PHYSICAL CHEMISTRY
OF SOLUTIONS

Heteropolynuclear Cobalt(II) and Nickel(II) Ethylenediaminetetraacetates in Aqueous Solutions of Aminoethanoic Acid

V. I. Kornev, Ghusoon Faidhi Alabdullah, T. N. Kropacheva, and E. V. Batueva

Udmurt State University, Universitetskaya ul. 1/1, Izhevsk, Udmurtia, 426034 Russia

e-mail: nah@uni.udm.ru

Received July 9, 2015

Abstract—Complexation in the Co(II)−Ni(II)−aminoethanoic acid (HGly)−EDTA (H_4Edta) system was studied at different molar ratios of components by absorption spectrophotometry. The mathematical modeling of $A = f(pH)$ curves was used to establish that bi-, tri-, and tetranuclear heteroligand complexes like $[(CoGly)Edta(NiGly)]^{2-}$, $[(CoGly_2)Edta(NiGly_2)]^{4-}$, $[(CoGly_2)Edta(NiGly_2)_2]^{4-}$, $[(CoGly_2)_2Edta(NiGly_2)]^{4-}$, and $[(CoGly_2)_2Edta(NiGly_2)_2]^{4-}$, whose accumulation fraction attained 80−100% at optimal pH values, were formed depending on the ratio of reagents and the acidity of a medium. The formation equilibrium and total stability constants of these complexes were calculated, and a hypothesis about their structure was made.

Studies of regularities in the formation of heteroligand polynuclear complexes are one new topic of coordination chemistry. Systems where a complex incorporates several different metal ions and several bulky organic ligands are of special interest. They raise the question about mutual effects of metals and ligands and their compatibility in the coordination sphere. In such systems, polynuclear heteroligand complexes can be formed alongside with mononuclear heteroligand complexes due to that a polydentate ligand does not completely unleash its donating ability in the inner coordination sphere of one central complexating ion. Just for this reason a mononuclear complex acts as a kind of metal chelating ligand, which can coordinate the second metal ion of the same or different nature.

In this work, the coordination equilibria of the formation of cobalt(II) and nickel(II) polynuclear heteroligand complexes with ethylenediaminetetraacetic (EDTA, H_4Edta) and aminoethanoic (glycine, HGly) acids were studied in details. There exist no literature information on this matter except [1], where the formation of the $[(CoGly_2)Edta(NiGly_2)]^{4-}$ complex ($\log\beta = 36.66$) was established when studying complexation in the Co(II)−Ni(II)−HGly−EDTA system.

EXPERIMENTAL

Complexation processes were studied spectrophotometrically. The absorbance of solutions was measured on an SF-2000 spectrophotometer using a specially manufactured setup for spectrophotometric titration with silica glasses ($l = 1$ cm). This setup provides the simultaneous measurement of pH and the absorbance of solution. Wavelengths were adjusted in the region of 300−1000 nm with an accuracy of ±0.1 nm. The activity of hydrogen ions was measured on an I-160 ion meter using an ES-10601/7 working electrode and an ESR-10101 reference electrode. Required pH values were adjusted with solutions of NaOH and $HClO_4$ (pure for analysis grade). A constant ionic strength ($I = 0.5$) was maintained with a solution of $NaClO_4$ (pure for analysis grade). Studies were performed at room temperature (20 ± 2)°C. Solutions of cobalt(II) and nickel(II) sulfates were prepared by dissolving $MSO_4 \cdot 7H_2O$ salts in water; the precise concentration of metal(II) ions in the resulting solution was established complexonometrically. Solutions of EDTA and aminoethanoic acids were prepared by dissolving their samples (chemically pure) in distilled water. The mathematical processing of results was performed using the software CPESSP [2] and HypSpec [3]. The models of complexes were constructed using the ACD/Labs software [4].

