PHYSICAL METHODS
OF INVESTIGATION

Cobalt(II) and Copper(II) Complexes with Carboxylic Acids, Imidazole, and 2-Methylimidazole

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Abstract—The compositions of $[MIm(MeIm)_x]L$ complexes synthesized by the reaction of cobalt(II) and copper(II) fumarates $ML \cdot nH_2O$ with imidazole (Im) and 2-methylimidazole (MeIm) were determined. The thermal decomposition of the salts was analyzed, and the pyridine nitrogen atom of imidazole and the oxygen atoms of carboxyl anions were shown to participate in complexation using electronic absorption spectra and IR spectra. The composition and stability of cobalt(II) and copper(II) imidazolatesuccinate complexes in an aqueous solution were determined photometrically and spectrophotometrically, and their higher stability in comparison with monoligand complexes was demonstrated.

Interest in the chelates of biogenic elements (Fe, Zn, Cu, Mn, Mo, and Co) with organic ligands of different chemical natures and bioactivities is currently kept undiminished. Most of the processes occurring in biological systems involve the interaction of metal ions with several ligands, so the synthesis of mixed-ligand complexes and the study of their properties and structure are of particular interest. In many cases, the ligand incorporated into such a complex exhibits bioactivity, which is not typical of it in the free state. Thus, the new zinc complexes with nitroimidazole, adamantine, and nitrofuran derivatives were established to have more pronounced antimicrobial activities than the initial ligands [1]. The metal ions in mixed-ligand complexes become less toxic and gain the ability to catalyze various biochemical processes. The frequent appearance of synergism for the ligands in mixed-ligand complexes with two bioactive ligands is also noteworthy. For this reason, biometal complexes can be used as a basis to create new medicines, bioactive supplements, biocatalysts, etc.

Moreover, the coordination compounds of *d*-elements with organic ligands containing various donor atoms are good models for studying the mutual effect of ligands in complexes. Such ligands, which are of both theoretical and practical interest, may be carboxylic acids, amino acids, oxyacids, vitamins, and azoles. For example, succinic and fumaric acids and some their salts with *d*-cations are applied in different fields, such as the production of food supplements, beverages, and medicinal, cosmetic, veterinary, and agricultural preparations, and fumarates are widely used as blood plasma substitutes. The physicochemical properties of succinates, hydrogen succinates, and fumarates of some metals were studied in [2]. The syn-

thesis of succinate dihydrates $MC_4H_4O_4 \cdot 2H_2O$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) by the reaction between the corresponding *d*-metal sulfate and a mixture of succinic acid and sodium hydroxide and the synthesis of iron(III) fumarate $Fe_2(C_4H_2O_4)_2(OH)_2 \cdot 2H_2O$ are described in [3, 4].

Succinic acid (H_2Suc) and fumaric acid (H_2Fum) are known to form complexes with transition-metal ions in solution. The survey of the stability of copper(II) succinate complexes [CuSuc] ($\log\beta_1 = 3.02$) and copper(II) hydrogen succinate complexes $[CuHSuc]^+$ ($\log\beta_{11} = 1.99$) is given in [5]. The copper(II)–fumaric acid system is found to contain only one predominant complex [CuFum] ($\log\beta_1 = 2.35$) [6].

Coordination compounds of *d*-metal ions on the basis of nitrogen-containing heterocycles, in particular, azoles, have efficient pharmacological activity and participate in key vital processes. Imidazole derivatives hold a great place in the field of medicinal chemistry. For example, 2-methylimidazole $C_4H_6N_2$ is used as an initial material for the synthesis of anti-infective agents. Some mixed-ligand complexes of metal salts with imidazole derivatives (1-ethylimidazole, 1-methylimidazole, etc.) have also been prepared. Syntheses with 2-methylimidazole (L) and copper(II) bromide from ethanol solutions yielded complexes of different compositions [7]: $[CuL_2Br_2]$ was prepared from neutral solutions; $(HL)_2[CuBr_4] \cdot H_2O$ was prepared from solutions in the presence of HBr at the ratio M : L = 1 : 2 and pH 1 (according to IR spectra, the ligand is in the outer sphere of the complex; and $(HL)_2[Cu_2Br_6]$ was prepared from solutions with pH 2–3, where HL^+ is the outer-sphere cation. The composition and structure of dimeric, monomeric, and polymeric copper(II) benzimidazole complexes synthesized by the

