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Comparative Study of the Formation of Heterometallic Diethylenetriaminopentaacetates of Cobalt(II), Nickel(II), and Copper(II) in Aqueous Solutions

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Abstract—The formation of heterobinuclear complexes of cobalt(II), nickel(II), and copper(II) with diethylenetriaminopentaacetic acid (dtpa, H₅dtpa) in aqueous solutions was studied by spectrophotometry. The effect the pH has on the formation of the coordination sphere of heterobimetallic complex particles in ternary systems with an equimolar ratio of components is established. The thermodynamic stability of homo- and heterobinuclear complexes is estimated via mathematical modeling of the formation of complex particles of a certain stoichiometry with limited logarithmic processing of experimental data for specific polycomponent systems. Numerical values of logarithms of the constant of stability ($\log \beta$) of homobinuclear chelates [Me₂dtpa][−] are 24.46 ± 0.1 ; 25.53 ± 0.1 and 27.03 ± 0.1 for Co(II), Ni(II), and Cu(II), respectively. Values $\log \beta$ are 25.43 ± 0.1 ; 25.60 ± 0.1 ; 17.83 ± 0.09 ; and 27.57 ± 0.1 for heterobimetallic diethylenetriaminopentaacetates [CoNi₂dtpa][−], [CoCu₂dtpa][−], [NiCuHdtpa]⁰, and [NiCu₂dtpa][−], respectively.

Keywords: heterobimetallic complexes of cobalt(II), nickel(II), and copper(II), polyaminopolycarboxylic acids

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INTRODUCTION

Studying conditions of the formation and stability of complex compounds containing heterometallic centers is a priority in the development of modern coordination chemistry. The combination of different central metal atoms in the composition of such compounds allows targeted regulation of the structure of substances and the creation of materials based on them with certain functional properties and characteristics. Bimetallic complex compounds of *d*-elements currently form the basis of heterogeneous catalysts for organic synthesis [1], chemotherapeutic drugs with improved pharmacokinetic and pharmacodynamic properties [2], and drugs with antifungal activity [3]. They are precursors for obtaining nanooxides of superparamagnets and ferromagnets [4–6]. Biochemical studies have also shown that heteronuclear complexes enhance the catalytic oxidase activity during the atmospheric fixation of carbon dioxide [7] and activate molecular oxygen during the formation of superoxide complexes [8].

The high potential denticity and geometric flexibility of diethylenetriaminopentaacetic acid (dtpa, H₅dtpa) and the dynamic ease of changing the lengths of coordination bonds when substituting one central

metal atom for another ensure the effectiveness of using this acid as a ligand for the joint chelation of cations of different metals. A variety of combinations of central atoms (germanium(IV)–copper(II) [9], samarium(III), europium(III), terbium(III), or dysprosium(III)–germanium(IV) [10], europium(III) or dysprosium(III)–ruthenium(II) [11], europium(III), gadolinium(III), or samarium(III)–cadmium(II) [12], oxovanadium(IV)–cobalt(II) or nickel(II) [13], oxovanadium(IV)–titanium(III), chromium(III), or manganese(II) [14], cobalt(II)–nickel(II) [15]) in the composition of complex particles in heterobinuclear chelates is determined in a number of ways to coordinate donor oxygen and nitrogen atoms of the dtpa molecule.

This work presents results of a comparative spectrophotometric study of the formation of heterobinuclear complex compounds dtpa with cobalt(II), nickel(II), and copper(II) cations to determine the features of chelation in ternary systems and the composition and stability of heterobimetallic chelates in aqueous solutions. The data can serve as a basis for targeted synthesis and isolation from solutions of polymeric organometallic compounds with certain functional properties.

