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Complexes of Co(II), Ni(II), and Cu(II) with (*Z*)-10-(2-(4-Amino-5-Thioxo-4,5-Dihydro-1*H*-1,2,4-Triazol-3-yl)hydrazono)-9-Phenanthrone: Synthesis, Spectral Studies, and Quantum Chemical Simulation of the Structures

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Abstract—The complexes of (*Z*)-10-(2-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)hydrazono)-9-phenanthrone (HL) with the Co(II), Ni(II), and Cu(II) salts, [CoLAcDMF] (**I**), [NiLAcDMF] (**II**), [CuL(H_2O)]ClO_4 (**III**), and [CuLAc] (**IV**), are synthesized and studied. The titration of a solution of HL in DMF with aqueous solutions of $CoAc_2$, $NiAc_2$, $Cu(ClO_4)_2$, $CuAc_2$, $Cd(NO_3)_2$, or $ZnSO_4$ leads to the bathochromic shift of the long-wavelength absorption band by 35–77 nm in the UV spectra. The formation constants and compositions of the complexes in solutions are determined from the results of titration. The structures of complexes **I**–**IV** are proposed on the basis of the DFT calculations and spectral data: the ligand being in the deprotonated form of the thione tautomer is coordinated by the metal cations through the oxygen atom of the carbonyl group and the nitrogen atoms of the hydrazo and amino groups to form two metallocycles, six- and five-membered (6 + 5). The coordination mode is completed by the acetate ion and DMF molecule (in **I** and **II**), acetate ion (in **IV**), or H_2O molecule (in **III**).

Keywords: quantum chemical calculations, heterocyclic azo derivatives, 9,10-phenanthrenequinone, spectral studies

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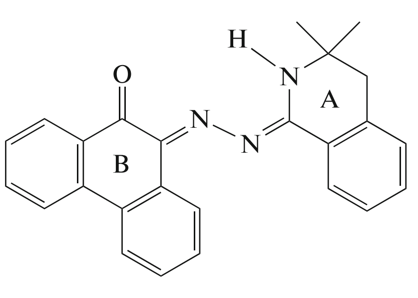
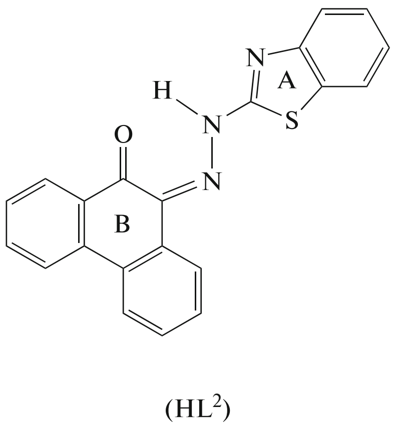
INTRODUCTION

Metal-containing compounds of heterocyclic azo derivatives of 9,10-phenanthrenequinone can be used as dyes for synthetic fibers [1] and color printing [2] and as carriers for information recording and storage [3]. However, they remain poorly studied.

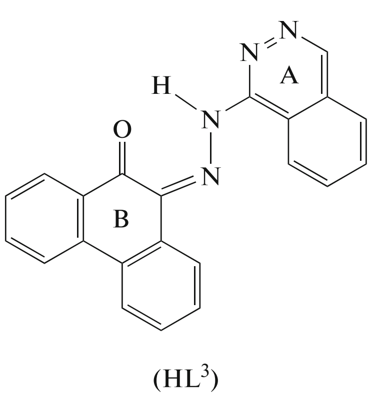
The structures of some heterocyclic azo derivatives of 9,10-phenanthrenequinone containing fragments of 3,3-dimethyl-3,4-dihydroisoquinoline (HL^1) [4], benzothiazole (HL^2) [5], and phthalazine (HL^3) [6] have been considered previously.



(HL^1)



(HL^2)



(HL^3)

These compounds are interesting for coordination chemistry, because they contain several electron-donor centers and can form with *d* metals complexes of various compositions, which can possess new useful properties. Each ligand, being in the anionic form, adds to the metal atom via the N,N,O-tridentate chelating mode with the closure of two five-membered (5 + 5) metallocycles to form 1 : 2 complexes for Co(II), Ni(II), and Cd(II) [6–9] and 1 : 1 complexes for Cu(II) [10, 11].

Various derivatives containing the 1,2,4-triazole cycle are characterized by a wide range of biological activity and are interesting from the viewpoint of the preparation of new drugs. They are used as anti-AIDS and antifungal drugs [12, 13], anti-inflammatory [14, 15] and antibacterial remedies [16], and agonists of benzodiazepine receptors [17]. The 4-amino-4*H*-1,2,4-triazole-3-thiol derivatives interact with transition metal salts by entering into the composition of metal complexes in the neutral thione form and forming chelate bonds involving the nitrogen atoms of the amino group and the sulfur atom [18].

This work continues our earlier studies [4–11] and is aimed at synthesizing and studying the structures and properties of the Co(II), Ni(II), and Cu(II) complexes with the new azo derivative of 9,10-phenanthrenequinone containing aminomercapto-4*H*-1,2,4-triazole as the heterocyclic component.