reaction between $CuCl_2$ and benzimidazole in ethanol were also determined [8]. The complexation of imidazole, 2-methylimidazole, benzimidazole, pyrazole, and 1,2,4-triazole was studied in [9], and they were found to have donating ability in reactions with salts (chlorides, acetates) of many metal ions (Cu^+, Ag^+, Pd^{2+}, Pt^{2+}, Pt^{4+}, Co^{2+}, Cu^{2+}). The ligands in these complexes behave as monodentate with coordination to the nitrogen atom. Crystal and molecular structures were also determined for the bis(1-vinylimidazole)diacetatozinc complex $C_{14}H_{18}N_4O_4Zn$, in which the apices of distorted zinc tetrahedra are occupied by the nitrogen atoms of imidazole ligands and the oxygen atoms of acetate groups [10]. The composition and stability constants of iron complexes with imidazole and benzimidazole were determined using the oxidation potential method, and the thermodynamic functions for the reactions of their formation were calculated [11].

A great number of patents are related to the synthesis of azole complexes with d-cation salts and the study of their bioactivity [12–17]. These are complexes of substituted imidazole with the general formula $(RIm)_nML_x$, where R is the allyl, vinyl, ethyl, allenyl, or other radicals; $M = Zn^{2+}$, Co^{2+}, Fe^{3+}, Cu^{2+}; and L is the chloride, succinate, acetate, ascorbate, or nicotinate ion. Bis-imidazole-(1,10)-phenantroline copper(II) dichloride $[CuIm_2Phen]Cl_2$ described in the patent [18] exhibits antibacterial and antiblastic activities.

The objective of this work is to determine the compositions and properties of mixed-ligand salts and the conditions of their formation in the ML−Im(MeIm) system ($M = Co^{2+}$, Cu^{2+}, L is the succinic and fumaric acid anions Suc^{2-} and Fum^{2-}); to study their bioactivity at a later stage; and to determine the compositions and stabilities of biligand $[MIm_xL]$ complexes formed in solution.

SUBJECTS AND METHODS

The cobalt(II) and copper(II) complexes with bioactive carboxylic ligands (succinic and fumaric acids)

$$H_2Suc \qquad\qquad H_2Fum$$
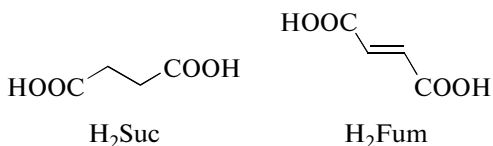
and some azoles, namely, imidazole and 2-methylimidazole, were studied in this work in the form of solid salts and in solution. Imidazole $C_3H_4N_2$ represents a five-membered ring with two nitrogen heteroatoms


Im
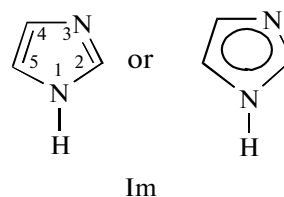
and has amphoteric properties (it is an acid for $N_{(1)}H$ and a base for $N_{(3)}$). The acidity constant (pK_a) of the $N_{(1)}$ pyrrol nitrogen atom of imidazole is ~14, so it can be protonated at pH > 10. The rigidly spatially oriented lone electron pair of the $N_{(3)}$ pyridine nitrogen atom can participate in protonation (log B_1 lies within a range of 7–7.7, where B_1 is the imidazole protonation constant) and in coordination of metal ions. 2-Methylimidazole, a substituted imidazole

MeIm

forms less stable complexes in comparison with imidazole due to the steric hindrances created by the substituent [19].

Thermal, thermogravimetric, and elemental analyses, potentiometry, photometry, spectrophotometry, and IR spectroscopy were used to analyze the synthesized salts, to study their properties, and to establish the composition and stability of mixed-ligand complexes in solution.

EXPERIMENTAL AND THEORETICAL

The initial monoligand cobalt(II) and copper(II) salts were prepared from aqueous solutions by the reaction of metal chloride or nitrate (MX_2) with succinic or fumaric acid (H_2L), which were partially neutralized with sodium hydroxide as

$$MX_2 + H_2L + (1.8-1.9)NaOH \rightarrow ML\downarrow$$
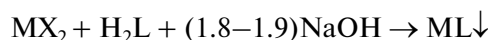
The final pH value of 4–5 was created in a solution using a NaOH solution, thereupon the suspensions were incubated on a bath and cooled, and the precipitates washed with water were air dried. The water, oxide, and ligand were determined by heating the salts at 125 and 900°C (by difference), and the metal ion was found trilonometrically (it was in satisfactory agreement with the metal determination in the oxide). The data on the analysis of the initial salts (cobalt(II) and copper(II) succinates and fumarates) are given in Table 1.

