

COORDINATION
COMPOUNDS

Formation of Heteropolynuclear Cobalt(II) and Nickel(II) Complexonates with EDTA and 2-Aminopropanoic Acid

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Abstract—Coordination equilibria in the Co(II)–Ni(II)–2-aminopropanoic acid (HAla)–EDTA system have been studied spectrophotometrically at different molar ratios of the reagents in a wide pH range. It has been found that, when metal ions are in excess with respect to EDTA at pH 5–9, polyheteronuclear complexonates $[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$, $[(\text{CoAla}_2)\text{Edta}(\text{NiAla}_2)]^{4-}$, $[(\text{NiAla}_2)\text{Edta}(\text{CoAla}_2)]^{4-}$, $[(\text{CoAla}_2)\text{Edta}(\text{NiAla}_2)_2]^{4-}$, and $[(\text{NiAla}_2)_2\text{Edta}(\text{CoAla}_2)_2]^{4-}$ form in a solution. The equilibrium constants of formation of these complexes and their overall stability constants have been calculated. Possible structures of the polynuclear complexonates are discussed.

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Conditions of formation of polynuclear complexes with participation of complexonates are relatively poorly understood [1]. A prerequisite for the formation of such complexes is a high denticity of the structure-forming complexone, which cannot be realized in the inner coordination sphere of one metal ion. Ethylenediaminetetraacetic acid (EDTA), being a hexadentate ligand, usually forms mononuclear complexes; however, when doubly charged metal ions (Ni(II), Co(II), Cu(II), Mn(II)) are in excess and additional bidentate ligands (ethylenediamine, oxalate, glycine) are present, bi-, tri-, and even tetranuclear complexonates can form [2–4]. In our previous studies of Ni(II)–EDTA–secondary ligand (L = amino acids, ethylenediamine, dipyridyl, iminodiacetic acid (IDA), nitrilotriacetic acid (NTA)) systems, we determined the stability constants and optimal conditions of formation of polynuclear mixed-ligand complexes $[(\text{NiL})_2\text{Edta}]$, $[(\text{NiL}_2)_2\text{Edta}]$, $[(\text{NiL}_2)_3\text{Edta}]$, and $[(\text{NiL}_2)_4\text{Edta}]$ (charges of the complexes are omitted) [5–7]. The bridging function of the chelating ligand, EDTA, afford a combination of different metal ions in the same complex; however, conditions of formation of heteropolynuclear complexonates should be further studied. In continuation of this research, here we have studied equilibria in aqueous solutions of the Co(II)–Ni(II)–EDTA system when the metal ions are in excess with respect to EDTA and in the presence of an additional ligand (2-aminopropanoic acid (alanine)) stabilizing polynuclear complexonates.

EXPERIMENTAL

Complex formation in solutions was studied by spectrophotometric titration. The absorbance of solutions was measured on an SF-2000 spectrophotometer equipped with a special unit containing a flow-type cell with quartz glasses and a path length of 1 cm. Such a setup allowed us to simultaneously determine pH and absorbance of solution. The hydrogen ion activity was measured on an I-160MI ionometer with the use of an ES-10601/7 working electrode and an ESR-10101 reference electrode. The required pH value was adjusted with NaOH and HClO₄ (pure for analysis) solutions. The ionic strength ($I = 0.2$) was maintained constant with a NaClO₄ (pure for analysis grade) solution. Studies were carried out at room temperature (20 ± 2)°C. Metal salt solutions were prepared by dissolving the CoSO₄ · 7H₂O and NiSO₄ · 7H₂O salts in water; the metal ion concentration in a solution was determined by complexometric titration. EDTA (chemically pure) and alanine (chemically pure) solutions were prepared by dissolving the reagents in distilled water. The results were mathematically processed with the HypSpec program [8]. Complex models were constructed with the ACD/Labs program [9].