EXPERIMENTAL

Synthesis of CoLAc · DMF (I), NiLAc · DMF (II), and $\mathbf{CuLClO_4 \cdot H_2O}$ (III) (L^- is (*Z*)-10-(2-(4-amino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)hydrazono)-9-phenanthrone anion). A corresponding metal ($CoAc_2 \cdot 4H_2O$, $NiAc_2 \cdot 4H_2O$, or $Cu(ClO_4)_2 \cdot 6H_2O$) (0.297 mmol) in DMF (5 mL) was added by small portions with stirring to a freshly prepared solution of HL (0.297 mmol) [19] in DMF (20 mL), and the mixture was kept in a water bath at ~90°C for 2 h. The reaction mixture was cooled to room temperature and left to stay over day. The precipitates formed were filtered off on a Schott glass filter, washed with ethanol and water, and dried under reduced pressure to a constant weight.

Synthesis of CuLAc (IV). A concentrated solution of NH_3 (1 mL) was poured to a freshly prepared solution of HL (0.149 mmol) in DMF (10 mL), after which a solution of $CuAc_2 \cdot H_2O$ (0.149 mmol) in DMF (3 mL) was added by small portions with stirring to the mixture, and the reaction mixture was kept in a water bath at ~90°C for 3 h. Then the reaction mixture was cooled to 8°C and left to stay for 3 days. The precipitate formed was filtered on a Schott glass filter, washed with ethanol and water, and dried under reduced pressure to a constant weight.

The data of elemental analysis and IR and UV spectroscopy for compounds **I–IV** and the results of studying the complex formation processes in solutions are presented in Table 1.

IR spectra were recorded on an Infralum FT-801 FTIR spectrometer for crystalline samples (KBr pellets) in a range of 4000–400 cm^{-1}. The accuracy of frequency determination depended on the band half-widths and was equal to ± 0.1 cm^{-1}.

The UV spectra of solutions of compounds **I–IV** in DMF were measured on a Varian Cary 50 Scan spectrometer in quartz cells 1.0 cm thick. The formation constants and compositions of the complexes in solutions (Table 1) were calculated from the results of the spectrophotometric titration of HL ($c = 3.4–3.5 \times 10^{-5}$ mol/L) with solutions of the corresponding metal salts ($c = 2.0–2.4 \times 10^{-3}$ mol/L) using the saturation method [20].

The quantum chemical simulation of the electronic structures of the molecular complexes was performed in terms of the density functional theory (DFT) approximation using Becke's hybrid three-parameter exchange functional [21] with the Lee–Yang–Parr correlation functional [22] (B3LYP) [23] in the def2-SV(P) and def2-TZVP basis sets [24]. The approach of natural bonding orbitals (NBO) was applied to examine the electronic structures of the ground states of molecules of the ligand and complexes [25]. All calculations were performed using the Firefly 7.1.G program package [26].

RESULTS AND DISCUSSION

An HL molecule (Fig. 1) contains two "mobile" hydrogen atoms, which assumes a potent possibility of both azo–hydrazone and thione–thiol tautomerism to occur in this molecule [19]. The most probable form of HL existing in the crystalline state and in saturated solutions is the thione quinonehydrazone tautomer stabilized by the intramolecular hydrogen bond O(1)···H–N(2), which does not exclude, however, a change in the tautomer form in dilute solutions and during complex formation.

An HL molecule contains several electron-donating atoms, which allows its coordination to *d* metals to occur via different modes. On the one hand, similarly to HL^1, HL^2, and HL^3 [7–11], an HL molecule, which exists in the anionic form and has changed its isomeric form, can interact with a metal cation through the O(1), N(1), and N(3) atoms to form two five-membered metallocycles. On the other hand, the presence in HL of the NH_2 group and S atom, which were absent from HL^1, HL^2, and HL^3, assumes two new coordination modes for the metals: in the anionic form with the formation of the five-membered and six-membered or six-membered and five-membered metallocycles involving the O(1), N(1) or N(2) and N(6) atoms, respectively; and in the neutral form involving the S and N(6) atoms with the formation of the five-membered metallocycles as shown for the

Table 1. Compositions and elemental analysis and IR and UV spectroscopy data for compounds **I–IV** and the results of the titration of HL with some *d*-metal salts

Compound	Empirical formula (color of crystals, yield, %)	Elemental analysis, %, found (calculated)					IR ν, cm^{-1}	UV λ_{max}, nm	Titration of HL with metal salts		
		C	H	N	S	M			UV λ_{max}, nm (log ε)	log β	M^{2+} : L
I	$C_{21}H_{21}N_7O_4SCo$ (green, 57.30)	47.72 (47.93)	4.74 (3.99)	18.49 (18.62)	5.86 (6.09)	10.90 (11.20)	1673 m 1607 w 1564 w 1535 w 1507 w	511	509^2 (4.16)	6.08	1 : 1
II	$C_{21}H_{21}N_7O_4SNi$ (violet, 42.50)	47.78 (47.95)	4.55 (3.99)	18.29 (18.63)	5.87 (6.10)	10.83 (11.16)	1677 w 1639 w 1540 w 1528 w	542	562^1 (4.11) 544^2 (4.23)	6.29	1 : 1
III	$C_{16}H_{13}N_6O_6SClCu$ (violet, 54.70)	38.67 (37.23)	2.66 (2.52)	16.87 (16.27)	6.37 (6.21)	12.15 (12.31)	1626 w 1576 w 1514 w	549	546^1 (4.09) 532^2 (4.20)	6.17	1 : 1
IV	$C_{18}H_{14}N_6O_3SCu$ (violet, 71.98)	46.84 (47.23)	3.65 (3.06)	18.06 (18.35)	6.95 (7.00)	13.69 (13.88)	1639 m 1589 w 1564 w 1540 w 1511 w	539	539^1 (4.07)	6.87	1 : 1

* Freshly prepared solution.