The mixed-ligand complexes were prepared from the obtained metal carboxylates $ML \cdot nH_2O$ and azoles, namely, imidazole and 2-methylimidazole by the reaction

Table 1. Elemental analysis of cobalt(II) and copper(II) succinates and fumarates

Complex formula	M^{2+}, %		Co_3O_4, CuO, %		H_2O, %	
	found	calcd	found	calcd	found	calcd
$CoC_4H_4O_4 \cdot 4H_2O$	24.5	23.79	32.4	32.49	28.7	29.07
$CoC_4H_2O_4 \cdot 3H_2O$	–	25.96	36.0	35.36	25.6	23.78
$CuC_4H_2O_4 \cdot 2H_2O$	29.7	29.75	37.2	37.23	16.6	16.85
$CuC_4H_4O_4 \cdot 2H_2O$	27.8	29.47	37.1	37.24	16.8	16.70

Table 2. Analysis of mixed-ligand cobalt(II) and copper(II) salts

Salt	N, %		C, %		H, %		O, %		Co_3O_4, CuO, %		H_2O, %	
	found	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	calcd
$Co(C_3H_4N_2)_2C_4H_4O_4 \cdot 2H_2O$	16.73	16.14	34.27	34.56	4.45	4.61	20.57	27.34	23.6	23.12	8.4	10.37
$Co(C_3H_4N_2)_2C_4H_2O_4 \cdot 2H_2O$	16.29	16.23	35.82	34.77	3.69	4.07	21.38	27.81	23.3	23.25	10.5	10.43
$Co(C_4H_6N_2)_2C_4H_4O_4 \cdot 2H_2O$	17.29	14.93	38.76	38.38	5.16	5.33	25.93	25.58	21.7	21.39	9.0	9.59
$Co(C_4H_6N_2)_2C_4H_2O_4 \cdot 2H_2O$	17.96	15.01	39.92	38.58	5.33	4.82	25.88	25.72	21.6	21.51	10.2	9.65
$Cu(C_3H_4N_2)_2C_4H_4O_4 \cdot 2H_2O$	16.35	15.93	33.74	34.11	4.53	4.55	24.29	27.30	22.6	22.61	7.3	10.23
$Cu(C_3H_4N_2)_2C_4H_2O_4 \cdot H_2O$	16.57	16.88	33.93	37.17	3.98	3.01	24.87	24.11	23.6	23.97	5.3	5.43
$Cu(C_4H_6N_2)_2C_4H_4O_4 \cdot 2.5H_2O$	15.01	14.41	36.51	37.05	5.57	5.40	25.29	26.76	23.9	20.47	14.5	11.58
$Cu(C_4H_6N_2)_2C_4H_2O_4 \cdot H_2O$	17.58	15.57	39.82	40.02	4.45	4.45	28.62	22.23	23.9	22.10	5.0	5.00

$ML \cdot nH_2O + x(Im, MeIm) \rightarrow M(Im, MeIm)_xL\downarrow$ from aqueous solutions within pH in a range of 6.5–8.5, except cobalt(II) imidazolatesuccinate and imidazolatefumarate, which were separated from water–acetone solutions. To accomplish this, a precisely weighed initial salt portion was dissolved in a small volume of water (8–10 mL), thereupon a calculated amount of imidazole or 2-methylimidazole was gradually added to the suspension to create the molar ratio ML : Im (MeIm) of 1 : 1, 1 : 2, etc. until the complete dissolution of the salt or the complete conversion of the carboxylic acid salt into a new vividly colored biligand salt. The suspension was allowed to stand on a bath and then at room temperature for 24 h.

The mixed-ligand salts were subjected to elemental analysis, thermal analysis for water and metal oxide, and thermogravimetric analysis, which quantitatively confirmed the contents of water, ligands, and metal oxide in the salt. The results of analyses were used to calculate the formulas of the synthesized biligand salts (Table 2). As can be seen from Table 2, the d-cation succinates and fumarates coordinate two (Im or MeIm) nitrogen molecules. Changing the molar ratio of components also makes it possible to separate salts containing different numbers of nitrogen molecules.