RESULTS AND DISCUSSION

The study of coordination equilibria in systems containing different metal(II) hydroxo complexes and various protonated forms of ligands is a complex problem. Since the results of modeling depend on the set of particles that describes the system, the selection of a correct set of complex forms is of principal importance. In the software used by us, the question about
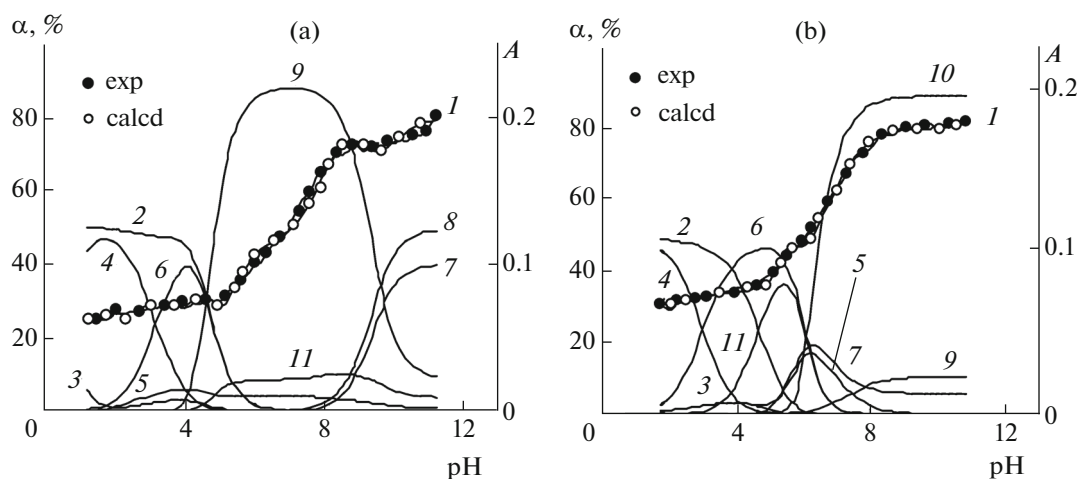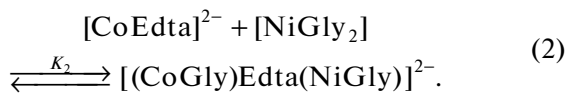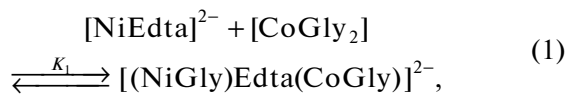
Fig. 1. Accumulation fraction (α) and absorbance (A) of the complexes in the Co(II)−Ni(II)−HGly−Edta system versus pH at a ratio of (a) 1 : 1 : 2 : 1 and (b) 1 : 1 : 4 : 1: (*1*) $A = f(\text{pH})$, (*2*) Co^{2+}, (*3*) Ni^{2+}, (*4*) $[NiHEdta]^-$, (*5*) $[CoEdta]^{2-}$, (*6*) $[NiEdta]^{2-}$, (*7*) $[NiGly_3]^-$, (*8*) $[CoGlyEdta]^{3-}$, (*9*) $[(CoGly)Edta(NiGly)]^{2-}$, (*10*) $[(CoGly_2)Edta(NiGly_2)]^{4-}$, and (*11*) $[NiGly_2]$. $c_{Co^{2+}} = c_{Ni^{2+}} = 1.25 \times 10^{-2}$ mol/L; $\lambda = 490$ nm.

the reasonability of taking into consideration a complex form of a metal or a ligand was solved by minimizing the Fischer criterion, which took into account the deviations between experimental and calculated absorbances (A) for each measured value. The software used in this work provides the possibility of estimating the parameters of an equilibrium system and their stoichiometry and the equilibrium formation and stability constants of complexes with sufficient reliability. The protolytic and coordination equilibria in a solution were described using the following literature data: the cobalt(II) and nickel(II) monomeric hydrolysis constants [5], the EDTA dissociation and protonation constants [6], and the aminoethanoic acid dissociation constants [5].
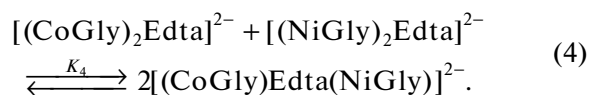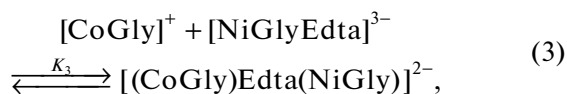
The modeling of equilibria in compliance with the selected complexation model was performed via the analysis of electron absorption spectra (EASs) used as the basis to obtain $A = f(\text{pH})$ curves at different wavelengths. In all cases, the consideration of $A = f(\lambda)$ and $A = f(\text{pH})$ curves showed that the formation of heteroligand polynuclear complexes must be taken into account in each of the studied systems. In the process of calculations, we considered several models consisting of different sets of particles, such as $[M(OH)_j]^{2-j}$ ($j = 0$–3), $[H_iEdta]^{i-4}$ ($i = 0$–6), $[MH_iEdta]^{i-2}$ ($i = 0$–2), $[M(OH)_jEdta]^{(j+2)-}$ ($j = 0$–1), $[MGly_n]^{2-n}$ ($n = 1$–3), and $[M_mGly_nEdta]^{2m-}$ ($m = 2$–4, $n = 2$–8).

