numbers of water and dioxane ($\bar{n}_{H_2O} + \bar{n}_{do}$)

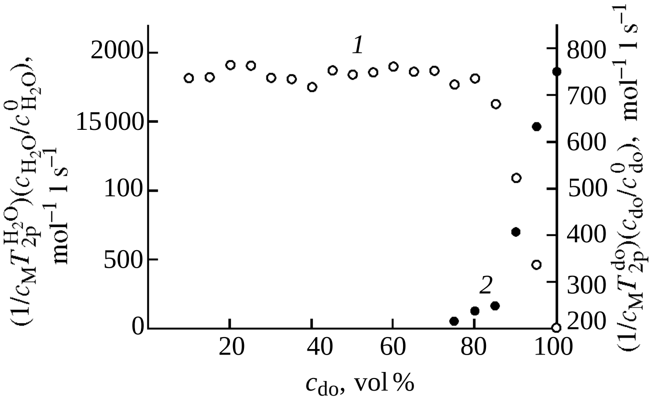

Fig. 1. Dependences of reduced spin-spin relaxation factors (*1*) $(1/c_M T_{2p}^{H_2O})(c_{H_2O}/c_{H_2O}^0)$ and (*2*) $(1/c_M T_{2p}^{do})\cdot(c_{do}/c_{do}^0)$ on the composition of the solvent in the system Ni(II)–H_2O–dioxane. $c_{Ni^{2+}}$ 2×10^{-2} M, 298 K (300 MHz).

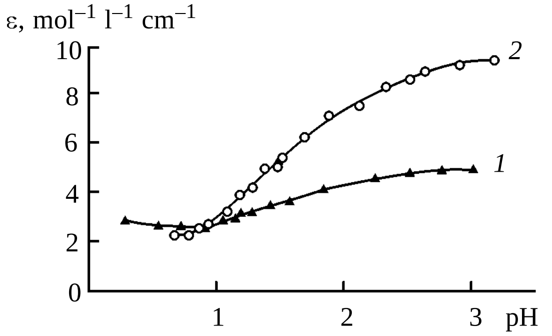

Fig. 2. Dependences of the extinction factors of solutions (ε) on pH in the system Ni(II)–*p*-methoxybenzoic hydrazide (L^3)–H_2O–dioxane (80 vol%, 0.45 mole fraction). $c_{Ni^{2+}}$ 5.00×10^{-2} M; c_{L^3}, M: (*1*) 5.50×10^{-2} and (*2*) 0.120; λ, nm: (*1*) 640 and (*2*) 600; 298 K.

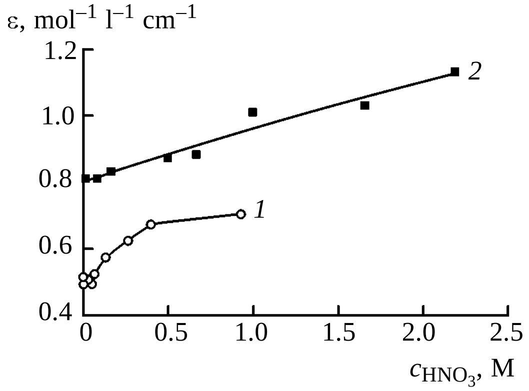

Fig. 3. Dependences of the extinction factors of solutions (ε) on pH in the systems Ni(II)–HNO_3–H_2O–dioxane [(*1*) 80 and (*2*) 90 vol%]. $c_{Ni^{2+}}$ 5.03×10^{-2} M, λ 600 nm, 298 K.

