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Quantum-Chemical Model for the Formation of the Coordination Mode Structure of Be(II), Ni(II), Pd(II), Pt(II), and Hg(II) Bis(chelate) Complexes with Polydentate Azomethine Ligands

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Abstract—The competitive coordination for the formation of the coordination mode (MN_2O_2 or MN_2S_2) of Be(II), Ni(II), Pd(II), Pt(II), and Hg(II) bis(chelate) complexes based on thioindanone derivatives of aromatic azomethines is studied using the density functional theory methods. The dependences of the relative stability of the complexes on the properties of the central metal atom and ligating donor atoms are qualitatively consistent with Pearson's principle of hard and soft acids and bases. The dependences of the MN_2Y_2 ($Y = O$, S) coordination mode configuration on the nature of the metal atom, donor atoms, and specific features of the ligand structure are explained on the basis of the calculated data obtained for the azomethine bis(chelates) of d^8 metals (Ni^{2+}, Pd^{2+}, and Pt^{2+}).

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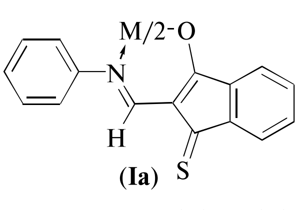
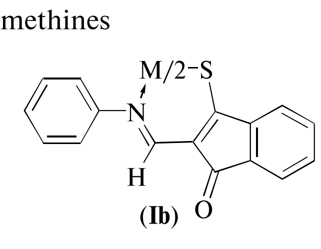
INTRODUCTION

Considerable attention is given to experimental studies of the molecular structures and spectral, magnetic, and other physical properties of chelate complexes of transition and nontransition metals with Schiff bases (coordination modes MN_2Y_2 ($Y = O$, S)) [1–4]. The complexes of transition d^8 metals (Ni^{2+}, Pd^{2+}, and Pt^{2+}) are characterized by the polyvariant configurations (*cis*- and *trans*-planar and *pseudo*-tetrahedral) of the coordination mode MN_2Y_2 ($Y = O$, S), depending primarily on the nature of the central metal atom, the choice of ligating donor atoms, and structural regularities of the ligands. The transition from the O-containing ($Y = O$) to S-containing ($Y = S$) complexes is accompanied by basic changes in the configuration of the coordination mode MN_2Y_2 and related properties of the complexes [1–6]. Therefore, complexes based on bifunctional donor systems capable of accomplishing one of two variants of the coordination mode MN_2O_2 (**a**) or MN_2S_2 (**b**), depending on the metal atom, are of special interest. They are simulated by the metal complexes of the thioindanone derivatives of aromatic azomethines



(Ia)



(Ib)

M = Be(II), Ni(II), Pd(II), Pt(II), Hg(II).

The competitive coordination of O- and S-donor centers leading to the formation of a(MN_2O_2) and b(MN_2S_2) isomers, respectively, of complexes **I** can be considered in terms of Pearson's principle of hard and soft acids and bases (HSAB) [7–9]. According to Pearson's "rule of relative stability of acid–base complexes" (HSAB principle), "hard acids interact preferentially with hard bases, and soft acids interact preferentially with soft bases" [9]. This means that the HSAB principle can be used for the prediction of the comparable stability of compounds (thermodynamic aspect) and the direction of chemical reactions (kinetic aspect). Basically empirical Pearson's concept initiated the development of theoretical models for the description of the acid–base equilibrium [10–14], including the earliest concept about the controlling effect of frontier molecular orbitals of interacting molecules [11] and the further developed concepts and formulations of the "chemical hardness" of molecules [12–14]. At the same time, theoretical substantiations of the main principle of the HSAB concept with respect to the competitive reactivity during the formation of coordination metal compounds (i.e., competitive coordination) on the basis of data calculated by modern quantum-chemical methods are nearly lacking.