The compositions of the complexes formed in the Co(II)−Ni(II)−HGly−EDTA systems and the character of coordination equilibria depend not only on the acidity of the medium, but also on the concentration ratios between the components.

At a molar component ratio of 1 : 1 : 2 : 1 in an acidic medium with pH < 4, a solution predominantly contains uncomplexed Co^{2+} ions and mononuclear metal ethylenediaminetetraacetates (Fig. 1a). In the region of 4 < pH < 8, heterobinuclear complexes are formed in the system and, probably, can be constituted by different initial complexes. For example, the possible reactions between $[MEdta]^{2-}$ and cobalt(II) or nickel(II) glycinate $[MGly_2]$ taken as reacting components are the following:

$$[NiEdta]^{2-} + [CoGly_2]$$
$$\xrightleftharpoons{K_1} [(NiGly)Edta(CoGly)]^{2-}, \quad (1)$$

$$[CoEdta]^{2-} + [NiGly_2]$$
$$\xrightleftharpoons{K_2} [(CoGly)Edta(NiGly)]^{2-}. \quad (2)$$

Binuclear complexes can decompose at pH > 8. The heterobinuclear complex can also be formed by the reactions

$$[CoGly]^+ + [NiGlyEdta]^{3-}$$
$$\xrightleftharpoons{K_3} [(CoGly)Edta(NiGly)]^{2-}, \quad (3)$$

$$[(CoGly)_2Edta]^{2-} + [(NiGly)_2Edta]^{2-}$$
$$\xrightleftharpoons{K_4} 2[(CoGly)Edta(NiGly)]^{2-}. \quad (4)$$

The maximum accumulation fraction of the heterobinuclear complexes formed by reactions (1)−(4) is nearly 90% (Fig. 1a and table). The structure of such complexes can be schematized as follows:
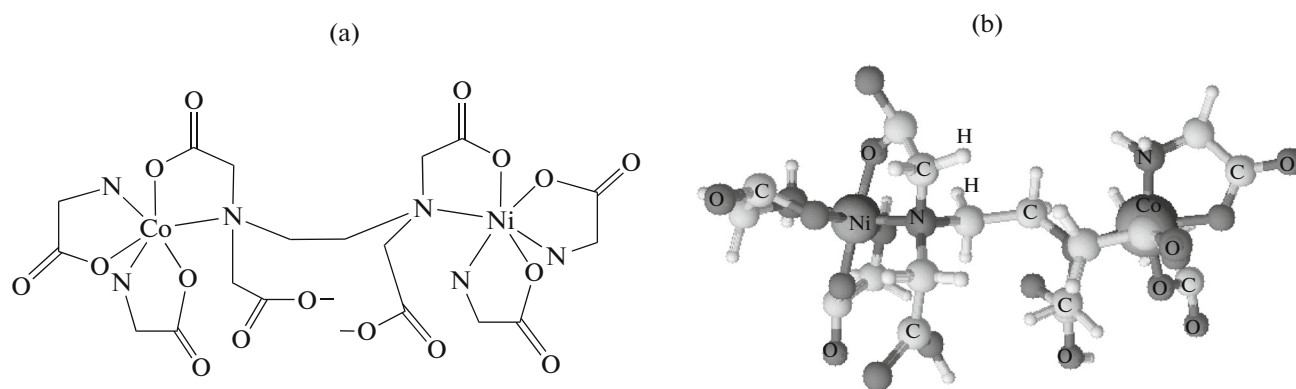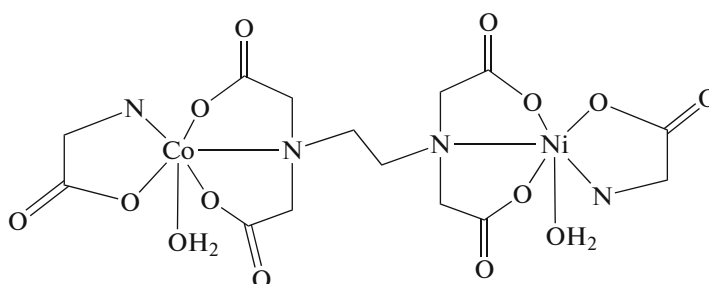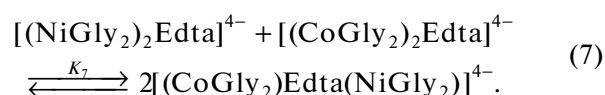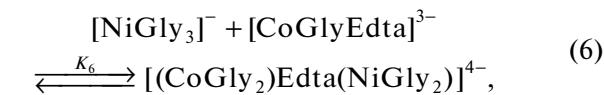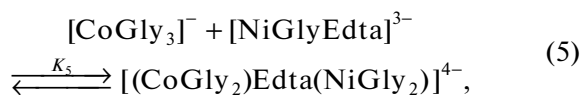
(a) (b)

