Homo- and Heteroleptic Cobalt(II) and Nickel(II) Complexes with Nitrilotriacetic and Dibasic Carboxylic Acids

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Abstract—Equilibria in binary and ternary systems containing cobalt(II) and nickel(II) salts, nitrilotriacetic acid, and dicarboxylates were studied by spectrophotometry with $NaClO_4$ as a supporting electrolyte ($I = 0.1$) at $T = 20 \pm 2°C$. The molar and proton compositions of the complexes and the pH ranges of their existence were determined. The stability constants of the homo- and heteroleptic complexes were calculated. The pH-distribution of the detected complexes was obtained. The experimental data were processed in terms of the mathematical models that predict the existence of a wide spectrum of complex species in solution and allow ignoring those species that are negligible for accurate reproduction of the observed pattern.

Dibasic carboxylic acids and their salts find wide application in diverse industries: the production of lacquers and dyes, synthetic fibers, and food. Dicarboxamides (dipeptides) coordinated by microelement metals are known to be biologically active drugs [1]. Nitrilotriacetic acid and its salts are used in textile, tanning, and food industries and in photography. This acid is a good eluent for chromatographic separation and purification of cations with similar properties (e.g., rare-earth elements [2–4]).

To date, much progress has been achieved in the investigations of coordination compounds of various metals with organic acids and complexones. Complexation often (especially in the presence of extra ligands) substantially enhances the functional activity of an organic compound, which can be associated with the electron density redistribution, the higher reactivity, the formation of new structures, etc. [4].

Cobalt(II) and nickel(II) are biologically active metals. Excessive "man-caused" intake of their compounds has been found to be toxic for an organism's metabolism. When present in excess, cobalt and nickel salts produce a carcinogenic effect on the cell [5]. In connection with this, an investigation of the quantitative characteristics of reactions of cobalt(II) and nickel(II) with organic compounds is of current interest.

Here we studied homo- and heteroleptic cobalt(II) and nickel(II) complexes with nitrilotriacetic acid (**H₃Nta**) and some saturated dicarboxylic acids: oxalic (**H₂Ox**), malonic (**H₂Mal**), and succinic acids (**H₂Suc**).

Complexes of these metals with nitrilotriacetic acid have been repeatedly examined by various methods. Polarographic studies at $I = 0.1$ (KNO_3) and $T = 20°C$ detected the complexes $[CoNta]^-$ ($\log\beta = 10.4$ [6] and

10.38 [7]), $[NiNta]^-$ ($\log\beta = 11.54$ [6] and 11.53 [7]), $[CoNta_2]^{4-}$ ($\log\beta = 14.31$ [7]), and $[NiNta_2]^{4-}$ ($\log\beta = 16.42$ [7, 8]). Chromatographic studies at $I = 0.1$ (KNO_3) and $T = 20°C$ detected the complexes $[CoNta]^-$ ($\log\beta = 10.0$) and $[CoNta_2]^{4-}$ ($\log\beta = 13.9$) [9]. Electrochemical studies at $I = 0.1$ (Cl^-) and $T = 20°C$ detected the complexes $[CoNta]^-$ ($\log\beta = 10.6$) and $[NiNta]^-$ ($\log\beta = 11.26$) [8]. According to spectrophotometric data, an aqueous solution with $I = 0.1$ (KCl) contains neutral Co(II) and Ni(II) nitrilotriacetates: $[CoNta]^-$ ($\log\beta = 10.05$), $[CoNta_2]^{4-}$ ($\log\beta = 14.32$) [10], $[NiNta]^-$ ($\log\beta = 10.95$), and $[NiNta_2]^{4-}$ ($\log\beta = 15.62$) [11]. The stability constants of metal complexes with H_3Nta have been surveyed critically and quite comprehensively in the literature. The dissociation constants of H_3Nta obtained by different researchers using different techniques have been analyzed in [2]. The most acceptable values of the logarithms of the stability constants of $[CoNta]^-$, $[CoNta_2]^{4-}$, $[NiNta]^-$, and $[NiNta_2]^{4-}$ at $I = 0.1$ (KNO_3) and $T = 20°C$ are believed to be 10.4, 14.41, 11.54, and 16.42, respectively [2].