EXPERIMENTAL

Electronic absorption spectra (EAS) of our solutions were recorded on an SF-2000 spectrophotometer (Spektr, Russia). The main characteristics of the solutions were monitored on an Anion-4100 pH meter (Infrapak-Analit, Russia) equipped with an ESLK-01.7 combined electrode. The absolute error of pH measurement was ± 0.01 . All measurements were performed in air at a temperature of $20 \pm 2^\circ\text{C}$. Chemically pure reagents were used in the work. The required acidity of the solutions was adjusted with 1.0 and 0.1 M solutions of hydrochloric acid and sodium hydroxide prepared from HCl (SigmaTek, Russia) and NaOH (LenReaktiv, Russia) reagents. The ionic strength was maintained with a 0.1 M potassium chloride solution prepared from the KCl reagent (Khimreaktiv, Russia). The initial 0.1 M solutions of cobalt(II) and nickel(II) chlorides, copper(II) sulfate, and diethylenetriamine-pentaacetic acid were prepared by dissolving accurately weighed portions of reagents $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Vekton, Russia) and H_5dtpa (Acros Organics, Belgium) in distilled water. H_5dtpa was dissolved by adding sodium hydroxide to form a soluble trisodium salt. Solutions of the studied binary and ternary systems were obtained by mixing the initial solutions of metal salts and a complexing agent in amounts corresponding to a certain molar ratio of the components, and subsequently adding an acid or alkali to create the required acidity of the medium. The formation of complex compounds was registered from changes in the electronic absorption spectra of solutions of binary and ternary systems and the optical density at the characteristic maxima of light absorption bands with varying composition of solutions.

The known limited logarithmic approach [16, 17] was used to calculate the quantitative characteristics of complexation and the resulting homo- and heterometallic complex particles, based on mathematical processing of the experimental dependences of the optical density on pH for specific multicomponent complex-forming systems. To model the formation of complexes of a certain stoichiometry with the dominant forms of ligand ionization in the pH range of complex formation in ternary systems, we used the data for constructing a diagram of the distribution of ligand ionization forms depending on pH, along with the constants of stability of homonuclear chelates, calculated earlier from the results of a similar spectrophotometric study of binary systems.

Complexation in binary and ternary systems was modeled based on the general scheme of interaction between metal cations (M) and the ligand:



where x is the number of complexing cations in the complex ion, and z is the number of protons split off

the dominant form of ligand ionization $\text{H}_y\text{dtpa}^{y-5}$ in the pH range of complexation.

Numerical values of the constants of equilibrium of complex formation (K_{eq}) and stability (β) of complex particles were calculated using the relations

$$K_{\text{eq}} = \frac{(A_x - A_{\text{min}})(A_{\text{max}} - A_{\text{min}})^x [\text{H}^+]^z}{(A_{\text{max}} - A_x)^x (pA_{\text{max}} - (p-1)A_{\text{min}} - A_x) C_{\text{M}}^x \varphi},$$

$$\beta = \prod_i K_{\text{ai}},$$

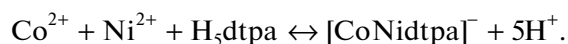
where A_{max} , A_{min} , and A_x are the maximum, minimum, and intermediate values of the optical density of solutions in the pH range of complexation; p is the multiplicity of the ligand excess in solution; φ is the average mole fraction of the ligand ionization form that dominates in the pH range of complexation; C_{M} is the molar concentration of metal cations in solution, mol L^{-1} ; and K_{ai} are the stepwise constants of ligand dissociation.

RESULTS AND DISCUSSION

Preliminary study of the electronic absorption spectra of binary systems Co(II)-dtpa, Ni(II)-dtpa, and Cu(II)-dtpa in the visible region with varying composition of the components and pH of the solutions confirmed that the high denticity of the polyaminopolycarboxylate complexing reagent allows us to form solutions of both mono- and bihomonuclear chelates. Table 1 lists the wavelengths of the characteristic maxima of the light absorption bands of chelate solutions formed in binary systems in the pH ranges optimal for the formation of the coordination sphere of mono- and bihomonuclear dtpa-complexonates. Complex formation reactions were modeled and the logarithms of the stability constants of the resulting complexes were calculated using the procedure described above. The numerical values were in good agreement with the known literature data [18].