Fig. 2. (a) Hypothetic structure and (b) 3D model of $[(CoGly_2)Edta(NiGly_2)]^{4-}$.

The experimental and calculated $A = f(pH)$ curves and the fractional distribution of the complexes depending on pH at a molar ratio of components in the Co(II)−Ni(II)−HGly−EDTA system of 1 : 1 : 4 : 1 are plotted in Fig. 1b. From Fig. 1b it follows that uncomplexed Co^{2+} ions and mononuclear cobalt(II) and nickel(II) complexes with EDTA and glycine predominate in the solution within a wide range of 2 < pH < 8.

The formation of the heterobinuclear complex can be described by the following particular reactions:

$$[CoGly_3]^- + [NiGlyEdta]^{3-} \xrightarrow{K_5} [(CoGly_2)Edta(NiGly_2)]^{4-}, \quad (5)$$

$$[NiGly_3]^- + [CoGlyEdta]^{3-} \xrightarrow{K_6} [(CoGly_2)Edta(NiGly_2)]^{4-}, \quad (6)$$

$$[(NiGly_2)_2Edta]^{4-} + [(CoGly_2)_2Edta]^{4-} \xrightarrow{K_7} 2[(CoGly_2)Edta(NiGly_2)]^{4-}. \quad (7)$$

It is possible to hypothesize that the octahedral spheres of the Co^{2+} and Ni^{2+} ions in the $[(CoGly_2)Edta(NiGly_2)]^{4-}$ complex are linked to each other via an EDTA bridge (Fig. 2). In this case, the two acetate groups belonging to different nitrogen atoms do not participate in the formation of the coordination sphere. The scheme and model constructed for this