Cobalt(II) and nickel(II) complexes with dicarboxylic acids have also been studied repeatedly. However, the data obtained are contradictory with respect to both the compositions and stability constants of the complexes (Table 1).

Numerous heteroleptic cobalt(II) and nickel(II) complexes M(Nta)X (where M = Co(II) and Ni(II) and X = glycine, alanine, aspartic acid, glycylglycine, dimethylglycine, histamine, histidine, pyridine, and the following anions: $S_2O_3^{2-}$, SCN^-, $C_2O_4^{2-}$, Cl^-, Br^-, J^-, etc.) were described in [2, 3]. No heteroleptic cobalt(II) and

Table 1. Compositions and stability constants of the cobalt(II) and nickel(II) complexes with the dicarboxylic acids

Ligand	T, °C	I	Medium	Method	$\log \beta$ [CoL]	[NiL]	$[CoL_2]^{2-}$	$[NiL_2]^{2-}$	References
Oxalic acid	25	0.5	NaCl	Potentiometry	3.21	4.05	5.39	6.01	[12]
	35	0.1	KNO$_3$	Potentiometry	4.97	5.23			[13]
	25	1.0	NaClO$_4$	Distribution method	3.33		6.20		[14]
	25	1.0	NaClO$_4$	Potentiometry	3.20		5.60		[15]
	25	0		Potentiometry	4.69		7.15		[16]
	25	0		Ion exchange	4.75		6.91		[17]
	25	0.16	NaCl	Ion exchange	3.72		6.03		[18]*
	0	0		Potentiometry	4.77	5.18			[19]
	15				4.78	5.14			[19]
	25				4.79	5.16			[19]
	35				4.81	5.17			[19]
	45				4.83	5.18			[19]
	25	0.1	KNO$_3$	Potentiometry		4.43			[20]
	25	0.1	indefinite	Potentiometry		5.30			[21]
	25	1.0	KNO$_3$	Potentiometry				7.64	[22]
	20	0.1	NaClO$_4$	Distribution method				7.88	[23]
	25	0		Dissolution				6.51	[24]
	25	0.1	KNO$_3$	Voltammetry		4.16		7.52	[25]
	25	1.0	NaClO$_4$	Distribution method		3.70		6.60	[26]
	20	0.1	NaClO$_4$	Distribution method		3.83		7.06	[27]
Malonic acid	25	0.5	NaCl	Potentiometry	2.37	2.74			[12]
	25	0		Potentiometry	3.74		5.14		[16]
	25	0		Ion exchange	3.77		5.12		[17]
	25	0.1	KNO$_3$	Potentiometry		4.58			[20]
	25	0.1	NaClO$_4$	Potentiometry	2.97				[28]
	7	0.1	NaClO$_4$	Potentiometry	2.78				[29]
	25	0.1	KCl	Potentiometry	2.92		4.6		[30]
	23	0		Ion exchange	2.5		3.93		[31]
	25	0.1	KNO$_3$	Potentiometry	2.95	3.27	4.43	4.94	[32]
	25	0.1	NaClO$_4$	Voltammetry		3.28		5.45	[33]
	25	50%	Dioxane/H$_2$O	Potentiometry		5.7		8.93	[34]
	25	0.1	NaClO$_4$	Potentiometry		3.29			[35]
	20	0.1	NaClO$_4$	Potentiometry		3.30			[36]
Succinic acid	25	0.5	NaCl	Potentiometry	1.26	1.47			[12]
	25	0		Potentiometry	2.37				[16]
	25	0		Ion exchange	2.41				[17]
	25	0.1	KNO$_3$	Potentiometry		5.92			[20]
	25	0.1	NaClO$_4$	Voltammetry		1.84			[33]
	25	0.5				1.18			[33]
	20	0.1	NaClO$_4$	Potentiometry	1.70				[36]*
	25	0.1	KNO$_3$	Potentiometry	1.71	1.62			[37]

* For [CoHL]$^+$ $\log \beta$ = 5.46 [18] and 6.27 [36], for [Co(HL)$_2$] $\log \beta$ = 10.51 [18].

nickel(II) complexes with H_3Nta and dicarboxylic acids were documented.