remains invariable within 6.00±0.24. As judjed from the inconsiderable varuation in the relation factors for water protons at the dioxane fractions $c_{do} \le 80$ vol% (Fig. 1), the coordination sphere of the metal ion does not contain dioxane molecules. These results are not consistent with data in [2, 3]. Note that the fraction of coordinated dioxane molecules $Y_{do} = \bar{n}_{do}/(\bar{n}_{H_2O} + \bar{n}_{do})$ is much lower than the dioxane content of the solution, expressed in mole fractions (X_{do}) (Table 1). This finding can be explained by the lower donor number of dioxane (14.8) compared with the "bulk donocity" of pure water (33) [4–6]. However, when the content of the organic component attains 95 vol%, the Y_{do} and X_{do} values come closer together. As with aqueous-DMSO solutions [1], as the concentration of dioxane is increased above 0.65 mole fraction, progressive cleavage of hydrogen bonds between H_2O molecules takes place, and the "bulk donocity" of water decreases, approaching, finally, the donor number of molecular water (18.0). As a result, in coordinative ability dioxane comes closer to water, and Y_{do} comes closer to X_{do}.

Complex-formation equilibria. The dependences of the extinction factors (ε) on pH for the systems nickel(II)–hydrazide (L^1–L^3)–water–1,4-dioxane at high dioxane contents (80 or 90 vol%) are curves with a minimum (Fig. 2). The increase in ε with increasing acidity of the medium to pH < 1 may imply formation of nickel(II) complexes with nitrate ion. To check this assumption, we obtained dependences of ε on the concentration of nitric acid in the aquoeus-dioxane solutions of nickel(II) with dioxane contents of 80 and 90 vol% (Fig. 3). Both dependences are fairly modeled by a single equilibrium of formation of the complex $Ni(NO_3)^+$ with the stability constants log β −0.19±0.12 and log β 0.57±0.07 for dioxane contents of 80 and 90 vol%, respectively. The fact that log β much increases when the concentration of 1,4-dioxane increases from 80 to 90 vol% can be explained by the considerable decrease in the dielectric constant of the medium [7]. As follows from the calculation results, the accumulation of the nitrate complexes can be neglected at pH > 1 and pH > 1.5 at 80 and 90 vol% dioxane, respectively. Since the water–1,4-dioxane solutions with dioxane contents of ≤70 vol% have higher dielectric constants, the accumulation of nickel(II) nitrate complexes in them under the conditions of the determination of stability constants for the hydrazide complexes can be neglected.

As seen from Table 2, the hydrazides in question form with nickel(II) 1:1 and 1:2 metal–ligand complexes. In the aqueous and aqueous-dioxane solvents studied the stability constants of the mono- and bis-

Table 1. Mean coordination numbers of water ($\bar{n}_{H_2O}$) and dioxane ($\bar{n}_{do}$) molecules in the system nickel(II)–water–1,4-dioxane by ^1H NMR data (298 K)

Dioxane content, vol%	Dioxane content, mole fraction (X_{do})	$\bar{n}_{H_2O}$	$\bar{n}_{do}$	$\bar{n}_{H_2O} + \bar{n}_{do}$	$\bar{n}_{do}/(\bar{n}_{H_2O} + \bar{n}_{do})$
50	0.17	6.00	0	6.00	0
60	0.23	6.00	0	6.00	0
70	0.32	6.00	0	6.00	0
80	0.45	5.90	0.34	6.24	0.05
85	0.55	5.31	0.46	5.77	0.08
90	0.65	3.56	2.21	5.77	0.38
95	0.81	1.51	4.71	6.22	0.76

Table 2. Formation constants (log $\beta \pm 0.10$) of nickel(II) complexes with benzoic (L^1), *p*-chlorobenzoic (L^2), and *p*-methoxybenzoic (L^3) in aqueous-dioxane media (298 K)

Equilibrium	Content of 1,4-dioxane, mole fraction								
	0	0.05	0.08	0.12	0.17	0.23	0.32	0.45	0.65
$Ni^{2+} + L^1 \rightleftarrows Ni(L^1)^{2+}$	3.00	2.76		2.95	2.96	2.99	3.09	3.12	3.68
$Ni^{2+} + 2L^1 \rightleftarrows Ni(L^1)_2^{2+}$	5.23	4.59		5.00	5.49	5.39	5.42	5.54	6.61
$Ni^{2+} + L^2 \rightleftarrows Ni(L^2)^{2+}$		2.57		2.76	2.77	2.84	2.93	3.02	3.43
$Ni^{2+} + 2L^2 \rightleftarrows Ni(L^2)_2^{2+}$				4.61	4.95	4.99	5.03	5.14	6.32
$Ni^{2+} + L^3 \rightleftarrows Ni(L^3)^{2+}$	3.09	2.91	2.99	2.96	3.14	3.17	3.33	3.31	3.82
$Ni^{2+} + 2L^3 \rightleftarrows Ni(L^3)_2^{2+}$	5.40	5.12	5.28	5.36	5.63	5.76	5.83	6.21	7.12