For the imidazole salts, thermoanalytical curves were recorded under air on a NETZSCH STA 449 C thermoanalyzer, and IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the region of 400–4000 cm^{-1} as KBr pellets. The IR spectra of salts were compared to the IR spectra of ligands, namely, carboxylic acids and imidazole.

pH in solutions was measured on a 673 pH meter, and the absorbance was determined on an SS2107UV LEKI spectrophotometer and KFK-2-UKhL4.2 photoelectrocolorimeter.

The isomolar series method (pH 6.8) was used to establish that the major solute species in $Co^{2+}(Cu^{2+})$–Im systems are 1 : 2 imidazolate complexes (Fig. 1) and in $Co^{2+}(Cu^{2+})$–Suc^{2-} systems, the major solute species are 1 : 1 complexes. The stability constants of the $[MIm]^{2+}$ and $[MIm_2]^{2+}$ complex cations were calculated from the isomolar series data using regions with different molar ratios of components.

The saturation curves method indicates the stepwise complexation of a metal ion with imidazole in the ternary M^{2+}–L^{2-}–xIm (Fig. 2). The stability constants β_{111} and β_{121} of $[MIm_{1, 2}Suc]$ mixed-ligand complexes were calculated from the saturation curves for MSuc–Im systems ($M^{2+} = Co^{2+}$, Cu^{2+}). The calculated stability constants of mono- and biligand cobalt(II) and copper(II) complexes at an ionic strength $I \sim 0.3$ are given in Table 3, and the confidence interval of $\log\beta_i$ values does not exceed 0.3.

The constants of mixed-ligand complexes were calculated as described in [20]. For the equilibrium, e.g., with participation of two predominant MIm_2Suc and $MSuc$ complexes absorbing at the same wavelength
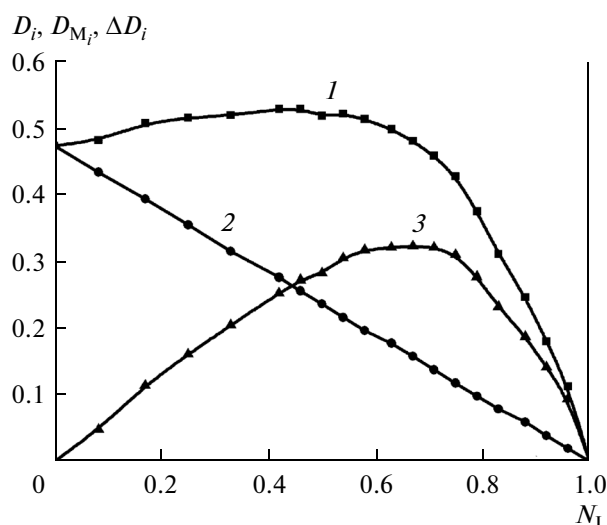
Fig. 1. Isomolar series for the $CoCl_2-Im$ system: (*1*) D_i, (*2*) D_{Mi}, (*3*) ΔD_i ($c_{Co}^0 = c_{Im}^0 = 0.12$ mol/L, $V_{tot} = 6$ mL, pH 6.8, $\lambda_{eff} = 490$ nm, $l = 10$ mm).
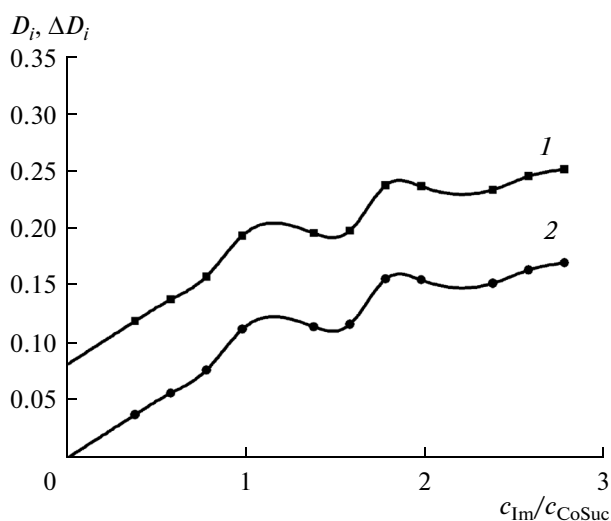
Fig. 2. Saturation curve for the $CoCl_2-H_2Suc-Im$ system: (*1*) D_i, (*2*) ΔD_i ($c_{Co} = c_{Suc} = 0.02$ mol/L, pH 6.8, $\lambda_{eff} = 490$ nm, $l = 10$ mm).