Understanding of complexation in ternary systems with H_3Nta and dicarboxylic acids is impossible without gathering information on processes in the corresponding binary systems containing a bivalent metal salt and H_3Nta, H_2Ox, H_2Mal, or H_2Suc. Because the literature data on homoleptic Co(II) and Ni(II) complexes with the ligands in question are contradictory, we had to thoroughly study complexation in binary systems under the same experimental conditions to refine the compositions and stability constants of the Co(II) and Ni(II) complexes with the reagents under consideration.

EXPERIMENTAL

We investigated complexation processes by spectrophotometry. The optical densities A of solutions were measured on an SF-26 spectrophotometer in a specially manufactured Teflon cell with quartz glasses (absorbing layer thickness 5 cm). Such a cell allows simultaneous measurements of pH and A. The relative error in the optical density determination was calculated by the formula $\Delta = 0.4343/(A \times 10^{-4})\%$. The wavelengths were set in the ranges from 500 to 540 nm for cobalt and from 380 to 420 nm for nickel to within ±0.1 nm. All curves $A = f(pH)$ were obtained by spectrophotometric titration at 20 ± 2°C. Twice-distilled water was used as a reference solution. The activity of H^+ ions was measured on an I-160 ionomer with an ES-10601/7 working electrode and an ESR-10101 reference electrode. The instrument was calibrated against standard buffers (prepared from titrating solutions) and tested on a UPKP-1 testing unit. To bring pH to a required value, a solution of NaOH or $HClO_4$ (analytical grade) was added. The constancy of the ionic strength ($I \approx 0.1$) was maintained with a solution of $NaClO_4$ (analytical grade). In the case of a great excess of dicarboxylic acids, all equilibrium constants were calculated for a basic ionic strength of 0.1. Solutions of cobalt(II) and nickel(II) perchlorates were prepared by dissolving CoO and NiO (reagent grade) in $HClO_4$. Solutions of complexones and dicarboxylic acids were prepared by dissolving their precisely weighed samples (reagent grade) in distilled water. Mathematical processing of the results obtained with our original programs and the CPESSP program [38] gave comparable results.

RESULTS AND DISCUSSION

The electronic absorption spectrum of the cobalt(II) hexaaqua complex shows two absorption bands at 560 ($^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$) and 550 nm (4 550 ($^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$). The electronic absorption spectrum of the octahedral nickel(II) aqua complex exhibits three absorption bands at 400 ($^3A_{2g} \longrightarrow {}^3T_{1g}(P)$), 714 ($^3A_{2g} \longrightarrow {}^3T_{1g}(F)$), and 1111 nm ($^3A_{2g} \longrightarrow {}^3T_{2g}$).

We studied complexation in binary and ternary systems by observing changes in the absorption spectra and optical densities of the solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ in the presence of the complexone and dicarboxylic acids. In addition, we constructed theoretical complexation models for ternary systems with no regard to mixed-ligand complexation. The discrepancies between the model and experimental curves $A = f(pH)$ are probably due to the formation of heteroleptic complexes. Measurements were performed at wavelengths of 520 (for Co(II) complexes) and 400 nm (for Ni(II) complexes) because the ligands themselves only slightly absorb at these wavelengths (regardless of pH), while the resulting complexes show a considerable hyperchromic effect. The curves $A = f(pH)$ plotted for binary and ternary systems suggest that the complexation in all the systems studied occurs over a wide pH range.