Formation equilibrium and stability constants of complexes

| Complex	Reaction	α_{max}, %	pH optimal	$\log K_i$	$\log \beta$
$[(CoGly)Edta(NiGly)]^{2-}$	(1)	88	6.0	3.74	31.39 ± 0.21
$[(CoGly)Edta(NiGly)]^{2-}$	(2)	87	7.0	4.59	31.62 ± 0.02
$[(CoGly)Edta(NiGly)]^{2-}$	(3)	94	8.0−10.0	4.86	31.56 ± 0.10
$[(CoGly)Edta(NiGly)]^{2-}$	(4)	87	9.0−11.0	1.34	31.27 ± 0.30
$[(CoGly_2)Edta(NiGly_2)]^{4-}$	(5)	87	9.0−11.0	3.66	36.83 ± 0.04
$[(CoGly_2)Edta(NiGly_2)]^{4-}$	(6)	87	8.0−11.0	3.86	36.26 ± 0.51
$[(CoGly_2)Edta(NiGly_2)]^{4-}$	(7)	79	8.0−11.0	1.76	36.61 ± 0.20
$[(CoGly_2)Edta(NiGly_2)_2]^{4-}$	(8)	95	7.0	3.83	52.18 ± 0.02
$[(CoGly_2)_2Edta(NiGly_2)]^{4-}$	(9)	92	>10	4.77	47.24 ± 0.04
$[(CoGly_2)_2Edta(NiGly_2)_2]^{4-}$	(10)	98	>10	9.07	61.74 ± 0.03
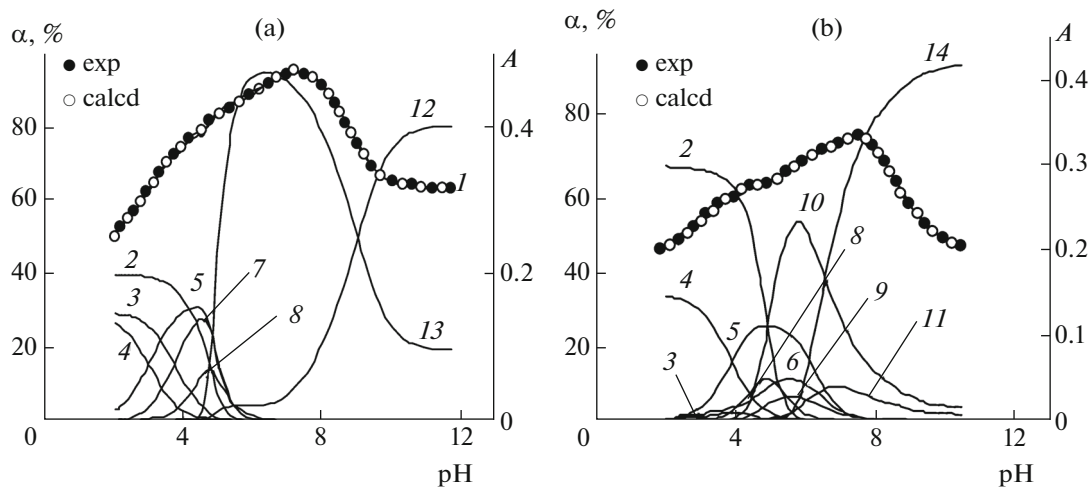
Fig. 3. Accumulation fraction (α) and absorbance (A) of the complexes in the Co(II)−Ni(II)−HGly−Edta system versus pH at a ratio of (a) $1 : 2 : 6 : 1$ and (b) $2 : 1 : 6 : 1$: (*1*) $A = f(\text{pH})$, (*2*) Co^{2+}, (*3*) Ni^{2+}, (*4*) $[\text{NiHEdta}]^-$, (*5*) $[\text{NiEdta}]^{2-}$, (*6*) $[\text{CoEdta}]^{2-}$, (*7*) $[\text{NiGly}]^+$, (*8*) $[\text{CoGly}]^+$, (*9*) $[\text{NiGly}_2]$, (*10*) $[\text{CoGly}_2]$, (*11*) $[\text{CoGlyEdta}]^{3-}$, (*12*) $[(\text{NiGly}_2)_2\text{Edta}]^{4-}$, (*13*) $[(\text{NiGly}_2)_2\text{Edta}(\text{CoGly}_2)]^{4-}$, and (*14*) $[(\text{CoGly}_2)_2\text{Edta}(\text{NiGly}_2)]^{4-}$. $c_{\text{Co}^{2+}} = 1.25 \times 10^{-2}$ mol/L (a), $c_{\text{Ni}^{2+}} = 1.25 \times 10^{-2}$ mol/L (b), $\lambda = 983$ nm.
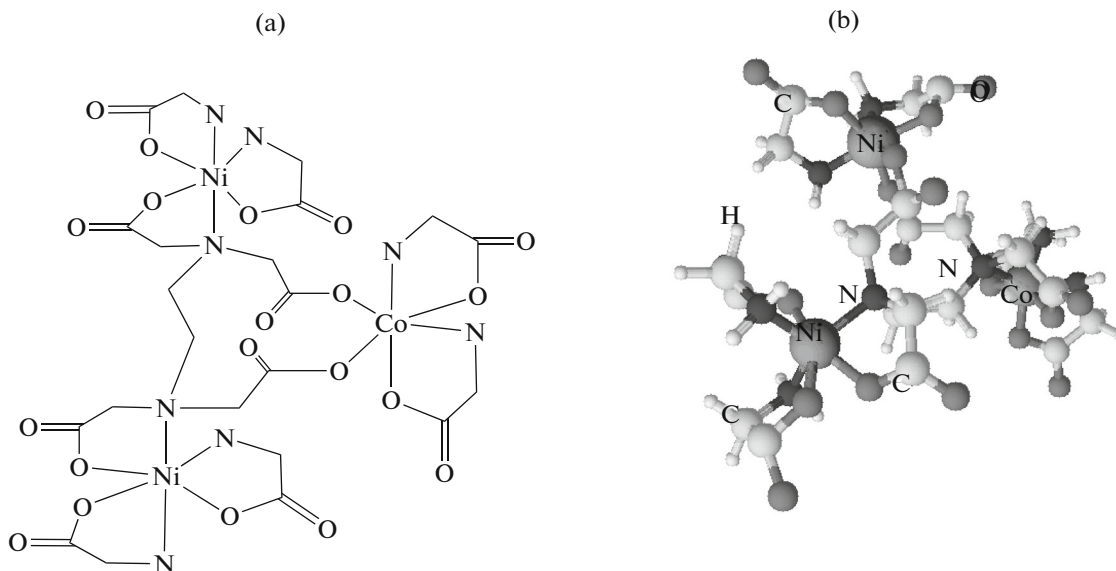