$$MSuc + 2Im \xrightleftharpoons{K} MIm_2Suc$$
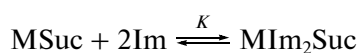
(charges are omitted for convenience), the equilibrium constant K and the stability constants β_1 and β_{121} of the monoligand MSuc and mixed-ligand MIm$_2$Suc complexes are correlated as $\beta_{121} = K\beta_1$. Using the photometric data, we have for each point on the saturation curve

$$\beta_{121} = \beta_1(\alpha_\infty f_{Im}^2)/((1 - \alpha_\infty) \times (c_{Im} - 2\alpha_\infty c_M)^2),$$

where α_∞ is the maximum yield of MIm$_2$Suc complex; $\alpha_\infty = (\varepsilon_i - \varepsilon_0)/(\varepsilon_\infty - \varepsilon_0)$, $\varepsilon_\infty = D_\infty/c_M$, $\varepsilon_i = D_i/c_M$, and ε are the molar extinction coefficients of corresponding species, namely, MSuc (ε_0), MIm$_2$Suc (ε_∞), and MSuc + MIm$_2$Suc (ε_i); f_{Im} is the imidazole protonation function equal to $1 + B_1[H^+]$; and B_1 is the imidazole pro-

Table 3. Results of assessing the stability of mono- and biligand cobalt(II) and copper(II) complexes with imidazole and the succinate ion ($\log B_{Im} = 7.69$, $I \sim 0.3$)

Complex composition	This work		$\log \beta_i$ [22]
	Assessment method	$\log \beta_i$	
[CoIm]$^{2+}$	Isomolar series	2.62	2.44
[CoIm$_2$]$^{2+}$	Isomolar series	4.72	4.34
[CoImSuc]	Saturation curve	5.34	–
[CoIm$_2$Suc]	Saturation curve	8.70	–
[CoSuc]	–	1.70	1.70
[CuIm]$^{2+}$	Isomolar series	3.85	4.33
[CuIm$_2$]$^{2+}$	Isomolar series	7.57; 7.72	7.60
[CuIm$_2$Suc]	Saturation curve	10.16	–
[CuSuc]			2.93

tonation constant ($\log B_1 = 7.69$ [21]). The stability constants of the cobalt(II) and copper(II) succinate complexes ($\log \beta_{CoSuc} = 1.70$ and $\log \beta_{CuSuc} = 2.93$) were taken from [22].

Electronic absorption spectra were taken for the aqueous $M^{2+}-H_2O$, $M^{2+}-L^{2-}$, $M^{2+}-Im$, $M^{2+}-L^{2-}-(1-2)Im$ systems ($M^{2+} = Co^{2+}$, Cu^{2+}, and L^{2-} is the succinate ion) in the UV and visible regions.

RESULTS AND DISCUSSION

The synthesized initial copper(II) salts, namely, CuSuc · 2H$_2$O and CuFum · 2H$_2$O, represent fine-crystalline blue compounds, which are poorly soluble in water (the solubility products determined by us for these salts at an ionic strength of 0.3 are 2.6×10^{-8} and 2.4×10^{-7}, respectively). The solubility of the cobalt(II) salts is better than for the copper(II) salts. Thus, the solubility product estimated for cobalt succinate CoSuc · 4H$_2$O from solubility data is 1.3×10^{-2}. The mixed-ligand salts containing a carboxylic acid ion and neutral azole molecules as ligands were synthesized from low-soluble cobalt(II) and copper(II) succinates and fumarates and azoles at pH of an aqueous solution of 6.5–8.5. A neutral imidazole HIm molecule coordinated to a metal cation is the dominant species within the mentioned range of pH. The constant B_1 for the protonation of the pyridine nitrogen atom of imidazole into an azolium ion [23] was used to plot the distribution diagram for the non-dissociated HIm and protonated H$_2$Im$^+$ imidazole forms in Fig. 3. From the distribution diagram it follows that the neutral HIm imidazole molecule has a wide pH region of predominance (curve *1*) from 5.35 to 13.0. For this reason, it is possible to hypothesize that the
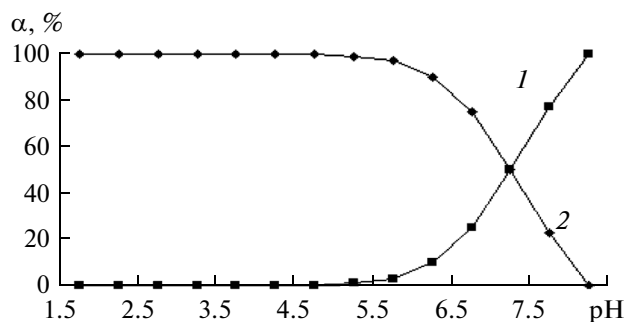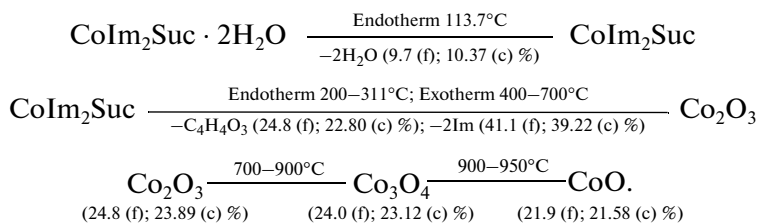
Fig. 3. Distribution of imidazole particles in an aqueous solution: (*1*) HIm, (*2*) H_2Im^+.