Description of equilibria in binary and especially ternary systems containing various hydroxo complexes and various protonated forms of polydentate ligands is a baffling problem. Since the estimated stability constants of the complexes depend on the set of species included in the description of the system, the choice of the right set of complex species is critical. In the programs we used, the problem of considering or ignoring a particular complex species of a metal or a ligand in the description of the system is solved by minimizing the Fisher test allowing for the discrepancies between the experimental and calculated optical densities for each component of the system. This approach allows sufficiently reliable estimation of the parameters of the system in equilibrium, their stoichiometry, and the thermodynamic characteristics of relevant processes. We described chemical equilibria in binary and ternary systems in terms of the ion-pair model supposing that a solution may contain a broad spectrum of complexes and associates.

The molar ratio of the complexes in binary systems (1 : 1 and 1 : 2) was determined by the saturation and isomolar series methods. Mathematical processing of the curves $A = f(pH)$ (Fig. 1) revealed the presence of several complexes in all the binary systems studied. The pH ranges in which these complexes exist were found from the distribution of their mole fractions at different pH values. It should be noted that the initial pH values for the existence of most complexes are distinct. However, the final pH value of a particular complex may be too basic (pH > 12) to be determined accurately (Table 2).

To identify the resulting complexes in binary and ternary systems, we used three constants of monomeric hydrolysis for cobalt(II) and nickel(II) [39], two dissociation constants of each dicarboxylic acid [40, 41], and four dissociation constants of nitrilotriacetic acid [42, 43]. We failed to determine the character of equilibria in the Co(II)–H_2Ox system since precipitates formed at all pH values, thus making the solutions turbid. The sta-
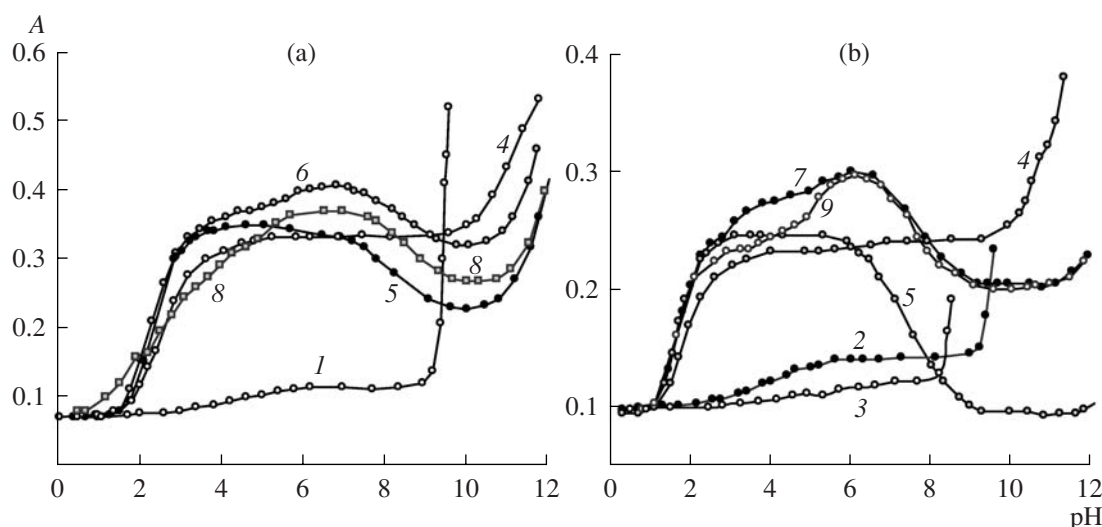
Fig. 1. Plots of the optical density vs. pH for solutions of (a) cobalt(II) and (b) nickel(II) with (*1, 2*) H_2Mal, (*3*) H_2Suc, (*4, 5*) H_3Nta, (*6, 7*) $H_3Nta + H_2Mal$, (*8*) $H_3Nta + H_2Ox$, and (*9*) $H_3Nta + H_2Suc$ for the ratio of the reagents: (*1*) 1 : 20, (*2*) 1 : 10, (*3*) 1 : 40, (*4*) 1 : 1, (*5*) 1 : 2, (*6*) 1 : 2 : 80, (*7*) 1 : 2 : 20, and (*8, 9*) 1 : 2 : 10; $c_{Co} = 3 \times 10^{-3}$ mol/l, $c_{Ni} = 4 \times 10^{-3}$ mol/l.

bility constants of homoleptic complexes (Table 2) were used to modify the equilibria in the formation of heteroleptic complexes. Note that a great excess of dicarboxylic acids is required to obtain homo- and heteroleptic complexes of both metals. However, the quantitative yields of the complexes cannot be achieved even at very great excesses of these ligands. We found that for the formation of heteroleptic complexes, the concentration of the ligand should be no lower than that in its homoleptic complexes obtained in maximum yields.