RESULTS AND DISCUSSION

Speciation in the systems was studied by monitoring changes in the absorption spectra (in the range 300–1000 nm) of the Co(II)–Ni(II)–HAla–EDTA systems at fixed molar ratios of the components induced by a change in solution acidity. The HyperSpec software makes it possible to calculate, for a

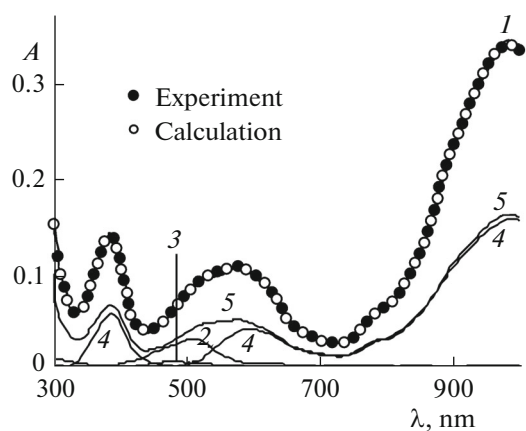


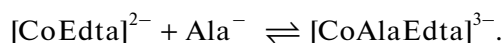
Fig. 1. Absorption spectra for (1) the Co(II)–Ni(II)–HAla–EDTA system at the 1 : 1 : 2 : 1 ratio, (2) Co^{2+} , (3) $[\text{CoEdta}]^{2-}$, (4) $[\text{NiEdta}]^{2-}$, and (5) $[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$ at pH 4.43. $C_{\text{Co}^{2+}} = C_{\text{Ni}^{2+}} = 1.25 \times 10^{-2}$ mol/L.

selected complexation model, formation constants of complex species and their spectral characteristics through minimization (by the iteration method) of the difference between the experimental and calculated absorbances for the entire spectral range [8]. In calculations, a large number of complexation models consisting of different sets of complex species composed of the starting components— M^{2+} (Co^{2+} , Ni^{2+}), EDTA (Edta^{4-}), and alanine (Ala^-)—were considered. The possible formation of mononuclear homoleptic complexes $[\text{MH}_i\text{Edta}]^{i-2}$ ($i = 0-2$), $[\text{MH}_i\text{Ala}]^{1+i}$ ($i = 0, 1$), and $[\text{MAla}_i]^{2-i}$ ($i = 0-3$); mononuclear heteroligand complexes $[\text{MAlaEdta}]^{3-}$, as well as of heteropolynuclear heteroligand complexes $[\text{M}_x\text{M}'_y\text{Ala}_i\text{Edta}]^{2x+2y-i-4}$ ($x = 1-2$, $y = 1-2$; $i = 2, 4, 6, 8$), was taken into account. In modeling equilibria, we used fixed values of the Co(II) and Ni(II) hydrolysis constants and EDTA and 2-aminoprop-

noic acid (alanine) dissociation constants taken from [10]. In the course of our initial study of binary systems (Co(II)–EDTA, Co(II)–HAla, Ni(II)–EDTA, and Ni(II)–HAla), we determined the stability constants of homoleptic complexes and their absorption spectra, which were used as fixed, known quantities in calculations of more complicated systems containing two metal ions and/or two ligands. The $A = f(\text{pH})$ dependences presented below are shown only for the most characteristic wavelengths corresponding to the absorption of Co(II) ($\lambda = 490$ nm) or Ni(II) ($\lambda = 985$ nm), although the entire absorption spectrum was used in calculation. As an example, Fig. 1 shows a good fit between the experimental and calculated absorption spectra for one of the systems studied, as well as the spectral contributions of separate components to the overall spectrum.

For modeling the equilibria of formation of heteropolynuclear Co(II) and Ni(II) complexes, information on mononuclear complexes is required. The composition and stability constants of these complexes for Ni(II) have been reported in [5, 6], whereas the present study deals with binary and ternary systems for Co(II). Mathematical processing of the $A = f(\text{pH})$ curves for the binary Co(II)–EDTA and Co(II)–HAla systems has demonstrated that completely deprotonated and monoprotonated complexonates are formed in the first system, and deprotonated mono-, bis-, and tris-ligand complexes are produced in the second system (Table 1). Comparison of stability constants for the Co(II) and Ni(II) complexes identified under identical conditions shows that the Ni(II) complexes are more stable than the Co(II) complexes, which is typical of many other ligands that form complexes with these metals.

