

**УСТОЙЧИВОСТЬ КОМПЛЕКСОВ КОБАЛЬТА И НИКЕЛЯ С СУКЦИНАТ И МАЛЕАТ ИОНАМИ, ИССЛЕДОВАННАЯ МЕТОДАМИ ПОТЕНЦИОМЕТРИЧЕСКОГО ТИТРОВАНИЯ, UV-VIS СПЕКТРОФОТОМЕТРИИ И КВАНТОВО-ХИМИЧЕСКИХ РАСЧЕТОВ**

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*В данной работе методом UV-Vis спектrophотометрии были изучены состав и устойчивость координационных соединений ионов никеля (II) и кобальта (II) с сукцинат-ионом ( $L^{2-}$ ) и малеат-ионом ( $Y^{2-}$ ) в водных растворах этанола с концентрацией этанола в диапазоне 0,0 – 0,3 мол. д., при ионной силе 0,1, поддерживаемой перхлоратом натрия. Результаты показали, что устойчивость монолигандных комплексов ионов  $Ni^{2+}$  и  $Co^{2+}$  с сукцинат-ионом и малеат-ионом увеличивается с ростом содержания этанола в растворителе. Это может быть связано, в основном, с изменением в сольватном состоянии лиганда при увеличении концентрации этанола в растворителе. Во всех исследованных составах водно-этанольных растворителей ион  $Co^{2+}$  образует менее устойчивые комплексы, чем ион  $Ni^{2+}$ , что соответствует ряду Ирвинга-Уильямса, установленному для водных растворов. Полученные в данной работе результаты были сопоставлены с представленными в литературе результатами для родственных соединений. Влияние изменения состава растворителя на структуру, заряд, общую энергию электронов и свободную энергию Гиббса было изучено с использованием уровней теории DFT и MP2 с использованием модели поляризуемого континуума (PCM). Результаты, полученные в этой статье методом UV-Vis спектrophотометрии, и теоретические расчеты были проанализированы совместно с результатами потенциометрического титрования, полученными нами ранее для координационных ионов никеля (II) и кобальта (II) с сукцинат-ионом и малеат-ионом в водных растворах этанола. Показано, что результаты теоретических расчетов хорошо согласуются с экспериментальными данными.*

**Ключевые слова:** комплексы никеля, комплексы кобальта, UV-Vis спектrophотометрия, устойчивость, квантово-химические расчеты, молекулярная структура

# STABILITY OF COBALT AND NICKEL COMPLEXES OF SUCCINIC AND MALEIC IONS STUDIED BY POTENTIOMETRIC TITRATION, UV-VIS SPECTROPHOTOMETRY AND QUANTUM CHEMICAL CALCULATIONS

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*In this study, composition and stability of coordination compounds of nickel (II) and cobalt (II) ions with succinate anion ( $L^{2-}$ ) and maleic anion ( $Y^{2-}$ ) in aqueous ethanol solutions with the molar concentration of ethanol ranging from 0.0 – 0.3 were studied by UV – Vis spectrophotometry at ionic strength of 0.1 maintained with sodium perchlorate. The result showed that, the formation of mono-ligand complexes of  $Ni^{2+}$  and  $Co^{2+}$  ions with succinate and maleic anions become stronger when the volume of ethanol rises. This may be due mainly to a change in the solvate state of the ligand with increasing ethanol concentration in the solvent. In all surveyed solvents,  $Co^{2+}$  forms less stable complexes than  $Ni^{2+}$  ion corresponding to the Irving-Williams series established for aqueous solutions. Obtained results were compared with literature data for akin compounds. The effect of solvent composition change on the geometry, charge, total electron and free Gibbs energies was studied using the DFT and MP2 levels of theory by using the Polarizable Continuum Model (PCM). The results obtained in this article by UV – Vis spectrophotometry and theoretical calculations were analyzed together with the potentiometric titration results obtained by us earlier for these complexes. The results of theoretical calculations are in good agreement with experimental data.*

**Key words:** nickel complex, cobalt complex, succinate anion, maleic anion, UV-Vis spectrophotometry, potentiometric titration, stability, quantum chemical calculation, molecular structure

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## INTRODUCTION

A wide practical application of carboxylic acids requires comprehensive study of their reactions in solutions. The study of composition and stability of *d*-metal complexes with carboxylic acids depending on the nature and concentration of a non-aqueous component of solvent is necessary for purposeful search of optimal conditions for the synthesis of coordination

compounds with prescribed thermodynamic properties [1, 2]. For this purpose, in continuation of works [3-8], we studied the effect of aqueous ethanol solvent compositions on the stability of coordination compounds of nickel (II) and cobalt (II) ions with succinic ( $L^{2-}$ ) and maleic ( $Y^{2-}$ ) ions and maleic anion using method UV – Vis spectrophotometry and quantum chemicals calculation. The results obtained in this article by UV – Vis spectrophotometry and theoretical calculations were

analyzed together with the potentiometric titration results obtained by us earlier [3-7] for these complexes. The results of theoretical calculations are in good agreement with experimental data.