It can be seen in Fig. 1 that the formation of heteroleptic Co(II) and Ni(II) complexes occurs over a wide pH range (0.1 < pH < 12.0). In all cases, H_3Nta acts as a primary ligand. In strongly acidic media, the curves $A = f(pH)$ for heteroleptic complexes are similar to the curves for Co(II) and Ni(II) mononitrilotriacetates. With an increase in pH, the protonated species of the secondary ligand (dicarboxylic acid **H_2Dik**) adds according to the equation

$$[MNta]^- + HDik^- \rightleftharpoons [MNta(HDik)]^{2-}. \quad (1)$$

Table 2. pH ranges of the existence of the homoleptic cobalt(II) and nickel(II) complexes and their stability constants at $I = 0.1$ (NaClO$_4$) and $T = 20 \pm 2$°C

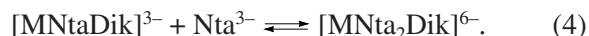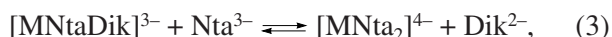| Complex	pH range of existence	log β	Complex	pH range of existence	log β
CoNta⁻	>1.0	10.10 ± 0.76	NiNta⁻	>0.8	11.38 ± 0.76
Co(Nta)$_2^{4-}$	>5.1	13.50 ± 0.12	Ni(Nta)$_2^{4-}$	>4.3	16.34 ± 0.05
Co(OH)Nta²⁻	>9.8	12.50 ± 0.01	Ni(OH)Nta²⁻	>9.6	13.95 ± 0.01
CoHMal⁺	0.4–5.5	5.18 ± 0.06	NiHOx⁺	0.0–3.2	6.30 ± 0.08
CoMal	>1.9	2.97 ± 0.08	NiOx	>0.2	5.35 ± 0.08
CoMal$_2^{2-}$	>3.2	4.51 ± 0.08	NiOx$_2^{2-}$	>1.0	9.25 ± 0.10
CoHSuc⁺	2.0–7.0	6.29 ± 0.09	NiHMal⁺	0.3–5.5	6.70 ± 0.07
CoSuc	>3.6	1.60 ± 0.10	NiMal	>1.9	3.50 ± 0.09
NiHSuc⁺	1.9–7.1	6.39 ± 0.10	NiMal$_2^{2-}$	>3.2	5.30 ± 0.07
NiSuc	>2.8	1.95 ± 0.08			
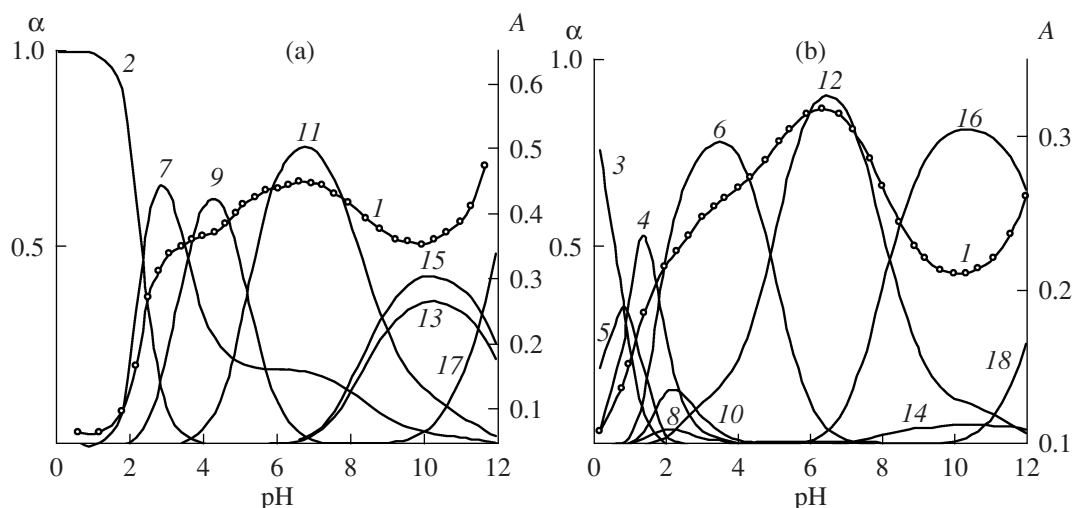
Fig. 2. Plots of the optical density A and mole fraction α of the complex vs. pH for (a) Co(II) and (b) Ni(II): (*1*) experimental curve, (*2*) Co^{2+}, (*3*) Ni^{2+}, (*4*) $[NiOx]$, (*5*) $[NiHOx]^+$, (*6*) $[NiOx_2]^{2-}$, (*7*) $[CoNta]^-$, (*8*) $[NiNta]^-$, (*9*) $[CoNta(HSuc)]^{2-}$, (*10*) $[NiNta(HOx)]^{2-}$, (*11*) $[CoNtaSuc]^{3-}$, (*12*) $[NiNtaOx]^{3-}$, (*13*) $[CoNta_2]^{4-}$, (*14*) $[NiNta_2]^{4-}$, (*15*) $[CoNta_2Suc]^{6-}$, (*16*) $[NiNta_2Ox]^{6-}$, (*17*) $[Co(OH)NtaSuc]^{4-}$, and (*18*) $[Ni(OH)NtaOx]^{4-}$ for (a) Co^{2+}: $H_3Nta : H_2Suc = 1 : 2 : 40$ and (b) Ni^{2+}: $H_3Nta : H_2Ox = 1 : 2 : 10$; $c_{Co} = 3 \times 10^{-3}$ mol/l, $c_{Ni} = 4 \times 10^{-3}$ mol/l.