** The solution was kept for 48 h.

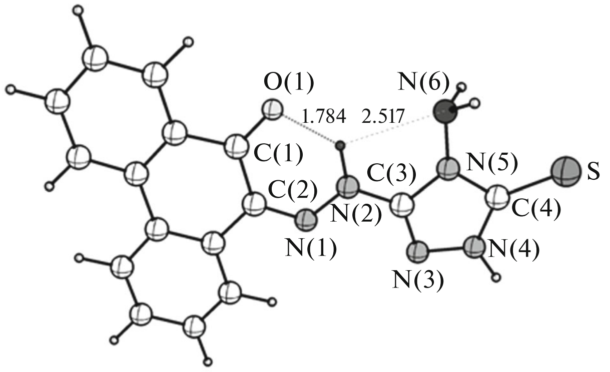


Fig. 1. Molecular structure of HL according to the DFT calculation.

compound containing the aminomercapto-4*H*-1,2,4-triazole moiety [18, 27].

The reactions of HL with the Co(II), Ni(II), and Cu(II) salts afford complexes CoLAcDMF, NiLAcDMF, CuL(H_2O)(ClO_4), and CuLAc in the crystalline state, whose compositions and structures were established on the basis of the data of elemental analysis, IR and UV spectroscopy, and DFT quantum chemical calculations.

In order to study complex formation in solutions, the spectrophotometric titration of HL with salts of some *d* metals was carried out using the saturation method, which enables one to determine long-wavelength absorption band maxima (LWBM), formation constants, and compositions of the complexes in solutions. Since the UV spectrum of compound HL in a solution undergoes changes with time (the LWAB maximum of a freshly prepared solution at 485 nm undergoes a hypsochromic shift to 474 nm after the solution was kept for 48 h [19]), the complex formation process was studied in both cases (Table 1).

A bathochromic shift by 77, 61, 54, 46, and 48 nm is observed for the titration of a freshly prepared solution of HL (λ_{max} = 485 nm) in DMF with aqueous solutions of $NiAc_2$, $Cu(ClO_4)_2$, $CuAc_2$, $Cd(NO_3)_2$, and $ZnSO_4$, respectively (Figs. 2, 3). The titration of a solution of HL kept for 48 h (λ_{max} = 474 nm) with solutions of $CoAc_2$, $NiAc_2$, and $Cu(ClO_4)_2$ results in a similar shift of the LWBM in the UV spectra (Fig. 4) by 35, 70, and 58 nm, respectively. It should be mentioned that all UV spectra exhibit one isosbestic point, indicating that the studied solutions contain two forms: the free ligand and the ligand in the composition of the complex. A significant increase in the LWBM intensity is observed in almost all cases. It can be asserted that the observed character of changing the UV spectrum is caused by complex formation processes. Since a similar change in the UV spectrum was observed for the titration of HL with a solution of NaOH [19], this indicates that the ligand enters into the compositions of the complexes in the deprotonated form.

An analysis of the saturation curves made it possible to determine the formation constants and the composition of the complexes in solutions (Table 1). It was found that the 1 : 1 complexes were formed upon the titration of HL with the Co(II), Ni(II), and Cu(II) salts in solutions, which is consistent with the compositions of synthesized complexes **I–IV**. The complexes with the 1 : 2 metal to ligand ratio are formed in solutions due to the titration with the Cd(II) and Zn(II) salts. However, these complexes were not isolated in the crystalline state. It has previously been shown [8] that HL^2, which differs from HL by the heterocyclic fragment only, in solutions and in the crystalline state forms the 1 : 2 complexes with the Co(II), Ni(II), Cd(II), and Zn(II) salts, but the difference is observed only for the Cu(II) salts, namely, the 1 : 2 complexes are formed for the crystalline state, whereas the 1 : 1 and 1 : 2 complexes are observed in solutions.

The LWBM positions in the UV spectra of complexes **I–IV** isolated in the crystalline state and the complexes formed in solutions upon the titration of HL with the Co(II), Ni(II), and Cu(II) salts are presented in Table 1. Freshly prepared solutions of HL were used for the synthesis of complexes **I–IV**, but the LWBM positions in the UV spectra of complexes **I** and **II** correspond to the LWBM positions for the titration of an HL solution kept for 48 h with the Co(II) and Ni(II) salts. This was not observed in the case of the Cu(II) complexes (**III** and **IV**) for which the LWBM position in the UV spectrum corresponds to the titration of a freshly prepared solution of HL.