Molecular studies of dicarboxylic acids and their complexes with transition metal play an important role in chemistry and biology. The structure and relative energies for conformers of succinic acid were studied by the gas-phase electron diffraction [9] and quantum chemical (QC) calculations [10, 11]. In the gas phase, this compound can exist in 18 conformers; nevertheless, from the PCM results in the aqueous solution the number of conformers decreases [12]. According to the QC calculations and experimental data (UV-vis, IR, ...), succinic acid forms three complexes with the uranyl ion (IV): 1:1, 1:2 and 1:3 U(IV)-suc [11].

The molecular structures of nickel and cobalt complexes with cyclic diphosphine ligands were studied by X-ray diffraction [13, 14]. From the X-ray experiments, the Co–O bond lengths in cobalt-pivalate complexes were found from 1.86 to 2.32 Å [15]. Calculation of electronic structure of nickel complex of corroles was performed using regular nonlocal density functional theory (DFT) with functional PW1 [16], structure of square planar nickel complexes [Ni(*o*-C<sub>6</sub>H<sub>4</sub>X<sub>2</sub>)<sub>2</sub>, where X = O, NH, S, Se, PH; Ni(*o*-C<sub>6</sub>H<sub>4</sub>XY)<sub>2</sub>, where XY = NH, NH<sub>2</sub> or S, NH<sub>2</sub>) were optimized at spin-unrestricted UB3LYP or spin-restricted RB3LYP level of theory [17]. Furthermore, geometry parameters of nickel complex of 2-hydroxyacetophenone thiosemicarbazone with triphenylphosphine have been investigated by X-ray diffraction and calculated at DFT/B3LYP level of theory [18]. Transition metal complexes (Ni, Co, ...) with Schiff base Bis-1,2 (2,4-dihydroxybenzylidene phylinediamine) were studied by IR and UV-vis spectroscopies [19]. In the paper [19], the authors investigated thermal decomposition of transition metal succinates M(CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·xH<sub>2</sub>O (M = Mn, Fe, Co, Ni, Cu, Zn) by many methods, but in which no molecular structure of complexes was determined.

In the literature no study for nickel and cobalt complexes with bidentate ligands in solutions was performed and therefore such work is desired. In this paper, we report the molecular structures of nickel and cobalt complexes with bidentate succinic ligand in gas phase and solutions using Quantum chemical calculations. The influence of solvents on structure was investigated. In addition, we compared the changes of energy in complexation reactions, obtaining from theoretical results with experimental data.

## EXPERIMENT SECTION

### Material and methods

#### Materials

In this work, the following reagents were used: succinic, maleic, perchloric acids, sodium (I), nickel (II), cobalt (II) perchlorates, sodium hydroxide and ethanol.

Solutions were prepared with double distilled water. Succinic acid and maleic acid, (high-purity grade) were used with additional purification. The purity of the preparations was determined by potentiometric titration (99.7 wt%).

Sodium perchlorate (Reakhimkomplekt, Russia) of “pure” mark was recrystallized and dried at 90 °C to a constant weight.

Hexahydrates of Nickel (II) and Co(II) perchlorate (high – purity grade) were recrystallized and dried at 80°C (for Ni(II)) and at room temperature (for Co(II)) to constant weight. The concentration of Ni(II) and Co(II) were determined by complexometric titration with trilon B.

Ethanol was purified by distillation. The water content determined by Fisher’s method was 0.5 wt%.

Sodium hydroxide NaOH grade “chemically pure” was used in the form of a saturated carbonate-free solution prepared according to the procedure previously described [20]. The content of carbonate was checked by titration with two indicators: phenolphthalein and methyl orange. The exact concentrations of prepared sodium hydroxide solutions were determined by potassium biphthalate.

Perchloric acid was used without additional purification. The concentration of HClO<sub>4</sub> was determined by titration of accurate weights of borax in the presence of methyl orange indicator.

#### Methods

##### 1. UV – spectrophotometry method

The absorption spectra of Ni<sup>2+</sup> and Co<sup>2+</sup> solutions in the presence of succinic and maleic acids in aqueous and aqueous ethanol solutions were taken on a Hitachi-U2001 spectrophotometer at room temperature in the wavelength range 360-900 nm (visible region, since the solutions are colored). Quartz glass cuvettes with an absorbing layer thickness of 1 cm were used to remove the spectra. A reference sample was prepared from distilled water and an aqueous ethanol solvent similar in ethanol content to the one under study. A solution of sodium perchlorate was used to create the ionic strength, and a solution of sodium hydroxide was used to create the pH.