A further increase in pH results in the deprotonation of the acid complexes:

$$[MNta(HDik)]^{2-} \rightleftharpoons [MNtaDik]^{3-} + H^+. \qquad (2)$$

In the pH range of the formation of Co(II) and Ni(II) dicomplexonates, one more mole of nitrilotriacetate adds according to the equations:

$$[MNtaDik]^{3-} + Nta^{3-} \rightleftharpoons [MNta_2]^{4-} + Dik^{2-}, \qquad (3)$$

$$[MNtaDik]^{3-} + Nta^{3-} \rightleftharpoons [MNta_2Dik]^{6-}. \qquad (4)$$

The yields of the complexes in reactions (3) and (4) vary with systems. At the same pH values, the dicomplexonate is dominant in some systems, while the heteroleptic complex is dominant in others. The latter complex is hydrolyzed in strongly basic media:

$$[MNta_2Dik]^{6-} + OH^- \rightleftharpoons [M(OH)NtaDik]^{4-} + Nta^{3-}. \ (5)$$

To determine the pH range in which heteroleptic complexes exist, we plotted species distribution diagrams for the systems Co(II)–H_3Nta–H_2Suc and Ni(II)–H_3Nta–H_2Ox (Fig. 2). The experimental curves $A = f(pH)$ subjected to mathematical modeling are shown in the same diagrams (Fig. 2, curve *1*). Note that the maximum yields of the heteroleptic complexes obtained in reactions (1), (2), (4), and (5) depend on not only the acidity of the medium but also the concentration of a secondary ligand (dicarboxylic acid) and noticeably differ for Co(II) and Ni(II) complexes. Obviously, this is associated with the stability of the metal complexes with dicarboxylic acids. For instance, homoleptic Co(II) complexes can hardly form in the presence of H_2Suc (Fig. 2a), while the system Ni(II)–H_3Nta–H_2Ox under acidic conditions produces the complexes

$[NiHOx]^+$ (35%), $[NiOx]$ (55%), and $[NiOx_2]^{2-}$ (75%) at pH 1, 1.5, and 3, respectively.