Fig. 4. (a) Hypothetic structure and (b) 3D model of $[(\text{NiGly}_2)_2\text{Edta}(\text{CoGly}_2)]^{4-}$.

complex in compliance with 3D optimization are shown in Fig. 2.

The experimental and calculated $A = f(\text{pH})$ curves and fractional distribution of complexes depending on pH at a molar component ratio of 1 : 2 : 6 : 1 in the Co(II)−Ni(II)−HGly−EDTA system are plotted in Fig. 3a.

From Fig. 3a it follows that mononuclear nickel(II) complexes with EDTA and glycine predominate in an acidic medium at 2 < pH < 5. The trinuclear heteroligand complexonate is formed at pH > 4 by the reaction

$$[\text{CoGly}_2] + [(\text{NiGly}_2)_2\text{Edta}]^{4-}$$
$$\xrightleftharpoons{K_8} [(\text{NiGly}_2)_2\text{Edta}(\text{CoGly}_2)]^{4-}. \quad (8)$$
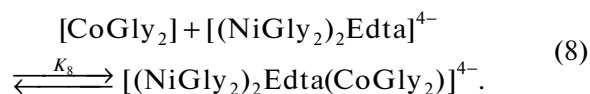
It is possible to hypothesize that Ni^{2+} ions in trinuclear complex $[(\text{NiGly}_2)_2\text{Edta}(\text{CoGly}_2)]^{4-}$ are linked to each other via a diaminoethane EDTA bridge (Fig. 4). The Co^{2+} ion is attached to the complex by means of bonding to two EDTA acetate groups. The octahedral spheres of all metal ions additionally contain two glycine residue each.

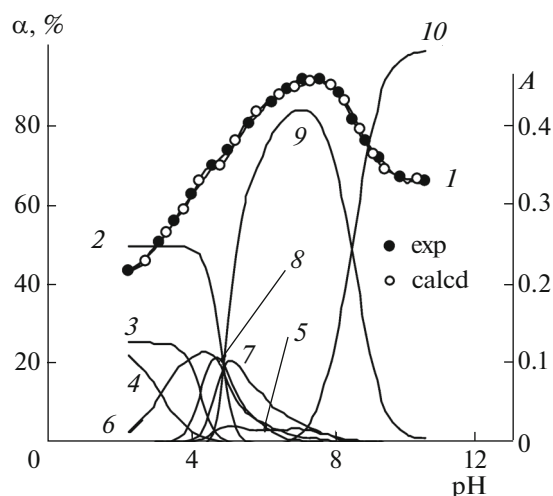The analysis of EAS for the solution containing cobalt(II) and nickel(II) salts, glycine, and EDTA at a