A series of solutions were prepared with a constant ligand concentration, a variable concentration of metal ions and a fixed pH value = 5.5, at which the

yield of the monoligand particle was at least 20% (potentiometric titration data). A solution of sodium hydroxide was used to maintain the set pH value. The ethanol content in the solutions varied from 0 to 0.3 mol. fr. With a higher content of the non-aqueous component, precipitation are formed.

The concentration of succinic and maleic acids in solutions containing nickel (II) ions was 0.1 mol/l, and in solutions containing cobalt (II) ions – 0.02 mol/L. The concentrations of  $\text{Ni}^{2+}$  ions in solutions varied from 0.01 to 0.15 mol/l, and  $\text{Co}^{2+}$  ions from 0.005 to 0.030 mol/l. The ionic force in the solutions was created by sodium perchlorate.

The experiments were carried out 5 times for each ethanol content in solutions. The experimental error in stability constants values of complexes  $\text{NiL}$  and  $\text{CoL}$  was determined as a standard root of mean square deviation for Student's test at confidence level 0.95 for the series of experiments at each mixed solvent composition.

In Uv-Vis spectroscopy, the quantification of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  ions concentrations in prepared samples were determined by Beer–Lambert's equation:  $A = \varepsilon \cdot l \cdot C$ , with  $A$  – absorbance;  $l$  – the path length of the cuvette (usually 1 cm);  $\varepsilon$  – the molar absorptivity of the compound ( $\text{M}^{-1} \cdot \text{cm}^{-1}$ );  $C$  – the concentration of the solution (M).

The results of measurement UV- Vis spectroscopy were processed mathematically by using FTMT software [21].

## 2. Computational details

Quantum chemical (QC) calculations of the  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{L}^{2-}$  ions and its complexes were performed with Gaussian 09 [22] program package. Geometry and vibrational calculations were performed by using DFT (with B3LYP, B3LYP-D3 and M06 functionals with multiplicity of 1 and 2 for Ni and Co, respectively) and MP2 methods with 6-311G(d,p) basic set and in solvents by using DFT-M06/6-311G(d,p) level of theory. The solvent influence was considered using polarized continuum model (PCM). The characteristic parameters, including static and dynamic dielectric constants, molar volume, radius and Abraham's hydrogen bond acidity and basicity parameters of solvent mixture, were estimated by analytical average values of parameters of each solvent:

$$P(\text{mixture}) = P(\text{H}_2\text{O}) \cdot \alpha(\text{H}_2\text{O}) + P(\text{EtOH}) \cdot (1 - \alpha(\text{H}_2\text{O}))$$

The Natural Bond Orbital (NBO) analysis was performed at the M06/6-311G(d,p) level of theory using the GenNBO program version 5.0.[23].

## RESULTS AND DISCUSSION

### The dissociation constant of complexes

The results of absorption spectra of nickel (II) and cobalt (II) ions in the presence of succinic acid in water and aqueous ethanol solvents with 0-0.3 mol. fr. of EtOH were determined.

As examples, Fig. 1 and 2 show the absorption spectra of complexes nickel (II) and Cobalt ions with succinic acid anion in water- ethanol solutions with an ethanol content of 0.1 mole fraction, at value pH 5.5 and an ionic strength of 0.1 maintained with sodium perchlorate, concentration of succinic acid anion ( $C_{\text{L}^{2-}} = 0.10 \text{ M}$ ) and  $\text{Ni}^{2+}$  ion from  $1 \cdot 10^{-2}$  -  $1.5 \cdot 10^{-1} \text{ M}$  and  $C_{\text{L}^0} = 2 \cdot 10^{-2} \text{ M}$  and  $\text{Co}^{2+}$  ions ranging from  $5 \cdot 10^{-3}$  –  $3 \cdot 10^{-2} \text{ M}$ , respectively.