It has been found that, at a 1 : 1 : 1 ratio of the components in the Co(II)–HAla–EDTA system, a precipitate was deposited at $\text{pH} > 10$, as well as in the Co(II)–EDTA system, which is evidence of Co(II) hydrolysis. However, in the presence of a tenfold excess of alanine, no precipitate is formed, since a ternary complex was produced in an alkaline medium by the scheme



This heteroligand complex can form through partial opening of two glycine rings of the $[\text{CoEdta}]^{2-}$ complex so that the vacant coordination sites are occupied by the alanine anion.

At the 1 : 1 : 2 : 1 molar ratio of the components in the Co(II)–Ni(II)–HAla–EDTA system in an acid medium, uncoordinated Co(II) ions and mononuclear complexes $[\text{NiHEdta}]^-$ and $[\text{NiEdta}]^{2-}$ are dominating (Fig. 2a). In the range $3.0 < \text{pH} < 8.0$, a binuclear heterometal complex is formed, with the maximal degree of accumulation $\alpha = 100\%$ at $\text{pH} > 8.0$. (It should be noted that here and hereinafter α was calculated with respect to the overall concentration of both

Table 1. Stability constant of Co(II) and Ni(II) complexes with 2-aminopropanoic acid and EDTA ($I = 0.2$ (NaClO_4), $T = (20 \pm 1)^\circ\text{C}$)

Complex	Co^{2+}	Ni^{2+} [6, 7]
	$\log\beta$	$\log\beta$
$[\text{MEdta}]^{2-}$	16.31 ± 0.06	18.61 ± 0.05
$[\text{MHEdta}]^-$	18.98 ± 0.02	21.60 ± 0.10
$[\text{MAla}]^+$	4.38 ± 0.09	6.49 ± 0.02
$[\text{MAla}_2]$	8.06 ± 0.06	13.91 ± 0.08
$[\text{MAla}_3]^-$	9.64 ± 0.06	22.78 ± 0.14
$[\text{MAlaEdta}]^{3-}$	21.17 ± 0.05	21.58 ± 0.03

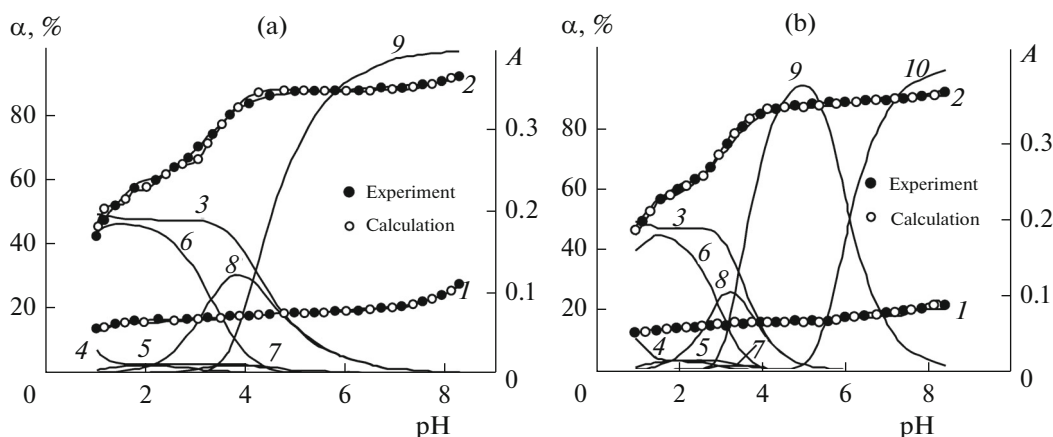
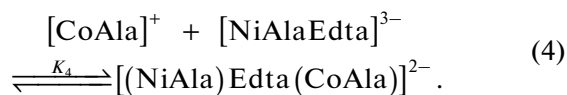
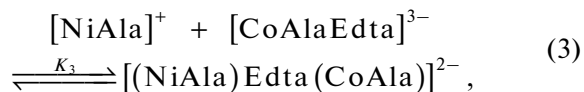
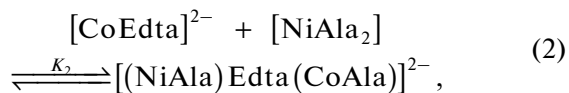
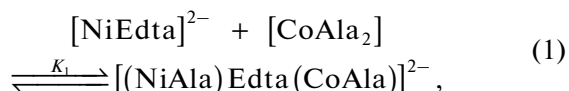