Fig. 5. Absorbance (A) and accumulation fraction (α) of the complexes in the Co(II)−Ni(II)−HGly−Edta system versus pH at a ratio of 2 : 2 : 8 : 1: (*1*) $A = f$(pH), (*2*) Co^{2+}, (*3*) Ni^{2+}, (*4*) $[NiHEdta]^-$, (*5*) $[CoEdta]^{2-}$, (*6*) $[NiEdta]^{2-}$, (*7*) $[CoGly_2]$, (*8*) $[NiGly_2]$, (*9*) $[(CoGly_2)_2Edta]^{4-}$, and (*10*) $[(CoGly_2)_2Edta(NiGly_2)_2]^{4-}$. $c_{Co^{2+}} = c_{Ni^{2+}} = 1.25 \times 10^{-2}$ mol/L, $\lambda = 983$ nm.

molar ratio of 2 : 1 : 6 : 1 shows that the mononuclear complexes are formed predominantly in weakly acidic or neutral media at 2 < pH < 10 (Fig. 3b). The trinu-

clear heteroligand complex is formed at pH > 5 by the reaction

$$[NiGly_2] + [(CoGly_2)_2Edta]^{4-}$$
$$\xrightarrow{K_9} [(CoGly_2)_2Edta(NiGly_2)]^{4-}. \quad (9)$$
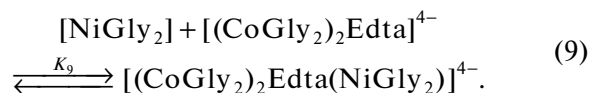
The modeling of complexation processes in the Co(II)−Ni(II)−HGly−EDTA system with a molar ratio of 2 : 2 : 8 : 1 shows that the mononuclear cobalt(II) and nickel(II) complexes with EDTA and glycine are formed in an acidic medium at 2 < pH < 8. A specific feature of this system is that the binuclear cobalt(II) complex with a maximum accumulation fraction of nearly 80% exists in solution within a wide range of 4 < pH < 10 (Fig. 5). The formation of the tetranuclear complex begins at pH > 6.0, and its yield attains 100% at pH > 9.0. The formation of the tetra-nuclear complex can be described by the following reaction:

$$2[NiGly_2] + [(CoGly_2)_2Edta]^{4-}$$
$$\xrightarrow{K_{10}} [(CoGly_2)_2Edta(NiGly_2)_2]^{4-}. \quad (10)$$
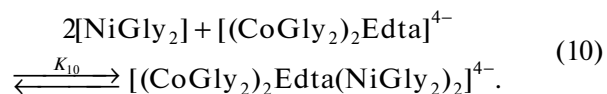
The octahedral spheres of all the four metal ions in this complex are linked to each other via an EDTA molecule, which forms two covalent bonds with each Co^{2+} and Ni^{2+} ions. The four bonds among them are formed by means of the EDTA carboxylate groups, and the other four coordination bonds appear due to the two nitrogen and two oxygen of carboxylate
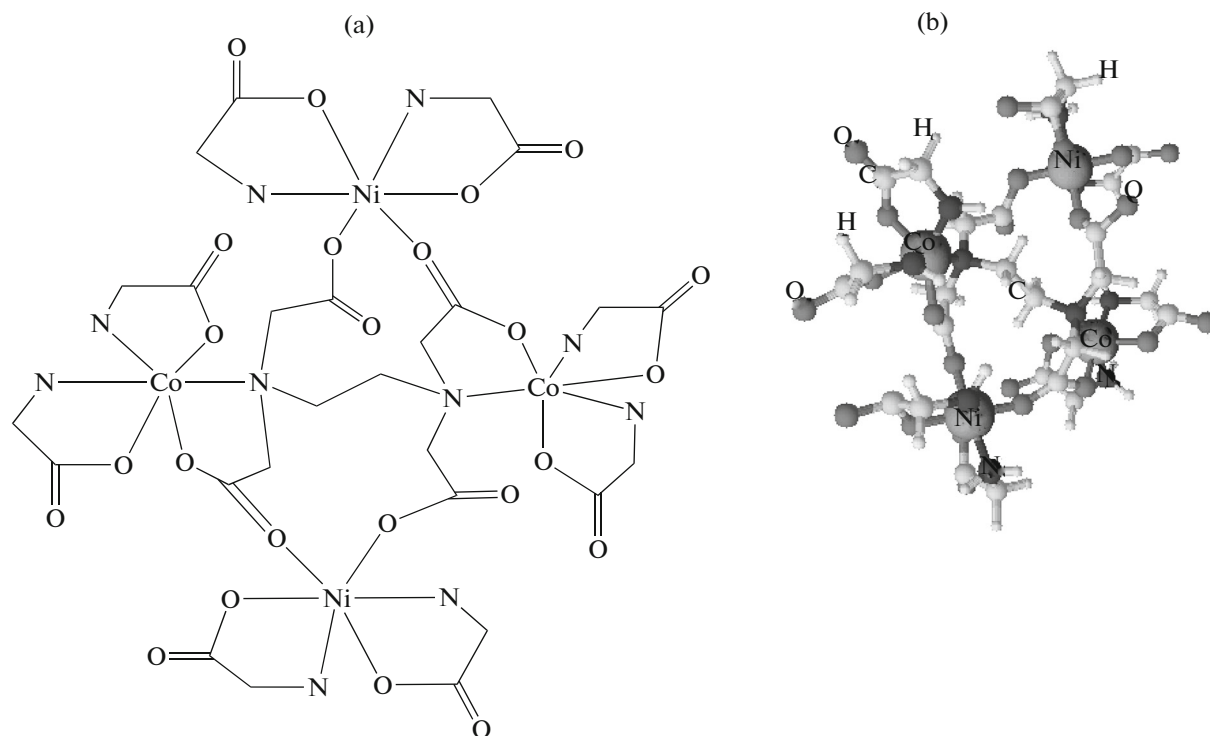