A possible reason for the observed difference can be the fact that HL in the crystalline form and in concentrated solutions exists in the dimeric "sandwich" form [28] in which the HL and HL' molecules are bound by the π–π-stacking interaction according to the parallel-displaced (PD) type [29], whereas in dilute solutions HL exists in the monomeric form. An assumption about the transition from the dimeric to monomeric form explains the hypsochromic character of changing the UV spectrum of compound HL in time. The observed difference in the UV spectra of the complexes can be explained by the fact that the ligand in the monomeric form enters into the compositions of complexes **I** and **II**, while the ligand has the dimeric form in the case of complexes **III** and **IV** as for the dimeric complex $[Cu_2(L^3)_2(H_2O)_4](ClO_4)_2$ [10]. Therefore, the structures of complexes **III** and **IV** can be described by the formulas $[Cu_2L_2(H_2O)_2](ClO_4)_2$ and $[Cu_2L_2Ac_2]$.

The IR spectra of isolated complexes **I–IV** in the polycrystalline state at ~3430 cm^{-1} contain a broad intense band assigned (in the case of HL) to stretching vibrations of the N(4)–H group and have no bands attributed [19] to stretching vibrations of the N(2)–H and NH_2 groups bound by an intramolecular hydro-

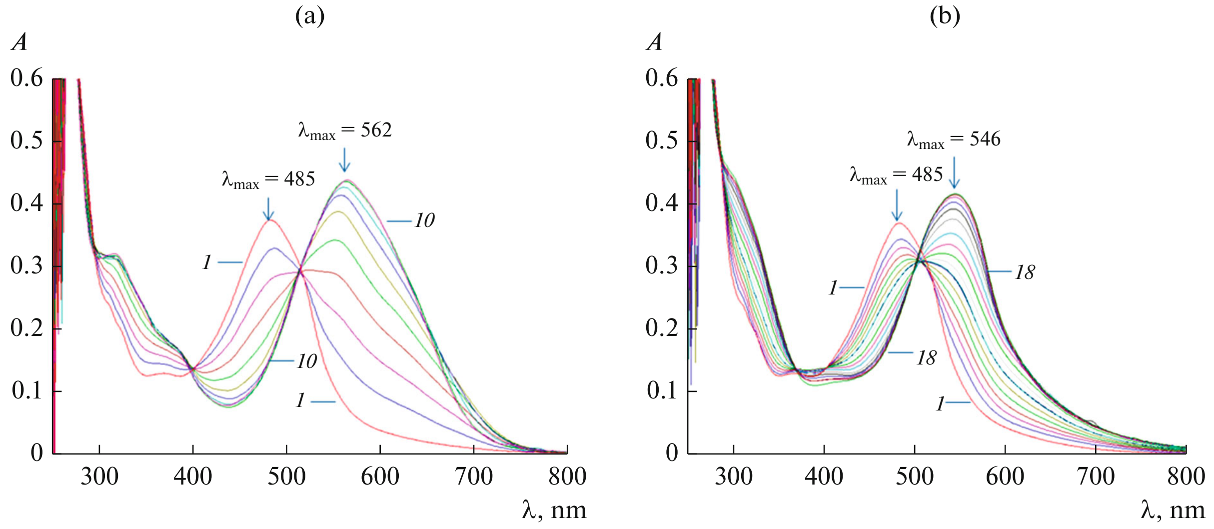


Fig. 2. UV spectra obtained by the results of titration of a freshly prepared solution of HL ($c = 3.4 \times 10^{-5}$ mol/L, line *1*) with solutions of (a) $Ni(Ac)_2$ ($c = 2.0 \times 10^{-3}$ mol/L, lines *2–10*) and (b) $Cu(ClO_4)_2$ ($c = 2.0 \times 10^{-3}$ mol/L, lines *2–18*).