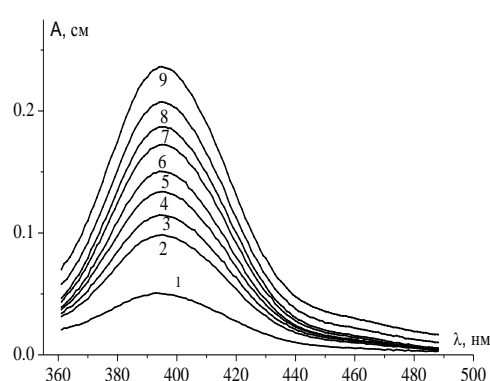


Fig. 1. Absorption spectra of  $\text{Ni}^{2+}$ (1) and  $\text{Ni}^{2+}$  solutions in the presence of succinic acid (2-9) in aqueous ethanol solutions with an ethanol content of 0.1 mol.fr.,  $I = 0.5 \text{ M}$  ( $\text{NaClO}_4$ ),  $C_{\text{L}^{2-}} = 0.10 \text{ M}$ ,  $C_{\text{Ni}^{2+}} = 1 \cdot 10^{-2}$  -  $1.5 \cdot 10^{-1} \text{ M}$ : 1 –  $C_{\text{Ni}^{2+}} = 0.01 \text{ mol/l}$ , 2 –  $C_{\text{Ni}^{2+}} = 3 \cdot 10^{-2} \text{ mol/l}$ , 3 –  $C_{\text{Ni}^{2+}} = 4 \cdot 10^{-2} \text{ mol/l}$ , 4 –  $C_{\text{Ni}^{2+}} = 5 \cdot 10^{-2} \text{ mol/l}$ , 5 –  $C_{\text{Ni}^{2+}} = 7 \cdot 10^{-2} \text{ mol/l}$ , 6 –  $C_{\text{Ni}^{2+}} = 8 \cdot 10^{-2} \text{ mol/l}$ , 7 –  $C_{\text{Ni}^{2+}} = 9 \cdot 10^{-2} \text{ mol/l}$ , 8 –  $C_{\text{Ni}^{2+}} = 0.1 \text{ mol/l}$ , 9 –  $C_{\text{Ni}^{2+}} = 0.15 \text{ mol/l}$

Рис. 1. Спектры поглощения растворов  $\text{Ni}^{2+}$ (1) и  $\text{Ni}^{2+}$  в присутствии янтарной кислоты (2-9) в водно-этанольных растворах с содержанием этанола 0,1 мол.д.,  $I = 0,5 \text{ M}$  ( $\text{NaClO}_4$ ),  $C_{\text{L}^{2-}} = 0,10 \text{ M}$ ,  $C_{\text{Ni}^{2+}} = 1 \cdot 10^{-2} - 1,5 \cdot 10^{-1} \text{ M}$ : 1 –  $C_{\text{Ni}^{2+}} = 0,01 \text{ моль/л}$ , 2 –  $C_{\text{Ni}^{2+}} = 3 \cdot 10^{-2} \text{ моль/л}$ , 3 –  $C_{\text{Ni}^{2+}} = 4 \cdot 10^{-2} \text{ моль/л}$ , 4 –  $C_{\text{Ni}^{2+}} = 5 \cdot 10^{-2} \text{ моль/л}$ , 5 –  $C_{\text{Ni}^{2+}} = 7 \cdot 10^{-2} \text{ моль/л}$ , 6 –  $C_{\text{Ni}^{2+}} = 8 \cdot 10^{-2} \text{ моль/л}$ , 7 –  $C_{\text{Ni}^{2+}} = 9 \cdot 10^{-2} \text{ моль/л}$ , 8 –  $C_{\text{Ni}^{2+}} = 0,1 \text{ моль/л}$ , 9 –  $C_{\text{Ni}^{2+}} = 0,15 \text{ моль/л}$

From Fig. 1 and 2, the wavelength of maximum absorbance of complexes  $\text{NiL}$  and  $\text{CoL}$  were observed at 396 nm and 513 nm, respectively. The other side, a change in the concentration of metal ions ( $\text{M}^{2+}$ ) leads to a change in the optical density of solutions (A).

The mathematical processing of spectrophotometric data was carried out using the FTMT program [21]. To calculate the stability constants of nickel(II) and cobalt(II) ion complexes with succinic and maleic acid anions, optical density values were used at, 396 (395) nm, 513 (519) nm, respectively.

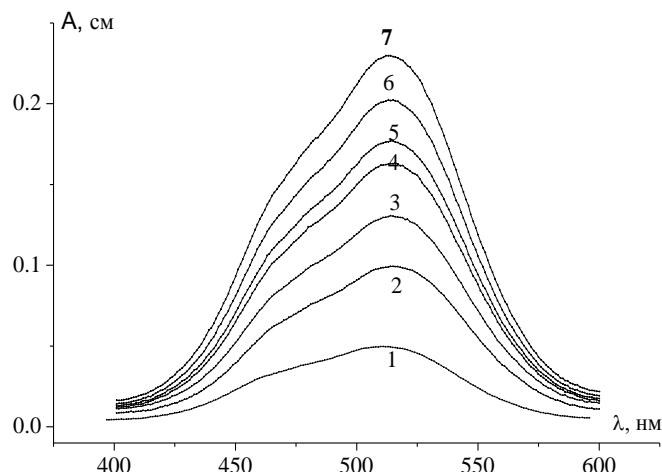
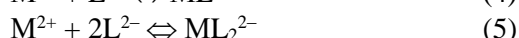
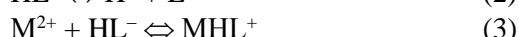