In our spectrophotometric study of the possibility of the formation of heterobinuclear dtpa-chelates in aqueous solutions in ternary systems containing cations of two different metals from the set of cobalt(II), nickel(II), copper(II), and a complexing agent in a molar ratio of 1 : 1 : 1, the electronic absorption spectra of solutions of ternary systems were compared to the corresponding spectral characteristics of solutions of mono- and bihomonuclear chelates of binary systems. It was established that the experimental electronic absorption spectra of solutions of ternary systems presented in Fig. 1 differ from those calculated according to the additivity principle for the optical characteristics of solutions of homonuclear complexonates, confirming the formation of heterobimetallic complex particles in solutions.

In the experimental determination of the pH ranges optimal for the existence of heterobinuclear dtpa-complexonates, differences were established in the chelation of cations of different metals in the joint presence in solutions. Formation of a heterobimetallic complex in the ternary system Co(II) : Ni(II) : dtpa = 1 : 1 : 1 in a solution at ΔpH 0.2–2.0 was accompanied by deprotonation of the neutral molecule of the complexing reagent with the release of five protons into the solution and the simultaneous chelation of both metal cations according to the equation



The resulting heterobinuclear dtpa chelate is stable over a wide pH range from 2.3 to 11.5 (Fig. 2).

In the ternary system Co(II) : Cu(II) : dtpa = 1 : 1 : 1, complexation begins in a strongly acidic medium (ΔpH 0.3–0.7) with the formation of a protonated mononuclear copper(II) chelate $[\text{CuHdtpa}]^{2-}$. An increase in the optical density of solutions was recorded when the pH of solutions was raised (ΔpH 1.4–3.6), due to the simultaneous deprotonation of $[\text{CuHdtpa}]^{2-}$ and incorporation of a second metal cation into the coordination sphere to form a heterobinuclear complex $[\text{CoCu}(\text{dtpa})]^-$ that was stable at pH values of 3.7 to 7.4. Upon moving to alkaline environments (pH >7.5), the heterobimetallic chelate undergoes hydrolytic decomposition with the release of copper(II) hydroxide into the solid phase, and only the mononuclear dtpa cobalt(II) chelate is fixed in alkaline solutions.

Table 1. Wavelengths of the maxima of the light absorption bands (λ_{max}), optimum pH intervals ($\Delta\text{pH}_{\text{opt}}$), and logarithms of the constants of stability of mono- and binuclear dtpa-complexes of cobalt(II), nickel(II), and copper(II)

Composition of complex	λ_{max} , nm	$\Delta\text{pH}_{\text{opt}}$	$\log \beta$
$[\text{CoH}_2\text{dtpa}]^-$	515	1.1–3.7	8.17 ± 0.04
$[\text{CoHdtpa}]^{2-}$			17.47 ± 0.09
$[\text{Co}(\text{dtpa})]^{3-}$		4.9–12.0	19.73 ± 0.1
$[\text{Co}_2\text{dtpa}]^-$		3.1–7.7	24.46 ± 0.1
$[\text{NiH}_2\text{dtpa}]^-$	340, 590	1.5–4.5	11.09 ± 0.05
$[\text{NiHdtpa}]^{2-}$			16.69 ± 0.08
$[\text{Ni}(\text{dtpa})]^{3-}$		6.3–12.0	20.78 ± 0.1
$[\text{Ni}_2\text{dtpa}]^-$		3.8–8.0	25.53 ± 0.1
$[\text{CuH}_2\text{dtpa}]^-$	330, 750	1.7–5.0	12.11 ± 0.06
$[\text{CuHdtpa}]^{2-}$			16.24 ± 0.06
$[\text{Cu}(\text{dtpa})]^{3-}$		7.0–10.0	22.14 ± 0.1
$[\text{Cu}_2\text{dtpa}]^-$	330, 750	2.2–7.5	27.03 ± 0.1