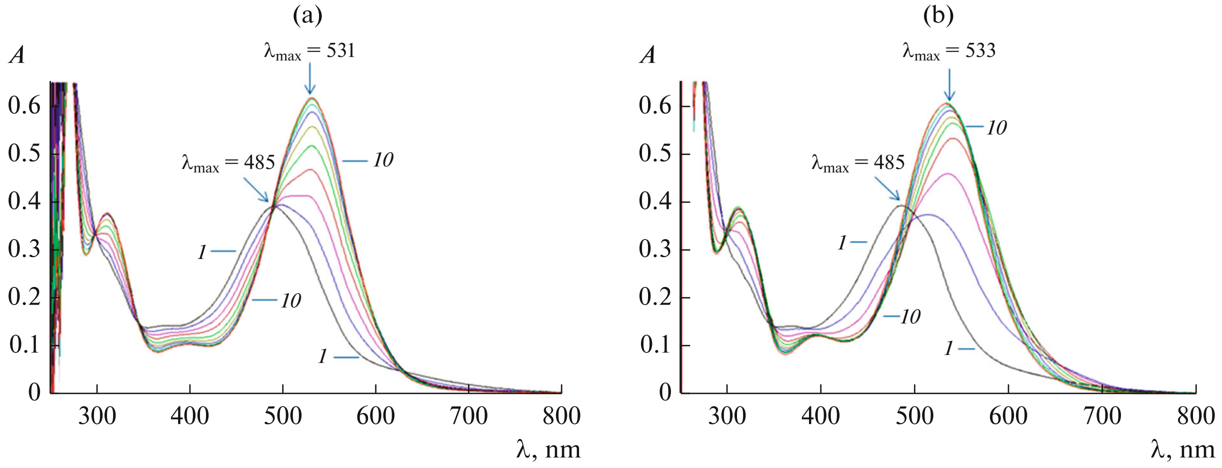


Fig. 3. UV spectra obtained by the results of titration of a freshly prepared solution of HL ($c = 3.4 \times 10^{-5}$ mol/L, line *1*) with solutions of (a) $Cd(NO_3)_2$ ($c = 2.05 \times 10^{-3}$ mol/L, lines *2–10*) and (b) $ZnSO_4$ ($c = 2.4 \times 10^{-3}$ mol/L, lines *2–10*).

gen bond. The ν(C=O) band at 1618 cm^{-1} characteristic of HL is absent, and the bands with the absorption maxima at 1573–1501 cm^{-1} assigned to the C=N and C=C bond vibrations are slightly shifted to the low-frequency range relative to HL with the simultaneous redistribution of their relative intensity. Complexes **I** and **II** contain DMF molecules, which is confirmed by their IR spectra exhibiting the ν(C=O) band at 1677 cm^{-1} characteristic of the coordinated DMF molecule [30]. Since the IR spectra of compounds **I**, **II**, and **IV** exhibit medium-intensity bands at 1639 cm^{-1}, which can be assigned to stretching vibrations of the coordinated carboxyl group of the acetate anion, it can be assumed that the acetate ion completes the internal coordination sphere of Co(II), Ni(II), and Cu(II) in these complexes.

The elemental analysis data indicate that the ligand enters into the composition of the complex as an anion. An analysis of the electron density distribution in an HL molecule shows a shift of 0.166 ē from the triazole moiety to the hydrazo group. This decreases the donor properties of the triazole moiety and makes the coordination of the neutral HL molecule involving the S and N(6) atoms poorly probable.

To determine the most probable coordination mode of L^- by the metal cations, we performed the quantum chemical calculation of the structure of the model complex ZnLAc · DMF (**V**). The composition of this complex is similar to those of isolated com-

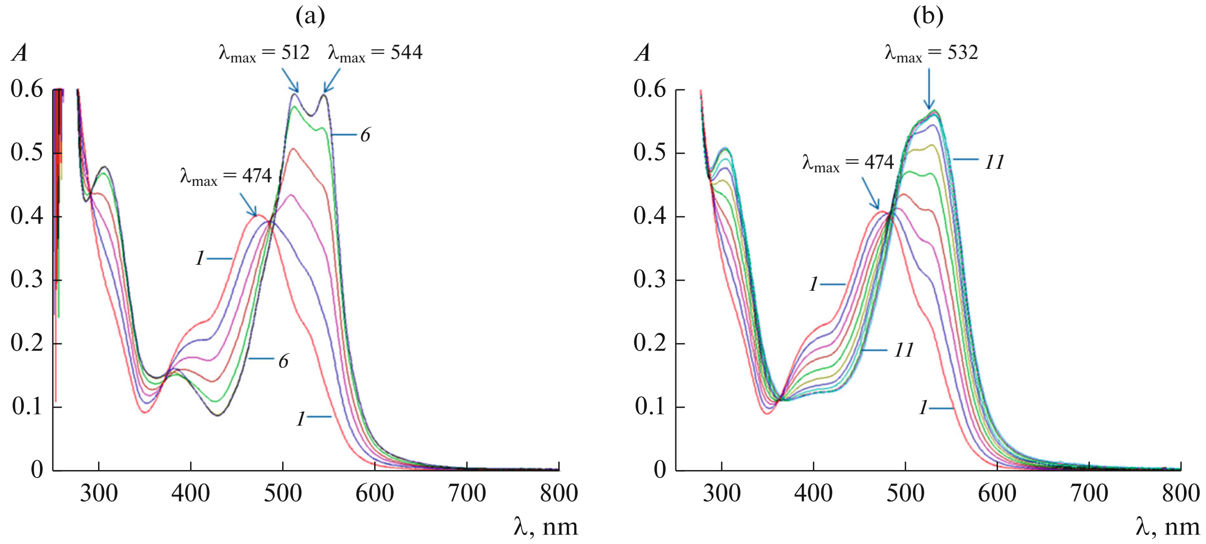


Fig. 4. UV spectra obtained by the results of titration of a solution of HL ($c = 3.52 \times 10^{-5}$ mol/L, line *1*) kept for 48 h with solutions of (a) $Ni(Ac)_2$ ($c = 2.0 \times 10^{-3}$ mol/L, lines *2–6*) and (b) $Cu(ClO_4)_2$ ($c = 2.0 \times 10^{-3}$ mol/L, lines *2–11*).

plexes **I** and **II**, but a similar complex itself was not isolated. The molecular structures of possible forms of complex **V** and the corresponding relative energies (kJ/mol) are presented in Fig. 5.