Fig. 2. Absorption spectra of  $\text{Co}^{2+}$  (1) and  $\text{Co}^{2+}$  solutions in the presence of succinic acid (2-7) in aqueous ethanol solutions with an ethanol content of 0.1 mol. fr.,  $C_{\text{L}^{2-}} = 0.02 \text{ mol/l}$  and  $C_{\text{Co}^{2+}} = 5 \cdot 10^{-3} - 3 \cdot 10^{-2} \text{ mol/l}$ : 1 –  $C_{\text{Co}^{2+}} = 5 \cdot 10^{-3} \text{ mol/l}$ , 2 –  $C_{\text{Co}^{2+}} = 10^{-2} \text{ mol/l}$ , 3 –  $C_{\text{Co}^{2+}} = 1.5 \cdot 10^{-2} \text{ mol/l}$ , 4 –  $C_{\text{Co}^{2+}} = 2 \cdot 10^{-2} \text{ mol/l}$ , 5 –  $C_{\text{Co}^{2+}} = 2.5 \cdot 10^{-2} \text{ mol/l}$ , 6 –  $C_{\text{Co}^{2+}} = 3 \cdot 10^{-2} \text{ mol/l}$

Рис. 2. Спектры поглощения растворов  $\text{Co}^{2+}$  (1) и  $\text{Co}^{2+}$  в присутствии янтарной кислоты (2-7) в водно-этанольных растворах с содержанием этанола 0,1 мол.д.  $C_{\text{L}^{2-}} = 0,02 \text{ моль/л}$  и  $C_{\text{Co}^{2+}} = 5 \cdot 10^{-3} - 3 \cdot 10^{-2} \text{ моль/л}$ : 1 –  $C_{\text{Co}^{2+}} = 5 \cdot 10^{-3} \text{ моль/л}$ , 2 –  $C_{\text{Co}^{2+}} = 10^{-2} \text{ моль/л}$ , 3 –  $C_{\text{Co}^{2+}} = 1,5 \cdot 10^{-2} \text{ моль/л}$ , 4 –  $C_{\text{Co}^{2+}} = 2 \cdot 10^{-2} \text{ моль/л}$ , 5 –  $C_{\text{Co}^{2+}} = 2,5 \cdot 10^{-2} \text{ моль/л}$ , 6 –  $C_{\text{Co}^{2+}} = 3 \cdot 10^{-2} \text{ моль/л}$

The following reactions for a system containing succinic acid ( $\text{H}_2\text{L}$ )/maleic acid ( $\text{H}_2\text{Y}$ ),  $\text{M}(\text{ClO}_4)_2$  ( $\text{M} = \text{Ni}^{2+}$  or  $\text{Co}^{2+}$ ), and  $\text{NaClO}_4$  are supposed: acid-base reactions of  $\text{H}_2\text{L}$  or  $\text{H}_2\text{Y}$  (1, 2), reaction of  $\text{M}^{2+}$  with the products of dissociation of succinic acid (3-5) or maleic acid and with hydroxide ion (6), as well as water dissociation (7).



Earlier, the pK values of stepwise succinic acid and maleic dissociation (1-2) were determined by potentiometric titration at 298 K and ionic strength of 0.1 maintained with sodium perchlorate at 0.0, 0.1, 0.3, 0.5 and 0.7 mol. fr. of EtOH [3, 24].

The values of the logarithms units of the stability constants of the formed complexes  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  ions with succinic acid and maleic acid anions in aqueous and in water-ethanol solutions obtained by spectrophotometry and potentiometric titration were showed in Table 1.

Table 1

Stability constants of complexes of Ni(II) and Co(II) ions with anions of succinic ( $\text{L}^{2-}$ ) and maleic ( $\text{Y}^{2-}$ ) acids in aqueous ethanol solvents,  $T=298.15 \text{ K}$

Таблица 1. Константы устойчивости комплексов ионов Ni(II) и Co(II) с анионами янтарной ( $\text{L}^{2-}$ ) и малеиновой ( $\text{Y}^{2-}$ ) кислот в водно-этанольных растворителях,  $T=298,15 \text{ K}$

$X_{\text{EtOH}}$ , mol.fr.	$\lg\beta$			
	NiL	NiY	CoL	CoY
0	$2.13 \pm 0.10^*$	$2.54 \pm 0.15^*$	$1.88 \pm 0.10^*$	$2.10 \pm 0.10^*$
	$1.96 \pm 0.04$ [24]	$2.83 \pm 0.06$ [4]	$1.64 \pm 0.07$ [24]	$2.07 \pm 0.04$ [3]
0.1	$2.57 \pm 0.10^*$	$3.22 \pm 0.10^*$	$2.09 \pm 0.15^*$	$2.03 \pm 0.20^*$
	$2.60 \pm 0.06$ [24]	$3.12 \pm 0.05$ [4]	$1.87 \pm 0.07$ [24]	$2.49 \pm 0.04$ [3]
0.3	$3.10 \pm 0.15^*$	$3.85 \pm 0.20^*$	$2.65 \pm 0.20^*$	$3.45 \pm 0.20^*$
	$3.02 \pm 0.04$ [24]	$3.37 \pm 0.05$ [4]	$2.07 \pm 0.04$ [24]	$3.07 \pm 0.06$ [3]