pyridine $N_{(3)}$ nitrogen atom of the neutral HIm molecule participates in complexation reaction within this pH range, as it contains a lone electron pair in the sp^2-hybrid orbital of the nitrogen atom.

The thermogravimetric data for biligand salt crystal hydrates confirms the composition established for the salts by other methods and allows us to suggest a scheme of their thermal decomposition. So, the thermal decomposition of cobalt(II) imidazolatesuccinate $CoIm_2Suc \cdot 2H_2O$ in air proceeds in several stages, which are quantitatively confirmed by the change in the salt weight:

$$CoIm_2Suc \cdot 2H_2O \xrightarrow[-2H_2O\ (9.7\ (f);\ 10.37\ (c)\ \%)]{\text{Endotherm } 113.7°C} CoIm_2Suc$$

$$CoIm_2Suc \xrightarrow[-C_4H_4O_3\ (24.8\ (f);\ 22.80\ (c)\ \%);\ -2Im\ (41.1\ (f);\ 39.22\ (c)\ \%)]{\text{Endotherm } 200-311°C;\ \text{Exotherm } 400-700°C} Co_2O_3$$

$$Co_2O_3 \xrightarrow[\substack{(24.8\ (f);\ 23.89\ (c)\ \%)}]{700-900°C} Co_3O_4 \xrightarrow[\substack{(24.0\ (f);\ 23.12\ (c)\ \%)}]{900-950°C} CoO.$$
$$\phantom{Co_2O_3 \xrightarrow{700-900°C} Co_3O_4} (21.9\ (f);\ 21.58\ (c)\ \%)$$

The endothermic dehydration of the salt is a single-stage process; two endotherms at 200–311°C correspond to the sublimation of succinic anhydride $C_4H_4O_3$, followed by the complete combustion of imidazole immediately with an exotherm in the temperature region of 400–700°C in air to form a Co_2O_3 residue, which is then converts consecutively into Co_3O_4 and CoO with loss of oxygen.

The functional groups participating in the complexation with cobalt(II) and copper(II) ions were determined using the IR spectra of the ligands and mixed-ligand salts. The IR spectra of succinic and fumaric acids contain the narrow intense bands of carbonyl C=O stretching vibrations at 1669.7 and 1667.9 cm^{-1}, respectively. The spectra of mixed-ligand complexes do not have these bands, but contain intense bands of the asymmetric and symmetric stretching vibrations of the ionized carboxylic COO$^-$ group involved into the coordination to a metal cation (e. g., the bands at 1548.2 and 1328.3 cm^{-1} for cobalt imidazolatesuccinate), thus confirming the incorporation of succinate and fumarate ions into the biligand salts.