Table 3. Step stability constants of nickel(II) complexes with benzoic (L^1), *p*-chlorobenzoic (L^2), and *p*-methoxybenzoic (L^3) hydrazides in aqueous-dioxane media (298 K) (charges are omitted)

Ligand	Constant	Content of 1,4-dioxane, mole fraction								
		0	0.05	0.08	0.12	0.17	0.23	0.32	0.45	0.65
L^1	$\log \beta'_{Ni(L^1)}$	6.49	6.06		6.00	5.88	5.68	5.57	5.26	5.20
	$\log K_{Ni(L^1)}$	3.00	2.76		2.95	2.96	2.96	3.09	3.12	3.68
	$\log K_{Ni(L^1)_2}$	2.23	1.83		2.05	2.44	2.43	2.33	2.42	2.93
	$\log (K_{Ni(L^1)}/K_{Ni(L^1)_2})$	0.77	0.93		0.90	0.52	0.59	0.76	0.70	0.75
L^2	$\log \beta'_{Ni(L^2)}$		5.87		5.81	5.69	5.56	5.41	5.16	4.95
	$\log K_{Ni(L^2)}$		2.57		2.76	2.77	2.84	2.93	3.02	3.43
	$\log K_{Ni(L^2)_2}$				1.85	2.18	2.15	2.10	2.12	2.89
	$\log (K_{Ni(L^2)}/K_{Ni(L^2)_2})$				0.91	0.59	0.69	0.83	0.90	0.54
L^3	$\log \beta'_{Ni(L^3)}$	6.58	6.21	6.19	6.01	6.06	5.89	5.72	5.45	5.34
	$\log K_{Ni(L^3)}$	3.09	2.91	2.99	2.96	3.14	3.17	3.24	3.31	3.82
	$\log K_{Ni(L^3)_2}$	2.31	2.21	2.29	2.40	2.49	2.59	2.50	2.90	3.30
	$\log (K_{Ni(L^3)}/K_{Ni(L^3)_2})$	0.78	0.70	0.70	0.56	0.65	0.58	0.74	0.41	0.52

complexes vary in the same ligand order $L^2 < L^1 < L^3$, as their acid dissociation constants (pK_a) [8]. This finding points to an important role the basicity of the ligands (electronic factor) plays in the stability of the hydrazide complexes. The fact that the formation constants of the complex $Ni(L^1)^{2+}$ increases with increasing dioxane content can not be explained in terms of metal dehydration in the course of reaction (2).

$$[Ni(H_2O)_6]_S^{2+} + L'_S = [Ni(H_2O)_{6-m}(L')]_S^{2+} + mH_2O, \tag{2}$$

$$\log \beta'_{Ni(L')^{2+}} = \log \beta_{Ni(L')^{2+}} + m\log [H_2O]. \tag{3}$$

Here L' is the common label for ligands L^1–L^3. Actually, with variation in the composition of the solvent, $\log \beta'_{Ni(L')^{2+}}$ at $m = 2$ (for bidentate coordination of L') do not remain constant with no one of the ligands (Table 3). This may point to an important role of ligand solvation in the complex formation.