In complexes **Va** and **Vb**, the ligand in the anionic form acts as a tridentate ligand and is coordinated by the metal cation through the O(1), N(1), and N(3) atoms to form two five-membered metallocycles as it took place earlier [7–11]. Complex **Vb** in which the ligand exists in the thione form is more stable than complex **Va** in which the ligand has the thiol form. It can be assumed that in complexes with other metals the HL ligand exists in the anionic form of the thione tautomer. However, HL can coordinate not only through the N(3) nitrogen atom of the heterocyclic fragment [7–11] but also through the N(6) nitrogen atom of the amino group. In this case, two metallocycles (five-membered and six-membered) are also formed. The most stable form is complex **Vd** in which the O(1) atom participates in the six-membered metallocycles and the N(6) atom is involved in the five-membered metallocycles.

In the calculated structures of complexes **Va–Vd**, the coordination polyhedron of zinc is a distorted octahedron. The L^- anion is tridentate, the acetate ion is bidentate, and DMF is a monodentate ligand (Fig. 5).

In addition to the choice of an optimum scheme of coordination, the simulation of the structure of the isolated complex CoLAc · DMF (**VI**) includes the choice of the spin state of the cobalt ion in the complex. Two variants are possible: the high-spin complex with a multiplicity of 4 and the low-spin complex with a multiplicity of 2. The high-spin complex is more stable than the low-spin one by 31 kJ/mol. The situation is similar for complex NiLAc · DMF: the high-spin complex with a multiplicity of 3 is more stable than the low-spin complex with a multiplicity of 1 by 41 kJ/mol. It follows from the values of energy that the high-spin cobalt and nickel complexes are more stable than the low-spin complexes, and synthesized complexes **I** and **II** can be assumed to have the structures presented in Fig. 6.

The coordination polyhedron of the metal in the high-spin cobalt and nickel complexes is a distorted octahedron. The L^- anion is tridentate, the acetate ion is bidentate, and DMF is a monodentate ligand (Fig. 6).

Copper complex **IV** has the composition CuLAc; i.e., the complex contains no DMF molecule. Therefore, we performed calculations for both complexes CuLAc (Fig. 7a) and CuLAc · DMF (Fig. 7b) similarly to the earlier considered nickel and cobalt complexes.

The coordination polyhedron of copper in the calculated CuLAc complex (**VIIa**) is a distorted square. The L^- anion is tridentate, and the acetate ion is a monodentate ligand. In the model CuLAc · DMF complex (**VIIb**), the coordination polyhedron of copper is an extended tetragonal pyramid in which the distance between the Cu atom and O(4) atom of DMF (2.302 Å) is longer than those in the cases of the cobalt (2.166 Å) and nickel (2.132 Å) octahedral complexes (Fig. 6). It can be assumed that the weakening of the bond between the copper atom and DMF molecule, which was mentioned in the calculation for the gas phase, results in the abstraction of the DMF molecule to form the square complex characteristic of copper in the solid phase.

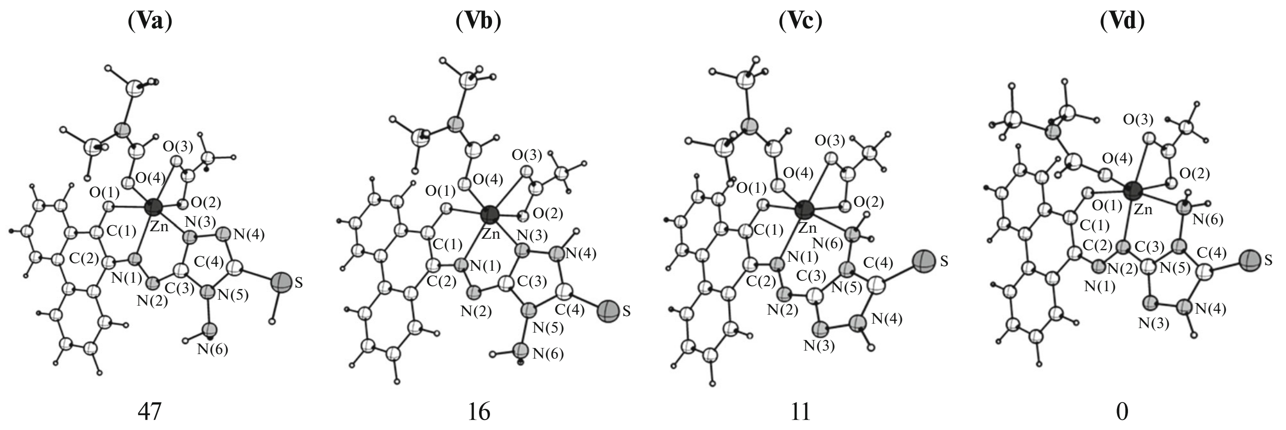


Fig. 5. Molecular structures of some forms of complex **V** (a–d) and their relative energies (kJ/mol).