Note: \*The values of the logarithms of the stability constants of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  complexes with succinic and maleic acid anions in aqueous and aqueous ethanol solutions obtained in this work by UV-Vis spectrophotometry

Примечание: \*Значения логарифмов констант устойчивости комплексов  $\text{Ni}^{2+}$  и  $\text{Co}^{2+}$  с анионами янтарной и малеиновой кислот в водных и водно-этанольных растворах, полученные в данной работе методом УФ-Вид спектрофотометрии

As can be seen from Table 1, in aqueous solutions  $\text{Ni}^{2+}$  ion forms stronger complexes with succinic acid anion than  $\text{Co}^{2+}$  ion. This fact is in the agreement with the Irving-Williams series ( $\text{Zn}^{2+} < \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$ ). The stability of the coordination compounds of ions of the studied metals with the succinic acid anion is less than with the maleic acid anion, which is obviously due to the presence of a double bond in the structure of the latter. The orientation and distance between two carboxyl groups in the molecular structure of maleic acid are more advantageous for the formation of complexes with transition metal ions than in the succinic acid molecule.

In the studied water – ethanol solution, analysis experimental results of the two independent methods was showed that, the increase in the content of ethanol in solution leads to the growth of NiL and CoL complexes stability. The both logarithms values of complexes NiL and CoL are in good agreement with one another. However the error in  $\lg\beta$  values using UV-vis spectroscopy method was higher than potentiometric titration method ranging from  $\pm 0.1$  to 0.2 units. The increase in the stability of complexes of cobalt and nickel with maleate and succinate anions is due to the destabilization of the ligand with increasing ethanol concentration [3, 4, 24].

Aqueous-ethanol solvent has similar effect on the stability of mono ligand  $\text{Ni}^{2+}$  complexes with ethylenediamine [25], as well as with anions aminoacetic [26], acetic [27] acids, and ammonium ion [28].

### Energies of complexation reaction

The structures of succinate anions and its complexes are shown in Fig. 3, the total electron and free Gibbs energies of reactions between metal ions and succinate ions in gas phase are given in Table 2. According to the structure of anion, two carboxylic groups point two different sides of the molecule. Therefore, for the reactions process, it is necessary to expend energy to rotate both carboxylic groups relative to C2–C3 bond. In the gas phase, structures of two complexes have a  $C_2$  symmetry. According to the QC calculations, both calculation methods, DFT and MP2, predict that the  $\Delta E$  and  $\Delta G$  values of reaction of succinate anion with  $\text{Co}^{2+}$  ion are 31–34 kcal/mol higher than those of reactions with  $\text{Ni}^{2+}$  ion. Thus, in the gas phase NiL complexes is more stable than CoL complexes.

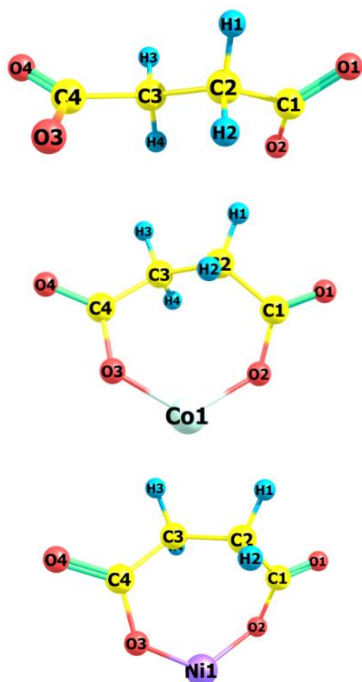


Fig. 3. Structure of succinate ion and its complexes with metal ions

Рис. 3. Структура сукцинат-иона и его комплексов с ионами металлов

Unlike gas phase, in the solvent, complex CoL exists in the  $C_1$  or  $C_2$  symmetry, a NiL complex – only  $C_1$  symmetry. Note that in the structure with  $C_1$  symmetry, the difference between Co–O bond length is from 0.0004 (in water) to 0.0010 Å (in ethanol). Moreover, the structure with  $C_1$  symmetry is stable with 10–12 kcal/mol higher than one with  $C_2$  symmetry. Fig. 4

shows change of reaction energies depending on composition of solvent components. It is important to note that the  $\Delta E$  and  $\Delta G$  values decrease with increasing molar fraction of ethanol, therefore stability of both complexes increase in this order. In the solvent the reaction energies are lower by ca. 6 times than in gas phase. Similar in the gas phase, NiL complex is more stable than CoL in solution. These results are in good agreement with experimental data in water and  $\text{H}_2\text{O}$ –EtOH mixtures.