Fig. 2. Degree of accumulation (α) and absorbance (A) vs. pH in the Co(II)–Ni(II)–HAla–EDTA system at the molar ratio (a) 1 : 1 : 2 : 1 and (b) 1 : 1 : 4 : 1: curves $A = f(\text{pH})$ for $\lambda = (1)$ 490 and (2) 985 nm; (3) Co^{2+} , (4) Ni^{2+} , (5) $[\text{CoHEDta}]^-$, (6) $[\text{NiHEDta}]^-$, (7) $[\text{CoEdta}]^{2-}$, (8) $[\text{NiEdta}]^{2-}$, (9) $[(\text{NiAla})\text{Edta}(\text{CoAla})]^{2-}$, and (10) $[(\text{NiAla})_2\text{Edta}(\text{CoAla})_2]^{4-}$. $C_{\text{Co}^{2+}} = C_{\text{Ni}^{2+}} = 1.25 \times 10^{-2}$ mol/L.

metals.) The heterobinuclear complex can form by the following equations (the corresponding equilibrium constants are presented in Table 2):



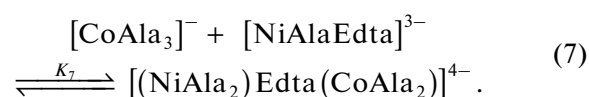
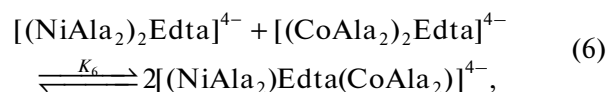
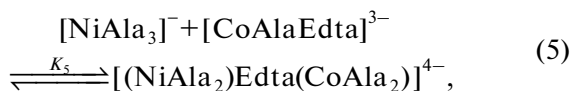
We can assume that the octahedral coordination polyhedra of the Co(II) and Ni(II) ions in the $[(\text{NiAla})\text{Edta}(\text{CoAla})]^{2-}$ complex share the diaminoethane bridge of EDTA, which is equivalently bound to each metal ion through the tridentate iminodiacetate moiety. The alanine residues partially saturate the metal coordination sphere to form five-membered chelate rings.

At the 1 : 1 : 4 : 1 molar ratio in the Co(II)–Ni(II)–HAla–EDTA system (Fig. 2b) in an acid medium ($\text{pH} < 4.0$), uncoordinated Co(II) ions as well as protonated

Table 2. Equilibrium constants of reactions and stability constants of heteropolynuclear Co(II) and Ni(II) complexes with 2-aminopropanoic acid and EDTA ($I = 0.2$ (NaClO_4), $T = (20 \pm 1)^\circ\text{C}$)