The signs of the coordination of imidazole in the inner sphere of a complex are the following [12]: For example, the IR spectrum of imidazole and the $CoIm_2Suc \cdot 2H_2O$ cobalt(II) complex contains the strong bands of the bending and out-of-plane vibra-

tions of the imidazole ring at 657.9, 1053.9 and 655.9, 1067.7 cm^{-1}, respectively. The nonappearance of the absorption bands of imidazole C=C and C=N stretching vibrations in the spectra in the region of 1700–1800 cm^{-1} (1829.0, 1770.6 cm^{-1}) and the sustention of the bands of NH group bending vibrations upon transition from the non-coordinated Im ligand (1668.6 cm^{-1}) to its complex salts (1668.3 cm^{-1}) indicate the participation of the pyridine $N_{(3)}$ nitrogen atom in the formation of coordination compounds due to its lone electron pair [24].

To provide an indirect proof for the composition of solid mixed-ligand salts, we studied complexation in the binary MCl$_2$–Im and MCl$_2$–Suc^{2-} and ternary Co(Cu)Suc–Im aqueous systems (pH 6.8). Copper(II) and cobalt(II) imidazolate 1 : 2 complexes were established to predominate in the binary systems (Fig. 1). The coordination of two imidazole molecules most often occurs during the synthesis of solid biligand complexes. The saturation curves for the ternary systems (Fig. 2) also indicate the formation of the 1 : 2 : 1 (MIm$_2$Suc) complex in addition to the 1 : 1 : 1 complex. As can be seen from Table 3, the mixed-ligand complexes are more stable than the monoligand complexes probably due to the different mutual effect of the inner-sphere ligands of the complex. The stability constants determined by us for the monoligand com-
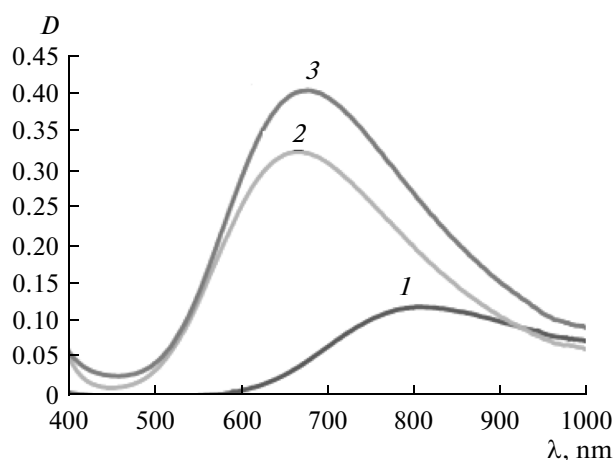
Fig. 4. Electronic absorption spectra of the systems (*1*) CuCl$_2$, (*2*) CuCl$_2$–Im, and (*3*) CuCl$_2$–H$_2$Suc–Im (c_{Cu} = c_{Suc} = 0.01 mol/L, c_{Im} = 0.02 mol/L, pH 6.8).
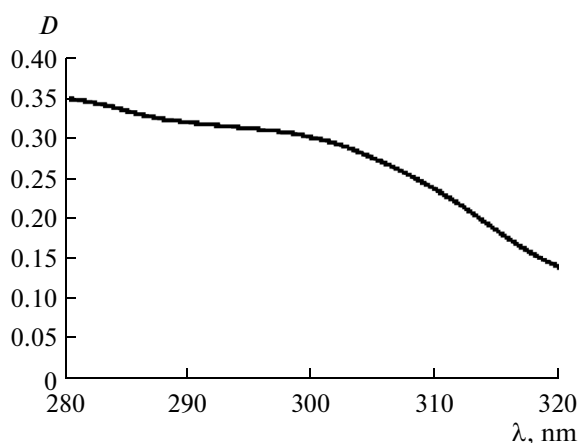
Fig. 6. Electronic absorption spectrum of imidazole (c = 0.12 mol/L, λ_{max} = 300 nm, l = 10 mm).
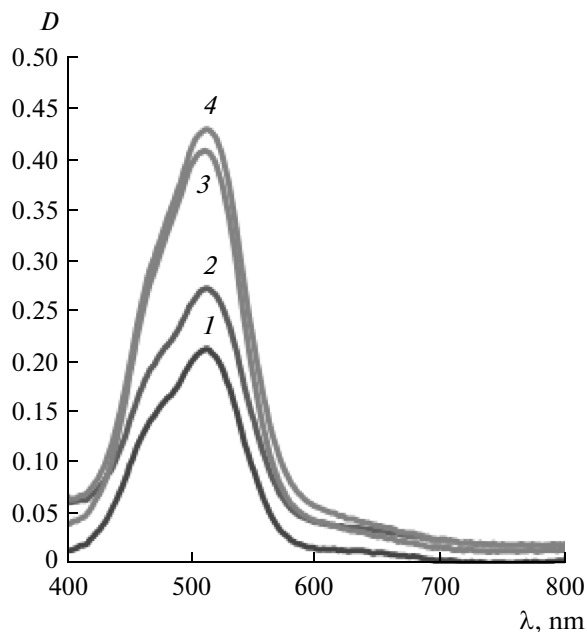
Fig. 5. Dependence of *D* on λ in the systems (*1*) CoCl$_2$, (*2*) CoCl$_2$–H$_2$Suc, (*3*) CoCl$_2$–Im, and (*4*) CoCl$_2$–H$_2$Suc–Im at pH 6.8 (c_i = 0.045 mol/L).
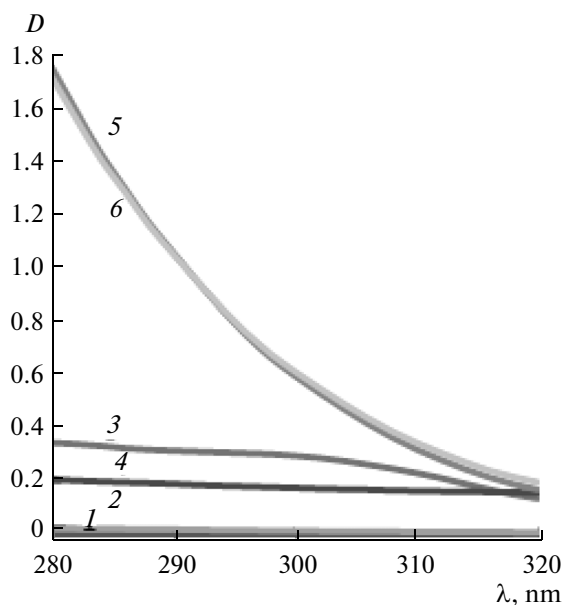
Fig. 7. Electronic absorption spectra of the systems (*1*) CoCl$_2$, (*2*) H$_2$Suc, (*3*) Im, (*4*) CoCl$_2$–H$_2$Suc, (*5*) Co–Im, and (*6*) CoCl$_2$–H$_2$Suc–Im (c_i = 0.06 mol/L, c_{Im} = 0.12 mol/L, pH 6.8).