Table 2

The total electron and free Gibbs energies (kcal/mol) of reactions between succinate anion and metal cations calculated at DFT (with B3LYP, B3LYP-D3 and M06 functionals) and MP2 levels of theory with 6-311G(d,p) basis set

Таблица 2. Полная энергия электронов и свободная энергия Гиббса (ккал/моль) реакций между сукцинат-анионом и катионами металлов, рассчитанные на уровнях теории DFT (с функционалами B3LYP, B3LYP-D3 и M06) и MP2 с базовым набором 6-311G(d,p)

Method	$\text{Co}^{2+} + \text{L}^{2-} = \text{CoL}$		$\text{Ni}^{2+} + \text{L}^{2-} = \text{NiL}$	
	$\Delta E$	$\Delta G$	$\Delta E$	$\Delta G$
B3LYP	-676.98	-665.03	-708.15	-696.22
B3LYP-D3	-677.45	-664.95	-710.63	-698.66
M06	-670.40	-657.69	-701.17	-688.88
MP2	-632.29	-619.69	-663.43	-652.17

$\Delta E = E(\text{MeL}) - E(\text{Me}^{2+}) - E(\text{L}^{2-});$   
 $\Delta G = G(\text{MeL}) - G(\text{Me}^{2+}) - G(\text{L}^{2-})$

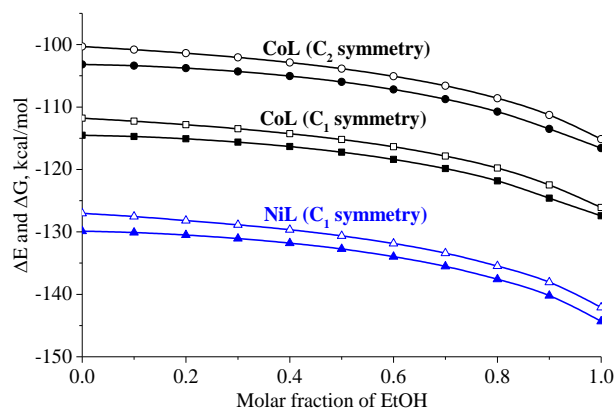


Fig. 4. Depending of  $\Delta E$  (solid symbol) and  $\Delta G$  (empty symbol) values on composition of solvent components

Рис. 4. Зависимость значений  $\Delta E$  (заполненные символы) и  $\Delta G$  (полые символы) от состава растворителя

### Geometry and NBO analysis

The calculated (QC) geometric parameters of the both complexes are compiled in Table 3. Comparing the two compounds, it can be seen that the C–C and C–O bond lengths in solvents are shorter than that in gas phase by 0.004–0.007 and 0.02–0.04 Å, respectively. In the contrary, the C=O and Me–O bond

lengths in solutions are larger than those in gas phase due to the interaction between oxygen and metal atoms with the solvents. Note that the double C=O bonds in two compounds are very close. From QC calculations, in the studied solvents, the Ni–O bond length is by *ca.* 0.06 Å shorter than Co–O bond. On account of this the NiL complex is more stable than CoL. Furthermore, according to QC calculations, the Me–O bond length decreases with increasing molar fraction of ethanol, therefore stability of both complexes increases in this order, which are in good agreement with experimental data. In addition, the Co–O bond length in structure with C<sub>2</sub> symmetry decreases from 1.7856 Å to 1.7824 Å with increasing of molar fraction of ethanol.

The C1–C2–C3, C2–C1=O1, C2–C1–O2 and C1–O2–Me bond angles in both compounds do not exceed 3° during the transition from the gas phase to the solution. At the same time, the O–Me–O bond angles are 13° and 8° in the CoL and NiL complexes, respectively. From Table 4, the C1, C2, O1, O2 and Co formed a plane in the gas phase. Nevertheless, in the solution, the Co atom does not lie in the plane forming by the C1, C2, O1 and O2 atoms. During the transition from the gas phase to the solution, the C1–O2–Me–O3 angle increases by 6°, 9° and 10° for CoL and NiL complexes, respectively. Thus, under the influence of

solvents the both complexes are more distorted than in gas phase.

The natural charges on atoms and the second-order perturbation energies E(2) (donor-acceptor) of both compounds calculated at M06/6-311G(d,p) level of theory are given in Table 4. The QC calculations show that the natural charges on carbon atoms do not change during from gas phase to the solvents. At the same time, the electron density on the oxygen atoms increases. It is important to note that charge on metal atoms increases from 1.10–1.11 in the gas phase to 1.35–1.51 e.u. in solution. Because the polarity of water is more than that of ethanol, charge on metal atoms slightly decreases with increasing molar fraction of ethanol.

According the NBO-analysis results the orbital interactions between electron lone pair (LP) of oxygen atom O2 or O3 and double bond C=O are most high. In the case of CoL, the energies E(2) LP2(O1)→σ\*(C1–C2) or LP2(O1)→σ\*(C1–O2) slightly decrease with increasing molar fraction of ethanol. In the contrary, these energies slightly increase for NiL complex. Note that the second-order perturbation energies E(2) (donor-acceptor) in NiL complex are twice of those in CoL. Thus, the NBO-analysis results conclude that NiL is more stable than CoL complex in the gas phase and in the solution.