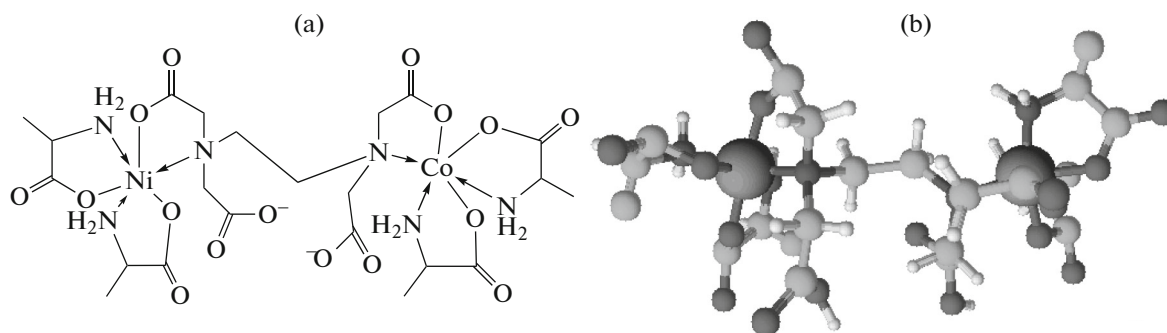
Complex	No. of reaction	$\log K_i$	$\log \beta$
$[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$	(1)	8.36 ± 0.07	35.03 ± 0.26
$[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$	(2)	8.87 ± 0.09	
$[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$	(3)	8.47 ± 0.05	
$[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$	(4)	9.07 ± 0.09	
$[(\text{CoAla}_2)\text{Edta}(\text{NiAla}_2)]^{4-}$	(5)	12.95 ± 0.12	46.98 ± 0.07
$[(\text{CoAla}_2)\text{Edta}(\text{NiAla}_2)]^{4-}$	(6)	1.23 ± 0.13	
$[(\text{CoAla}_2)\text{Edta}(\text{NiAla}_2)]^{4-}$	(7)	15.76 ± 0.07	
$[(\text{NiAla}_2)\text{Edta}(\text{CoAla}_2)]^{4-}$	(8)	7.5 ± 0.13	61.60 ± 0.07
$[(\text{CoAla}_2)\text{Edta}(\text{NiAla}_2)]^{4-}$	(9)	7.1 ± 0.10	63.64 ± 0.44
$[(\text{NiAla}_2)_2\text{Edta}(\text{CoAla}_2)]^{4-}$	(10)	8.82 ± 0.11	73.42 ± 0.11

and deprotonated mononuclear Ni(II) complexones are dominating. In the range $3.0 < \text{pH} < 8.0$, the heterometal complex $[(\text{NiAla})\text{Edta}(\text{CoAla})]^{2-}$ is formed, with a maximal degree of accumulation of 94% at pH 5.0. The second complex $[(\text{NiAla})_2\text{Edta}(\text{CoAla}_2)]^{4-}$ is formed at $\text{pH} > 5.0$, and its 100% yield is reached at $\text{pH} > 8.0$. The formation of this complex can be described by the following partial equations:



The equilibrium constants of these reactions and stability constants of the heterobinuclear complex are presented in Table 2.

In complexes with the 1 : 1 : 4 : 1 molar ratio of the components, each iminodiacetate moiety of EDTA is bound to the metal ion only through one carboxyl group, while the second remains free, and the coordination sphere of the metal ions is completely saturated with alanine. The schematic structure (a) and model (b) of a molecule of this complex, obtained by 3D optimization, can be visualized as follows:



Mathematical modeling in the Co(II)–Ni(II)–HAla–EDTA system with the 1 : 2 : 6 : 1 and 2 : 1 : 6 : 1 molar ratios of the components has shown that uncoordinated Co(II) and Ni(II) ions as well as mononuclear Ni^{2+} complexes with EDTA are dominating in an

acid medium. In weak acid and neutral solutions, homo- and heterobinuclear complexes with EDTA and alanine are formed (Fig. 3). The maximum degree of accumulation 100% of trinuclear complexes is observed at $\text{pH} > 8.0$. Trinuclear heteroligand com-