To estimate the contributions of ligand L^1 and L^3 solvation in the complex-formation processes, we estimated, from the solubilitiles of the ligands, the free energies of transfer of their molecular forms [$\Delta G^t_N(L')$] from water to aqueous-dioxane media. The calculations were performed as described in [9] with use of Eq. (4):

$$\Delta G^t_N(L') = -2.303RT\log (c_S/c_w) + 2.303RT\log \{([H_2O] + [S])/55.56\}. \tag{4}$$

Here c_w and c_S are the solubilities of hydrazides in aqueous and aqueous-organic solvents, respectively, $[H_2O]$ and [S] are the concentrations of water and

Table 4. Solubilities (c_S, M) and free energies of transfer (ΔG^t_N, kJ/mol) of benzoic (L^1) and *p*-methoxybenzoic (L^3) hydrazides in aquoeus-dioxane media (298 K)

Parameter	Content of 1,4-dioxane, mole fraction									
	0	0.05	0.08	0.12	0.17	0.23	0.32	0.45	0.65	1.00
c_S (L^1)	0.2132	0.2262	0.2678	0.2866	0.2898	0.2961	0.3192	0.3213	0.3360	0.2898
c_S (L^3)	0.0707	0.4130	0.5932	1.0185	1.0513	1.0762	1.3505	1.4490	1.2993	0.7297
$\Delta G^t_N(L^1)$	0	–0.5	–1.2	–1.6	–1.9	–2.3	–2.9	–3.4	–4.2	–4.6
$\Delta G^t_N(L^3)$	0	–4.2	–5.9	–7.5	–7.9	–8.3	–9.2	–9.9	–10.3	–9.7

dioxane (M). The calculated “unitary” ΔG^t_N(L') values are listed in Table 4.

As seen from Table 4, as the content of dioxane increases, the free energies of ligand transfer ΔG^t_N(L') decrease, indicating stabilization of L'. Therewith, the ΔG^t_N(L') values for L^3 are much lower than for L^1 over the entire range of compositions, probably due to additional hydrophobic interaction between the CH_3 group of ligand L^3 and the four hydrophobic CH_2 groups of dioxane, which does not hinder interaction of the dioxane oxygens with water molecules. However, such hydrophobic interaction of the ligand L^3 remote from the coordinating hydrazide fragment may also involve the ligand L^3 bound with nickel(II). Therefore, the additional stabilization of L^3 with respect to L^1 should not substantially affect variations in log $\beta'_{Ni(L')^{2+}}$ for L^3, produced by increasing content of dioxane, compared with L^1. This is indeed the case (Table 3). Similarly we can assume that different solvation in the periphery of ligands L^1 and L^2 will not appreciably affect their complex-forming ability. Consequently, the decrease in $\Delta G^t_N(L^1)$ is the primary reason for the deacrese in log $\beta'_{Ni(L')^{2+}}$ with increasing dioxane content for all the three ligands (Table 3). Thus, the peaked shapes of the dependences of log $\beta_{Ni(L')^{2+}}$ on dioxane content (Table 2) are explained by the opposition of two tendencies: (1) decrease in the stability constant of $Ni(L')^{2+}$ as the result of decrease in the free energies of transfer of L', ΔG^t_N(L') (stabilization of L'); (2) increase in the stability constant due to dilution.

Comparison of the step stability constants log $K_{Ni(L')_n^{2+}}$ of the complexes (Table 3) shows that the ratio log ($K_{Ni(L')^{2+}}/K_{Ni(L')_2^{2+}}$) is almost independent on the composition of the medium is close to the statistically expected value for binding of bidentate ligands in the absence of steric effects (0.68 [10]). This circumstance allows us to neglect the steric repulsion between two ligands L' and dioxane molecules in the coordination sphere of nickel(II). The latter is in complete agreement with the weak coordinating ability of 1,4-dioxane.