It should be emphasized that in almost all the systems studied, the increase in the concentration of the secondary ligand (dicarboxylic acid) increases the yields of the heteroleptic complexes, simultaneously lowering the yields of the homoleptic complexes (Fig. 3). Indeed, an increase in the concentration of malonic acid from 0.06 to 0.24 mol/l in the system Co(II)–H_3Nta–H_2Mal increases the yields of the heteroleptic complexes by 30%.

However, in the system Ni(II)–H_3Nta–H_2Ox, the opposite pattern is observed: a gradual increase in the concentration of H_2Ox lowers the yields of all heteroleptic complexes but increases the yields of nickel(II) oxalates. The mole fractions of the heteroleptic complexes at the optimal pH values and their stability constants are given in Table 3.

The neutral Co(II) and Ni(II) complexes with nitrilotriacetate and dicarboxylate can be arranged in the increasing order of their stability constants as follows:

$$[MNtaSuc]^{3-} < [MNtaMal]^{3-} < [MNtaOx]^{3-},$$

$$[MNta_2Suc]^{6-} < [MNta_2Mal]^{6-} < [MNta_2Ox]^{6-}.$$

The stabilities of neutral Co(II) and Ni(II) dicarboxylates change in the same order. Obviously, the ligating properties of the dicarboxylic acids depend on the number of methylene groups in their molecules, which affects their dissociation constants.
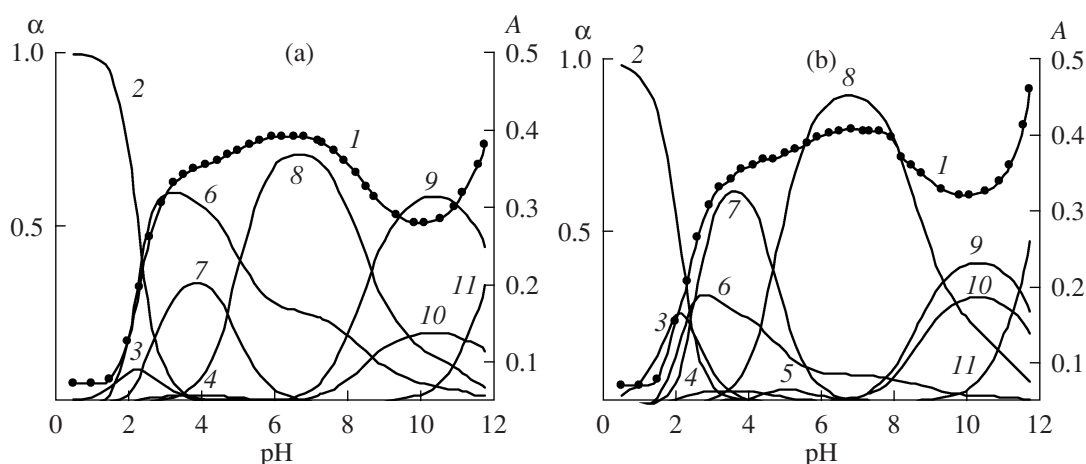
Fig. 3. Plots of the optical density A and mole fraction α of the complex vs. pH for Co(II) : H_3Nta : H_2Mal = (a) 1 : 2 : 40 and (b) 1 : 2 : 80: (*1*) experimental curve, (*2*) Co^{2+}, (*3*) $[CoHMal]^+$, (*4*) $[CoMal]$, (*5*) $[CoMal_2]^{2-}$, (*6*) $[CoNta]^-$, (*7*) $[CoNta(HMal)]^{2-}$, (*8*) $[CoNtaMal]^{3-}$, (*9*) $[CoNta_2]^{4-}$, (*10*) $[CoNta_2Mal]^{6-}$, and (*11*) $[Co(OH)NtaMal]^{4-}$; $c_{Co} = 3 \times 10^{-3}$ mol/l.