plexes are in satisfactory agreement with the literature data [22].

The electronic absorption spectra of the binary and ternary systems confirm the formation of mixed-ligand complexes. A higher absorbance *D* in the biligand CuCl$_2$–H$_2$Suc–Im system in comparison with the CuCl$_2$–Im system, in which a monoligand complex predominates (the spectrum of the CuCl$_2$–H$_2$Suc system can not be recorded because of the precipitation of copper succinate), and a considerable shift of absorption peaks toward shorter wavelengths for the systems with complexes in comparison with hydrated

copper ion indicate the formation of a new mixed-ligand complex (Fig. 4).

The substitution of water molecules in the coordination sphere of the Cu^{2+} ion by strongly bonded ligands (the best donors of electron pairs) increases the difference between the energies of split *d* sublevels of the complex-forming agent, and its *d–d* absorption band shifts toward shorter wavelengths (a hypsochromic effect). The shift of absorption peaks in the binary and ternary systems of cobalt complexes relative to the absorption peak of CoCl$_2$ solution is small (Fig. 5) due to a lower stability of the mono- and biligand cobalt

complexes in comparison with the copper(II) complexes according to the Irving—Williams stability series (Table 3), but the hypsochromic effect is also observed. From the electronic absorption spectra of imidazole (Fig. 6) and the mono- and biligand cobalt complexes with imidazole and the succinate anion (Fig. 7) it can be seen that the low-intensity absorption band of imidazole at 300 nm, which is assigned to the $n \rightarrow \pi^*$ transition of the unshared electron pair of nitrogen, disappears after imidazole is incorporated into a complex [24].

Hence, relying on the data of electron and IR spectroscopy, we can state that the bond between a metal ion and ligands in the mixed ligand complexes is formed due to the pyridine nitrogen atom of imidazole and the oxygen atoms of the carboxyl groups of a carboxylic acid anion. The formation of mixed-ligand salts and complexes in solution is associated with the affinity of the Cu^{2+} and Co^{2+} d-cations for both the donating nitrogen and the oxygen atoms of selected ligands.

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