EXPERIMENTAL

Nickel(II) nitrate of analytical grade was used. The hydrazides were synthesized by a standard procedure [11] with subsequent recrystallization from water and ethanol and drying at 60°C. 1,4-Dioxane was purified by the procedure described in [12]. pH measurements were performed on a pH-673M instrument. The glass electrode was preliminarily calibrated for every concentration of dioxane [13]. Required pH values were set up by means of titrated solutions of nitric acid. The optical densities were measured on an SF-46 spectrophotometer to an accuracy of ±1%. The proton spin-spin relaxation times (T_2) for H_2O and dioxane were determined from the NMR spectra measured on a Varian Unity-300 spectrometer (300 MHz) by the half-widths-at-half-heights of the corresponding signals [$\Delta\nu_{1/2} = (\pi T_2)^{-1}$] to an accuracy of 3–5%. The compositions and stability constants of the complexes were calculated by the CPESSP program [14] from the pH dependences of the extinction factors of the solutions (ε) at various metal-to-ligand ratios. The constants of acid dissociation of protonated forms of the hydrazides (pK_a) in aqueous and aqueous-dioxane media, required for calculation of the complex-formation parameters, were taken from [8] (parenthesized are the mole fractions of dioxane): L^1: 3.27 (0), 2.84 (0.05), 2.84 (0.12), 2.80 (0.17), 2.89 (0.23), 2.89 (0.32), 2.99 (0.45), and 3.31 (0.65); L^2: 3.03 (0), 2.78 (0.05), 2.67 (0.12), 2.66 (0.17), 2.70 (0.23), 2.73 (0.32), 2.84 (0.45), and 2.98 (0.65); L^3: 3.37 (0), 3.08 (0.05), 3.01 (0.12), 2.99 (0.17), 2.99 (0.23), 3.09 (0.32), 3.22 (0.45), and 3.42 (0.65).

REFERENCES

1. Bychkova, T.I., Shtyrlin, V.G., Sadykova, E.R., and Zakharov, A.V., *Zh. Neorg. Khim.*, 2000, vol. 45, no. 3, pp. 401–406.

2. Devyatov, F.V., Safina, V.F., Lazareva, L.G., and Sal’nikov, Yu.I., *Zh. Neorg. Khim.*, 1993, vol. 38, no. 6, pp. 1085–1088.
3. Devyatov, F.V., Safina, V.F., Sal’nikov, Yu.I., and Nozdrina, O.A., *Koord. Khim.*, 1998, vol. 24, no. 7, pp. 557–560.
4. Gutmann, V., *The Donor-Acceptor Approach to Molecular Interactions*, New York: Plenum, 1978.
5. Marcus, Y., *J. Solut. Chem.*, 1984, vol. 13, no. 9, pp. 599–624.
6. Zakharov, A.V. and Shtyrlin, V.G., *Bystrye reaktsii obmena ligandov* (Fast Ligand-Exchange Reactions), Kazan: Kazan. State Univ., 1978.
7. Akhadov, Ya.Yu., *Dielektricheskie svoistva binarnykh rastvorov* (Dielectric Properties of Binary Solutions), Moscow: Nauka, 1977.
8. Bychkova, T.I., Boos, G.A., and Dmitruk, I.Yu., Available from ONIITEKhim., 1994, Cherkassy, no. 114khp-94.
9. Bychkova, T.I., Boos, G.A., and Pichugina, M.V., *Zh. Fiz. Khim.*, 1992, vol. 62, no. 2, pp. 254–257.
10. Beck, M. and Nagypal, I., *Chemistry of Complex Equilibria*, Budapest: Akad. Kiado, 1990.
11. Smith, P.A.S., *Organic Reactions*, Adams, R., Ed., New York: Wiley, 1947, vol. 3. Translated under the title *Organicheskie reaktsii*, Moscow: Inostrannaya Literatura, 1951, vol. 3, pp. 322–426.
12. *Organic Solvents. Physical Properties and Methods of Purification*, Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Eds., New York: Interscience, 1955.
13. Aleksandrov, V.V., *Kislotnost’ nevodnykh rastvorov* (Acidity of Nonaqueous Solutions), Kharkov: Vysshaya Shkola, 1982.
14. Sal’nikov, Yu.I., Glebov, A.N., and Devyatov, F.V., *Poliyadernye kompleksy v rastvorakh* (Polynuclear Complexes in Solutions), Kazan: Kazan. State Univ., 1989.