In solutions of the ternary system Ni(II) : Cu(II) : dtpa = 1 : 1 : 1, chelation also begins in strongly acidic media. In the pH range of 0–0.2, however, the formation of mono- and diprotonated mononuclear nickel(II) complexonates $[\text{NiH}_2\text{dtpa}]^-$ and $[\text{NiHdtpa}]^{2-}$ and the subsequent increase in pH to 2.7 leads to the formation of heterobimetallic chelates $[\text{NiCuHdtpa}]^0$

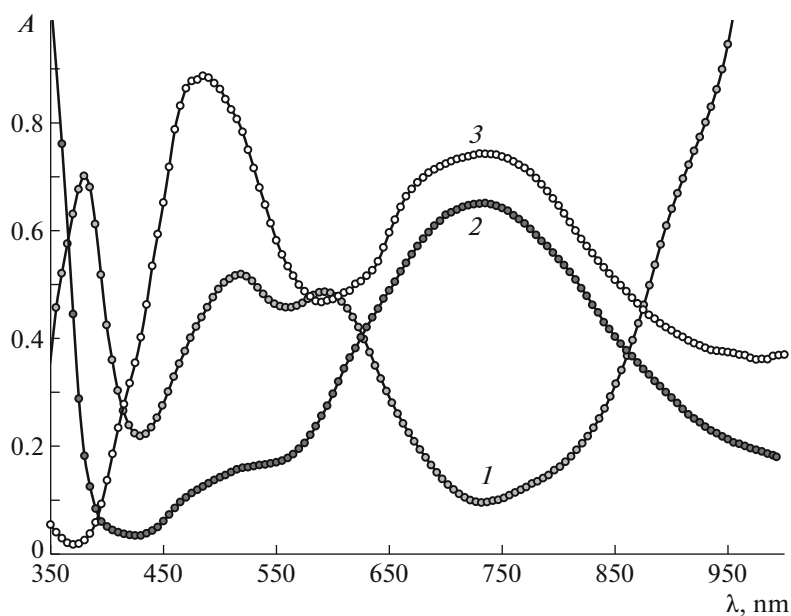


Fig. 1. Electronic absorption spectra of solutions of heterobinuclear complexes: (1) Co(II) : Ni(II) : dtpa = 1 : 1 : 1; (2) Co(II) : Cu(II) : dtpa = 1 : 1 : 1; (3) Ni(II) : Cu(II) : dtpa = 1 : 1 : 1. $C(\text{Co}^{2+}) = C(\text{Ni}^{2+}) = C(\text{Cu}^{2+}) = C(\text{dtpa}) = 1.0 \times 10^{-2} \text{ mol L}^{-1}$; $l = 1 \text{ cm}$; pH (1) 5.5, (2) 7.0, and (3) 5.1.