Table 3

Theoretical geometric parameters of the CoL (with the C1 symmetry) and NiL complexes in the gas phase and solutions calculated at M06/6-311G(d,p) level of theory

Таблица 3. Теоретические геометрические параметры CoL (с симметрией C1) и комплексов NiL в газовой фазе и растворах, рассчитанные на уровне теории M06/6-311G(d,p)

Complex Solvent	CoL (Multiplicity = 2)			NiL (Multiplicity = 1)		
	Gas	H <sub>2</sub> O	EtOH	Gas	H <sub>2</sub> O	EtOH
Bond distance, Å						
C1–C2	1.517	1.512	1.513	1.515	1.507	1.508
C2–C3	1.540	1.534	1.534	1.536	1.532	1.532
C1=O1	1.196	1.217	1.217	1.198	1.214	1.213
C1–O2	1.338	1.299	1.300	1.330	1.305	1.307
Me–O2	1.785	1.824	1.819	1.722	1.766	1.765
Me–O3	1.785	1.825	1.820	1.722	1.766	1.764
Bond angle, °						
C1–C2–C3	115.8	113.7	114.7	115.5	113.1	113.2
C2–C1=O1	123.9	121.4	121.2	123.8	122.4	122.4
C2–C1–O2	114.4	116.0	116.4	115.0	116.0	116.0
C1–O2–Me	128.2	129.8	130.5	129.3	130.5	130.3
O2–Me–O3	124.2	113.4	113.4	120.2	112.5	112.8
Dihedral angle, °						
C1–C2–C3–C4	104.8	105.8	104.4	102.4	101.4	101.5
C3–C2–C1–O2	–56.8	–51.5	–48.2	–52.1	–52.7	–52.2
C2–C1–O2–Me	–1.6	–15.6	–16.3	–10.5	–18.1	–18.6
C1–O2–Me–O3	14.2	23.1	20.1	19.9	29.9	30.1

Table 4

Selected natural charges and the second-order perturbation energies E(2) (donor-acceptor) of both complexes calculated at M06/6-311G(d,p) level of theory

Таблица 4. Выбранные заряды и энергии возмущений второго порядка E(2) (донор-акцептор) для обоих комплексов, рассчитанные на уровне теории M06/6-311G(d,p)

Complex Solvent	CoL			NiL		
	Gas	H <sub>2</sub> O	EtOH	Gas	H <sub>2</sub> O	EtOH
Natural charge, e.u.						
C1	0.856	0.860	0.859	0.849	0.859	0.860
C2	-0.503	-0.502	-0.501	-0.505	-0.502	-0.500
O1	-0.576	-0.702	-0.697	-0.584	-0.682	-0.679
O2	-0.772	-0.843	-0.841	-0.755	-0.795	-0.796
Me	1.106	1.514	1.498	1.100	1.358	1.346
E(2) (donor → acceptor), kcal/mol						
LP2(O1)→σ*(C1-C2)	9.77	9.01	8.78	19.08	17.75	17.81
LP2(O1)→σ*(C1-O2)	17.77	14.28	14.19	34.96	29.81	30.05
LP2(O2)→π*(C1=O1)	21.58	33.85	30.36	49.07	45.64	44.22
LP2(O3)→π*(C4=O4)	21.58	0.53	32.69	49.07	41.15	40.93
LP2(O4)→σ*(C4-C3)	9.77	9.03	8.83	19.08	17.64	17.70
LP2(O4)→σ*(C4-O3)	17.77	14.29	14.26	34.96	29.66	29.91

## CONCLUSIONS

The stability of complexes Ni<sup>2+</sup>, Co<sup>2+</sup> ions with succinic and maleic acids anions increase with increasing the content of EtOH in solutions. This was proven by experimental result of independence two methods UV – Vis spectroscopy and potentiometric titration. Maleate complexes of Ni<sup>2+</sup>, Co<sup>2+</sup> ions are more stable than succinate complexes. This was due to the orientation of two carboxyl group -COOH in structure of maleic was more suitable for formation chelating complexes with Ni, Co metals than in structure of succinic acid. Our previous published studies on calculation Gibbs energy changes for transfer of complexes components of NiL and CoL from water to water – ethanol solvent was specified that, the increase in the stability of complexes of cobalt and nickel with maleate and succinate anions is due to the destabilization of the ligand with increasing ethanol concentration. Cation solvation of Ni<sup>2+</sup> does not contribute to the stability of NiL and NiY complexes.

The QC calculations show that the NiL complex is more stable than CoL in the gas phase and in

the solution and are in good agreement with experimental data. According to the NBO-analysis, there is the electron density transfer from metal atom to oxygen atoms during the transition from the gas phase to the solution.

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