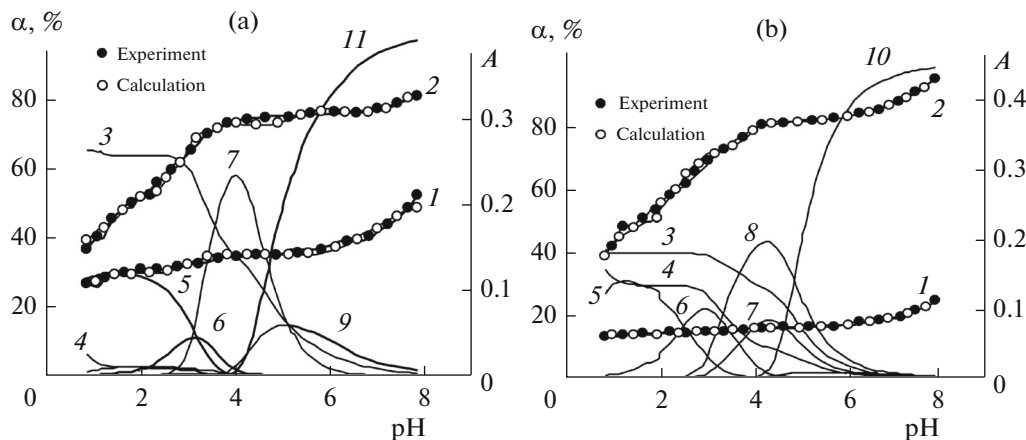
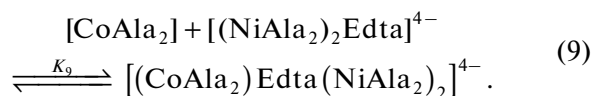
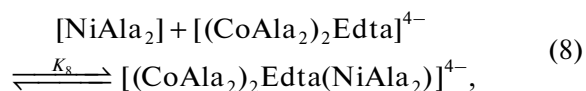
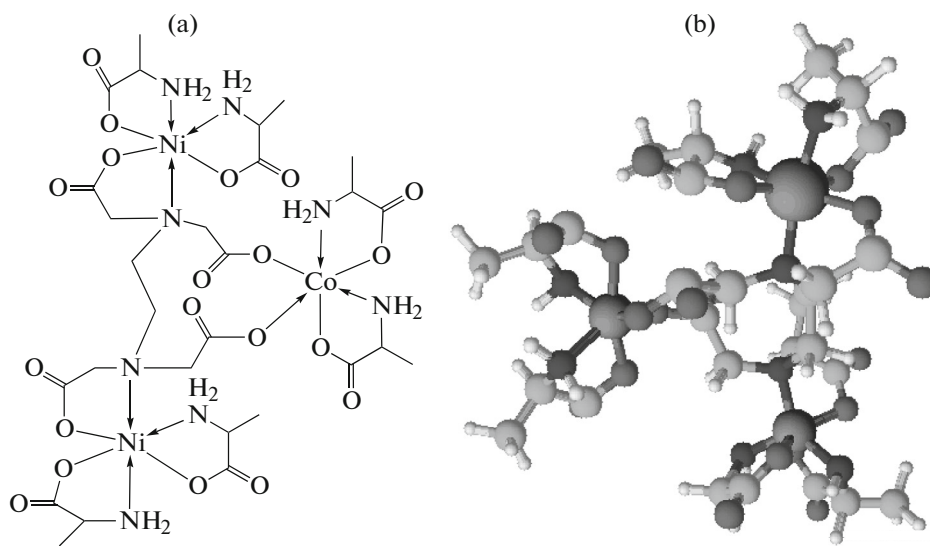


Fig. 3. Degree of accumulation (α) and absorbance (A) vs. pH in the Co(II)–Ni(II)–HAla–EDTA system at the molar ratio (a) 2 : 1 : 6 : 1 and (b) 1 : 2 : 6 : 1: curves $A = f(\text{pH})$ for $\lambda = (1)$ 490 and (2) 985 nm; (3) Co^{2+} , (4) Ni^{2+} , (5) $[\text{NiHEDta}]^-$, (6) $[\text{NiEdta}]^{2-}$, (7) $[(\text{NiAla})\text{Edta}(\text{CoAla})]^{2-}$, (8) $[(\text{NiAla})\text{Edta}(\text{NiAla})]^{2-}$, (9) $[(\text{NiAla})_2\text{Edta}(\text{CoAla}_2)]^{4-}$, (10) $[(\text{NiAla}_2)_2\text{Edta}(\text{CoAla}_2)]^{4-}$, and (11) $[(\text{CoAla}_2)_2\text{Edta}(\text{NiAla}_2)]^{4-}$. (a) $C_{\text{Ni}^{2+}} = 1.25 \times 10^{-2}$ mol/L; (b) $C_{\text{Co}^{2+}} = 1.25 \times 10^{-2}$ mol/L.