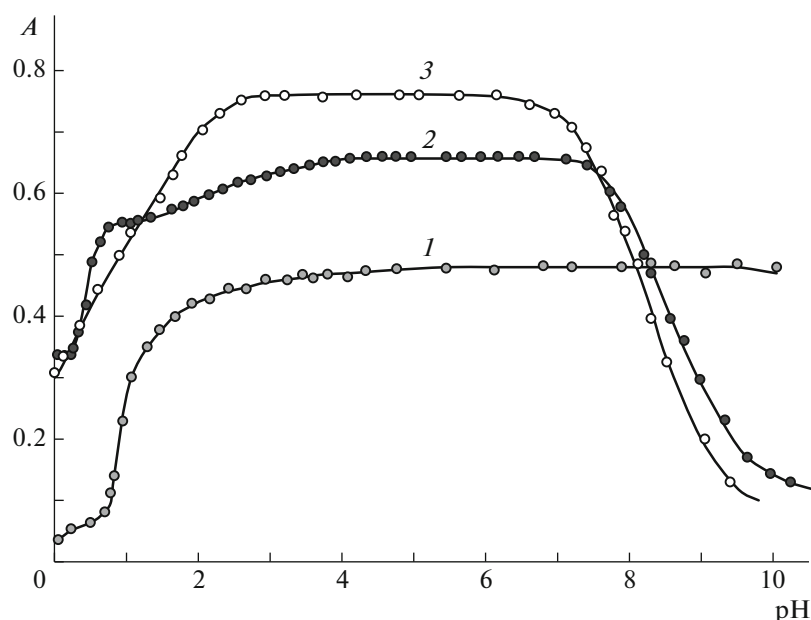


Fig. 2. Dependences of the optical density of solutions (A) on pH: (1) Co(II) : Ni(II) : dtpa = 1 : 1 : 1; (2) Co(II) : Cu(II) : dtpa = 1 : 1 : 1; (3) Ni(II) : Cu(II) : dtpa = 1 : 1 : 1. $C(\text{Co}^{2+}) = C(\text{Ni}^{2+}) = C(\text{Cu}^{2+}) = C(\text{dtpa}) = 1.0 \times 10^{-2} \text{ mol L}^{-1}$; $l = 1 \text{ cm}$; $\lambda =$ (1) 580, (2) 740, and (3) 690 nm.

and $[\text{NiCu}(\text{dtpa})]^-$ (Fig. 2), for which the optimum pH range of stable existence in solution is limited to pH 7.2. With a subsequent reduction in the acidity of the medium, there is a violation of the homogeneity of the system with the release of copper(II) hydroxide into the solid phase and the formation of mononuclear nickel(II) dtpa-chelate in the solution, as in the Co(II) : Cu(II) : dtpa = 1 : 1 : 1 system. The presence of oxophilic copper(II) cations in the composition of heterobimetallic complexes is therefore the reason for the drop in the hydrolysis resistance of Ni(II)–Cu(II) and Co(II)–Cu(II) dtpa chelates in alkaline solutions.

The molar ratio of the components in the heterobimetallic complexes of the studied ternary systems was confirmed experimentally from saturation series in solutions with optimum acidity of the medium. To calculate the quantitative characteristics of the resulting heterobinuclear dtpa complexes Co(II)–Ni(II), Ni(II)–Cu(II), and Co(II)–Cu(II), the same means and approaches were used as in the mathematical processing experimental spectrophotometric data for homobinuclear systems. To confirm the reliability of the obtained experimental data, all measurements were made in triplicate. The obtained values of parallel measurements were used to determine the confidence interval when calculating the logarithms of the stability constants of mononuclear, homobinuclear, and heterobinuclear homoleptic dtpa-chelates formed in aqueous solutions. Numerical values of the logarithms of the constants of stability of heterobimetallic diethylenetriaminepentaacetates $[\text{CoNi}(\text{dtpa})]^-$, $[\text{CoCu}(\text{dtpa})]^-$, $[\text{NiCu}(\text{dtpa})]^0$, and $[\text{NiCu}(\text{dtpa})]^-$ were 25.43 ± 0.1 ,

25.60 ± 0.1 , 17.83 ± 0.09 , and 27.57 ± 0.1 , respectively. The high coordinating ability of copper(II) cations with respect to the aminocarboxylate ligand ensures the higher thermodynamic stability of heterobimetallic chelates containing this metal center.

CONCLUSIONS

A comparative spectrophotometric study of the reactions of formation of heterobinuclear complex compounds of cobalt(II), nickel(II), and copper(II) with diethylenetriaminepentaacetic acid allowed us to establish differences in the coordination sequence of the aminocarboxylate ligand by two different central atoms. The presence of copper(II) cations in the composition of heterobimetallic dtpa-chelates contributes simultaneously to a rise in the thermodynamic stability of complex heterobinuclear particles and a drop in their resistance to hydrolysis in alkaline media.

ADDITIONAL INFORMATION

Materials from this work were presented at the XIV International Scientific Conference held in Ivanovo from September 20 to 24, 2021.

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