Fig. 6. (a) Hypothetic structure and (b) 3D model of $[(CoGly_2)_2Edta(NiGly_2)_2]^{4-}$.

groups. The coordination spheres of metals additionally containe two glycine molecules each (Fig. 6).

Hence, the results of this work show that mixed-ligand heteropolynuclear compelxes $[Co_xNi_yGly_zEdta]^{2x+2y-4-z}$ (x, y = 1, 2; z = 2, 4, 6, 8) are formed at an excess of Co^{2+} and Ni^{2+} cations in an EDTA solution. This logically supplements our earlier obtained data on the formation of homopolynuclear EDTA complexes with Ni^{2+} cations and a wide range of low-dentate ligands $[Ni_yL_zEdta]^{2y-4-nz}$ (y = 1, 2; z = 2, 4, 6, 8) (L^{n-} is dipyridyl, ethylenediamine, amino acids, IDA, NTA) [7–9]. In these complexes, EDTA acts as a tri- or bidentate structure-forming ligand (with respect to each metal cation), and the further saturation of the coordination capacity of cations occurs due to secondary low-dentate ligands. The similarity between the electronic structure and ionic radii of Co^{2+} and Ni^{2+} cause their good compatibility in polynuclear EDTA complexes, though no completely equivalent coordination of these ions takes place in them. The role of the nature of a secondary ligand in the stabilization of polynuclear EDTA complexes seems to be small, as proved by a wide spectrum of such ligands incorporated into these complexes.

REFERENCES

1. N. N. Barkhanova, N. M. Dyatlova, and A. Ya. Fridman, Zh. Neorg. Khim. **18**, 1489 (1973).

2. Yu. I. Sal'nikov, A. N. Glebov, and F. V. Devyatov, *Polynulear Complexes in Solution* (Izd–vo Kazansk. Univ., Kazan, 1989) [in Russian].

3. P. Gans, A. Sabatini, and A. Vacca, Talanta **43**, 1739 (1996).

4. www.acdlabs.com (addressed 2013-08-25).

5. Yu. Yu. Lur'e, *The Handbook of Analytical Chemistry* (Khimiya, Moscow, 1979) [in Russian].

6. G. S. Tereshin and I. V. Tananaev, Zh. Anal. Khim. **16**, 523 (1961).

7. V. I. Kornev, N. S. Buldakova, and M. V. Didik, Russ. J. Inorg. Chem. **59**, 626 (2014).

8. V. I. Kornev and N. S. Buldakova, Russ. J. Gen. Chem. **84**, 1587 (2014).

9. V. I. Kornev and N. S. Buldakova, Butlerovsk. Soobshch. **34** (6), 98 (2013).

Translated by E. Glushachenkova