When comparing the dissociation constants of the dicarboxylic acids, one should consider the presence of two acid centers in their nondissociated molecules (and two basic centers in the corresponding anions). Because of this, the first dissociation constants mono-

Table 3. Selected characteristics of the heteroleptic cobalt(II) and nickel(II) complexes with nitrilotriacetic and dicarboxylic acids at $I = 0.1$ (NaClO$_4$) and $T = 20 \pm 2°C$

Complex	pH range of existence	pH$_{opt}$	log β	Maximum mole fraction of the complex at pH$_{opt}$, %
CoNta(HOx)$^{2-}$	1.3–5.0	3.0	15.53 ± 0.31	6
CoNtaOx^{3-}	>2.2	7.0	12.31 ± 0.22	80
Co(OH)NtaOx^{4-}	>9.3		14.95 ± 0.01	
CoNta(HMal)$^{2-}$	1.5–7.0	3.6	16.49 ± 0.34	62
CoNtaMal^{3-}	>2.6	6.8	11.80 ± 0.17	90
Co(Nta)$_2$Mal^{6-}	>6.2	10.3	15.25 ± 0.04	42
Co(OH)NtaMal^{4-}	>8.6		14.95 ± 0.01	
CoNta(HSuc)$^{2-}$	1.8–7.5	4.3	16.84 ± 0.34	63
CoNtaSuc^{3-}	>3.4	6.7	11.65 ± 0.17	75
Co(Nta)$_2$Suc^{6-}	>6.3	10.3	15.50 ± 0.10	43
Co(OH)NtaSuc^{4-}	>9.2		15.05 ± 0.03	
NiNta(HOx)$^{2-}$	1.0–4.0	2.2	17.60 ± 0.56	15
NiNtaOx^{3-}	>1.4	6.4	14.75 ± 0.24	90
Ni(Nta)$_2$Ox^{6-}	>5.4	10.3	18.98 ± 0.05	82
Ni(OH)NtaOx^{4-}	>9.6		17.70 ± 0.01	
NiNta(HMal)$^{2-}$	1.3–6.0	3.6	16.93 ± 0.46	10
NiNtaMal^{3-}	>2.8	5.1	13.20 ± 0.45	78
Ni(Nta)$_2$Mal^{6-}	>5.7	10.5	17.50 ± 0.16	48
Ni(OH)NtaMal^{4-}	>10.7		15.85 ± 0.01	
NiNta(HSuc)$^{2-}$	2.0–7.0	4.5	17.79 ± 0.34	25
NiNtaSuc^{3-}	3.0–11.0	6.3	12.85 ± 0.18	46
Ni(Nta)$_2$Suc^{6-}	>6.0	10.0	17.03 ± 0.06	15
Ni(OH)NtaSuc^{4-}	>9.2		16.50 ± 0.13	

tonically decrease, while the second dissociation constants change "anomalously" [40, 41]:

Acid	H_2Ox	H_2Mal	H_2Suc
pK_1	1.54	2.73	4.00
pK_2	4.10	5.34	5.24

The stabilities of the protonated heteroleptic complexes change in a similar way; at least, this is true for the nickel complexes:

$$[NiNta(HMal)]^{2-} < [NiNta(HOx)]^{2-} < [NiNta(HSuc)]^{2-}.$$

The problem of ligand compatibility in a heteroleptic complex can be solved by determining the coproportionation constant K_a [3]. For instance, for the reaction

$$[MNta_2]^{4-} + [MDik_2]^{2-} \rightleftharpoons 2[MNtaDik]^{3-}$$
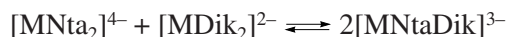
K_a is much greater than unity for all neutral heteroleptic Co(II) and Ni(II) complexes and the stability constants of the heteroleptic complexes are higher than the geometric mean of the stability constants of the corresponding homoleptic dicomplexes of these metals. This suggests that H_3Nta and H_2Dik are compatible in octahedral heteroleptic Co(II) and Ni(II) complexes.

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