plexes are formed at $\text{pH} > 4.0$ by the following equations (the corresponding equilibrium constants are presented in Table 2):

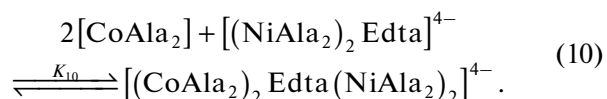


We can assume that the coordination spheres of two metal ions in the trinuclear complex are linked with each other through the EDTA diaminoethane bridge with the bidentate coordination of two iminodiacetate groups. The third metal ion is bound through the two remaining acetate groups from different "halves" of the EDTA molecule. The coordination sphere of each metal ion also contains two alanine residues. As an example, the schematic structure (a) and the model of the $[(\text{NiAla}_2)_2\text{Edta}(\text{CoAla}_2)]^{4-}$ complex (b) obtained by 3D optimization are shown below:

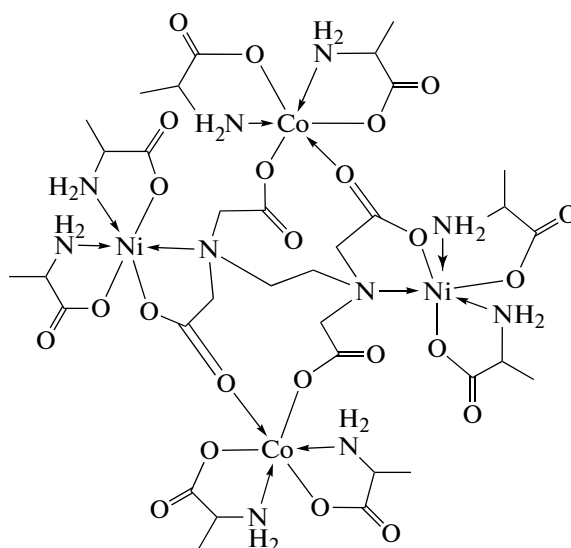


Mathematical modeling of speciation equilibria in the $\text{Co(II)}-\text{Ni(II)}-\text{HAla}-\text{EDTA}$ system at the 2 : 2 : 8 : 1 molar ratio of the components in the range $3.0 < \text{pH} < 8.0$ shows that the major species in solution are various homo- and heterobinuclear complexonates. At $\text{pH} > 5.0$, the tetranuclear $[(\text{NiAla}_2)_2\text{Edta}(\text{CoAla}_2)_2]^{4-}$ complex accumulates in solution (Fig. 4). The formation of the

tetranuclear complex can be represented by one of several possible equations:

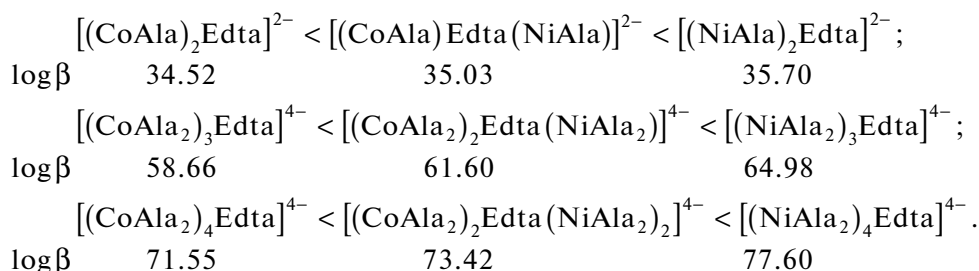


The structure of the tetranuclear complex can be schematically presented in the following manner:



Thus, our results are evidence that, when the Co(II) and Ni(II) ions are in excess with respect to EDTA and an additional ligand, alanine, is present in solution, heteropolynuclear heteroligand complexes $[\text{Co}_x\text{Ni}_y\text{Ala}_z\text{Edta}]^{2(x+y)-z-4}$ ($x = 1-2, y = 1-2, z = 2, 4, 6, 8$) are formed. This logically completes our previous data on the formation of homopolynuclear Ni(II) complexes with EDTA and a number of low-denticity ligands, such as ethylenediamine, dipyriddy, amino acids (glycine, alanine, serine, histidine), IDA, and NTA [5–7]. The coordination modes of the Ni(II) and Co(II) ions in tri- and tetranuclear complexes are nonequivalent; however, available spectral characteristics do not allow a conclusion about the mutual

arrangement of these metals. Even in simpler complexes $[(\text{NiX}_2)_4\text{Edta}]$ ($X = \text{En, Gly}$), the shape of absorption bands does not reflect differences between the coordination spheres of Ni(II) ions [3]. Similar electronic structures and close ionic radii of Co(II) ($3d^7, r = 72 \text{ pm}$) and Ni(II) ($3d^8, r = 69 \text{ pm}$) are responsible for their good compatibility in polynuclear ethylenediaminetetraacetates and makes it possible to substitute one cation for the other without noticeable changes in the complex structure. The stability of the heteropolynuclear complexes is intermediate between the stabilities of the corresponding homopolynuclear complexes and increases in the following series:



In all polynuclear complexes, EDTA acts as a structure-forming tri- or bidentate (with respect to each metal cation) ligand; in the tetranuclear complexes, eight of the ten donor atoms of EDTA are involved in coordination, which is possible because of the high flexibility of the EDTA molecule. For stabilization of polynuclear ethylenediaminetetraacetates, a

stoichiometric excess of the secondary bidentate ligand is necessary to achieve complete saturation of the coordination spheres of all metal ions.

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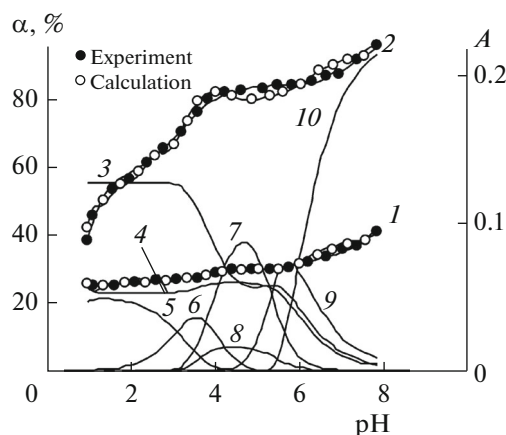


Fig. 4. Degree of accumulation (α) and absorbance (A) vs. pH in the Co(II)–Ni(II)–HAla–EDTA system at the molar ratio 2 : 2 : 8 : 1: curves $A = f(\text{pH})$ for $\lambda = (1)$ 490 and (2) 985 nm; (3) Co^{2+} , (4) Ni^{2+} , (5) $[\text{NiHEdta}]^-$, (6) $[\text{NiEdta}]^{2-}$, (7) $[(\text{NiAla})\text{Edta}(\text{CoAla})]^{2-}$, (8) $[(\text{CoAla})\text{Edta}(\text{NiAla})]^{2-}$, (9) $[(\text{NiAla}_2)\text{Edta}(\text{NiAla}_2)]^{4-}$, and (10) $[(\text{NiAla}_2)_2\text{Edta}(\text{CoAla}_2)]^{4-}$. $C_{\text{Co}^{2+}} = C_{\text{Ni}^{2+}} = 1.25 \times 10^{-2} \text{ mol/L}$.

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