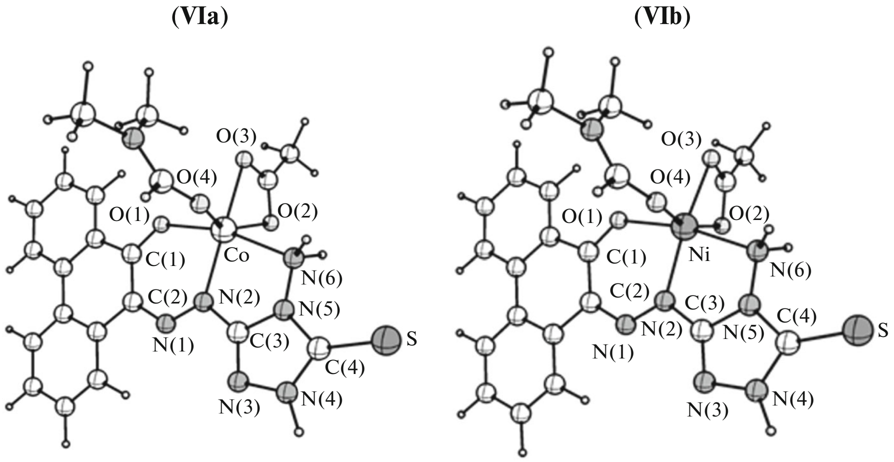
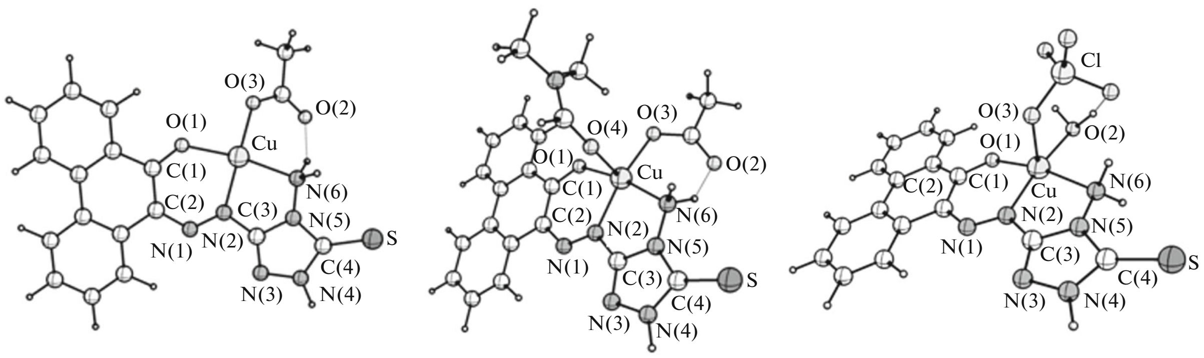


Fig. 6. Molecular structures of complexes CoLAc · DMF (**VIa**) and NiLAc · DMF (**VIb**) according to the DFT calculations.

The copper complex isolated by us (**III**) has the composition $CuLClO_4 \cdot H_2O$. The calculation of this complex (Fig. 7c) shows that the coordination polyhedron of copper is an extended tetragonal pyramid in which the distance between the metal and oxygen atom of the perchlorate ion (2.284 Å) is noticeably longer than the distances between the copper atoms and O(1), O(2), N(2), and N(6) atoms (Table 2). In spite of the hydrogen bond (1.760 Å) between the hydrogen atom of the amino group and one of the oxygen atoms of the perchlorate ion (Fig. 7c), the weak bond of the perchlorate ion with the metal can result in the shift of the perchlorate ion from the internal sphere of complex **III** to which the composition $[CuL(H_2O)]ClO_4$ can be ascribed. In this case, the coordination polyhedron of copper is a distorted square. A similar situation was observed for the calculated complex CuLAc · DMF containing a weak bond between the copper atom and oxygen atom of DMF, whereas isolated complex **IV** contained no DMF molecules. The conclusion that the perchlorate ion exists in the external sphere of complex **III** is consistent with the data on the structure of the $[Cu_2(L^3)_2(H_2O)_4](ClO_4)_2$ complex [10]. Based on the aforesaid, we can assume that complexes **III** and **IV** are also dimeric: $[Cu_2L_2(H_2O)_2](ClO_4)_2$ and $[Cu_2L_2Ac_2]$.

The calculated lengths of some bonds in HL, CoLAc · DMF, NiLAc · DMF, CuLAc, and $CuLClO_4 \cdot H_2O$ are given in Table 2, and the calculated charges of selected atoms in these molecules are listed in Table 3.

The calculated bond lengths of the metal with the O(1), O(2), O(3), O(4), N(2), and N(6) atoms in the cobalt and nickel complexes (Table 2) lie in comparatively narrow ranges, and the bonds of the metal with the O(4) atom of DMF are shorter than the bonds of the metal with the N(6) atoms. Therefore, it can be concluded that the DMF molecule is localized in the internal sphere of complexes **I** and **II**, and possible formulas of the complexes are [CoLAc · DMF] and



(VIIa) **(VIIb)** **(VIIc)**

Fig. 7. Molecular structures of complexes CuLAc (**VIIa**), CuLAc · DMF (**VIIb**), and $CuLClO_4 \cdot H_2O$ (**VIIc**) according to the DFT calculations.

[NiLAc · DMF]. In the Co–Ni–Cu series, the lengths of the bonds of the metal with the oxygen and nitrogen atoms are somewhat shortened (Table 2). However, the bond of Cu with O(3) of the perchlorate ion in the $CuLClO_4 \cdot H_2O$ complex (2.284 Å) is appreciably longer than other bonds of the metal with the heteroatoms, in particular, the bond of Cu with O(2) of water (2.024 Å). It can be assumed that the internal sphere of the complex contains a water molecule and the perchlorate ion is localized in the external sphere and is retained by hydrogen bonds. As earlier, this allows one to propose the formula $[CuL(H_2O)]ClO_4$ or $[Cu_2L_2(H_2O)_2](ClO_4)_2$ for complex **III**.

The calculated charges of the metal atoms range from +1.482 to +1.261 and differ appreciably from a value of +2, indicating the electron density transfer from the ligands to the metal cation (Table 3). The value of the electron density transfer from the L^- monoanion to the metal cation is 0.248, 0.279, 0.452,

Table 2. Selected bond lengths (Å) in an HL molecule and in the CoLAc · DMF, NiLAc · DMF, CuLAc, and $CuLClO_4 \cdot H_2O$ complexes according to the DFT calculations

Bond	Molecule				
	HL	CoLAc · DMF	NiLAc · DMF	CuLAc	$CuLClO_4 \cdot H_2O$
M–O(1)*		2.028	2.011	1.952	1.941
M–O(2)		2.118	2.115		2.024
M–O(3)		2.168	2.096	1.924	2.284
M–O(4)		2.166	2.132		
M–N(2)		2.072	2.036	1.979	1.963
M–N(6)		2.248	2.179	2.086	2.139
O(1)–C(1)	1.239	1.263	1.262	1.265	1.268
C(1)–C(2)	1.481	1.451	1.453	1.455	1.454
C(2)–N(1)	1.312	1.334	1.336	1.328	1.328
N(1)–N(2)	1.314	1.293	1.289	1.289	1.282
N(2)–C(3)	1.375	1.378	1.375	1.382	1.380
C(3)–N(3)	1.302	1.306	1.306	1.302	1.301
C(3)–N(5)	1.382	1.387	1.389	1.384	1.384
N(3)–N(4)	1.372	1.371	1.371	1.371	1.370
N(4)–C(4)	1.360	1.363	1.362	1.368	1.367
C(4)–N(5)	1.395	1.387	1.387	1.391	1.391
N(5)–N(6)	1.382	1.385	1.386	1.384	1.386
C(4)–S	1.659	1.660	1.660	1.653	1.653

* M = Co, Ni, and Cu.

Table 3. Charges on the atoms in an HL molecule calculated using the NBO approach and in the CoLAc · DMF, NiLAc · DMF, CuLAc, and $CuLClO_4 \cdot H_2O$ complexes according to the DFT calculations

Atom	Molecule				
	HL	CoLAc · DMF	NiLAc · DMF	CuLAc	$CuLClO_4 \cdot H_2O$
M*		+1.482	+1.433	+1.261	+1.289
O(1)	–0.613	–0.736	–0.725	–0.698	–0.710
O(2)		–0.787	–0.762	–0.714	–0.960
O(3)		–0.793	–0.802	–0.825	–0.895
O(4)		–0.740	–0.734		
C(1)	+0.511	+0.498	+0.503	+0.508	+0.513
C(2)	+0.114	+0.077	+0.070	+0.088	+0.088
N(1)	–0.199	–0.188	–0.182	–0.165	–0.148
N(2)	–0.385	–0.498	–0.478	–0.493	–0.458
C(3)	+0.614	+0.607	+0.607	+0.599	+0.601
N(3)	–0.334	–0.326	–0.326	–0.318	–0.311
N(4)	–0.383	–0.379	–0.379	–0.380	–0.377
C(4)	+0.217	+0.221	+0.221	+0.214	+0.213
S	–0.233	–0.239	–0.240	–0.199	–0.195
N(5)	–0.292	–0.289	–0.291	–0.295	–0.293
N(6)	–0.637	–0.684	–0.683	–0.729	–0.705

* M = Co, Ni, and Cu.

and 0.536 ē for four isolated complexes, respectively. The electron density on the O(1), N(2), and N(6) atoms directly bound to the metal increases substantially upon coordination (Table 3), and the density is transferred from the atoms that are not directly bound to the metal, including the hydrogen atoms.

Taking into account the character of the IR and UV spectra and the quantum chemical calculation data, it can be asserted that the ligand enters into the composition of the complex as an anion to form the 1 : 1 coordination compounds. According to the DFT quantum chemical calculations, the most probable is the formation of the complexes in which the metal atom is coordinated by the O(1) atom to form the six-membered ring and by the N(6) atom to form the five-membered ring (6 + 5). The coordination polyhedron in the high-spin nickel and cobalt complexes is a distorted octahedron, and that in the copper complexes is a distorted square. It is assumed that the ligand enters into the compositions of the copper complexes in the dimeric sandwich form.

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