The purpose of this work is the theoretical (based on quantum-chemical calculations by the density functional theory (DFT) method) analysis of the competitive coordination during the formation of molecular structures of the polyvariant (by composition (MN_2O_2 or MN_2S_2) and configuration (*trans*- and *cis*-

Table 1. Total E (au), relative ΔE (kcal/mol), and relative with allowance for zero-point vibrations ΔE_{ZPE} (kcal/mol) energies of the a(MN_2O_2) and b(MN_2S_2) isomers of complexes **I** (M = Be(II), Hg(II)) calculated by the DFT method

DFT method	Isomer	E	ΔE	ΔE_{ZPE}
M = Be(II)				
B3LYP	a(BeN_2O_2)	–2303.162692	0.0	0.0
	b(BeN_2S_2)	–2303.130707	20.1	19.5
PBE0	a(BeN_2O_2)	–2301.076248	0.0	0.0
	b(BeN_2S_2)	–2301.024741	15.5	15.0
TPSSh	a(BeN_2O_2)	–2303.259158	0.0	0.0
	b(BeN_2S_2)	–2303.232913	16.5	15.8
M = Hg(II)				
B3LYP	a(HgN_2O_2)	–2441.077725	3.8	4.4
	b(HgN_2S_2)	–2441.083704	0.0	0.0
PBE0	a(HgN_2O_2)	–2439.001154	6.1	6.7
	b(HgN_2S_2)	–2439.010834	0.0	0.0
TPSSh	a(HgN_2O_2)	–2441.114878	5.1	5.7
	b(HgN_2S_2)	–2441.122977	0.0	0.0

planar or *pseudo*-tetrahedral)) coordination modes of the Be(II), Ni(II), Pd(II), Pt(II), and Hg(II) bis(chelate) azomethine complexes and the comparison of the obtained results with the concepts of the HSAB principle.

The range of the considered complexing d^8 metals (Ni^{2+}, Pd^{2+}, and Pt^{2+}) was extended by to the central Be^{2+} and Hg^{2+} ions as polar representatives of hard and soft Lewis acids in the classification series of Pearson's concept [7–9]. The calculation scheme (as an investigation method) was chosen on the basis of results of an analysis of the applicability of the DFT method to the solution of molecular problems [15–17], including the studies of the coordination compounds [17].

The Be(II) and Hg(II) complexes. The calculations of four complexes as possible combinations of a pair of hard (Be^{2+}) and soft (Hg^{2+}) Lewis acids with a part of the hard O- and soft S-donor centers competing with each other for the formation of the a(MN_2O_2) or b(MN_2S_2) isomers of complexes **I** make it possible to theoretically study the dependences of the relative stability of acid–base complexes on the degree of hardness or softness of acids and bases. Note that the specific feature of the molecular structures of the complexes chosen as models allows one to estimate the energy effect of the variation of the hard O- and soft S-donor centers by the quantitative comparison of the energies of the a(MN_2O_2) and b(MN_2S_2) isomers of complexes **I** separately for each metal (Table 1).

Taking into account the known dependence of the DFT calculation results on the functional type [16, 17], we calculated the a(MN_2O_2) and b(MN_2S_2) isomers of the Be(II) and Hg(II) complexes using three hybrid functionals: B3LYP [18, 19], PBE0 [20], and TPSSh [21]. The 6-311++G(d,p) basis set was used for the Be(II) complexes, and the Hg(II) complexes were calculated in the SDD basis set.

The calculations of the Be(II) complex show that the **a** isomer with the coordination mode BeN_2O_2 (Fig. 1) is energetically more preferable than the **b** isomer with the coordination mode BeN_2S_2 for all variants of the functionals used (Table 1). Similar calculations of the Hg(II) complex show that the **b** isomer with the coordination mode HgN_2S_2 is the most stable one, unlike the Be(II) complex (Fig. 1, Table 1).

The results obtained are entirely consistent with the thermodynamic representation of the HSAB principle about the preference of the hard–hard (Be–O) or soft–soft (Hg–S) type compared to the mixed (Be–S or Hg–O) type of acid–base interactions.

Thus, the quantum-chemical calculations confirm that Pearson's HSAB principle makes it possible to qualitatively predict the relative stability of the complexes from the properties of the central complexing atom and ligating donor atoms.

The results of calculations of the **a** and **b** isomers of the Be(II) and Hg(II) complexes obtained using different functionals are in good agreement (Table 1). Based on this, the most frequently used B3LYP density functional was applied further for similar studies of the a(MN_2O_2) and b(MN_2S_2) isomers of the Ni(II), Pd(II), and Pt(II) complexes. The geometric parameters of complexes **I** (M = Be(II), Ni(II), Pd(II), Pt(II), and Hg(II)) calculated in this approximation (DFT/B3LYP) are given in Table 2. In particular, it follows from Table 2 that all **a** and **b** isomers of the Be(II) and Hg(II) complexes have the coordination mode configuration of the same type (*pseudo*-tetrahedral).

The Pd(II) and Pt(II) complexes. According to the classification concepts of the HSAB principle [7–9],

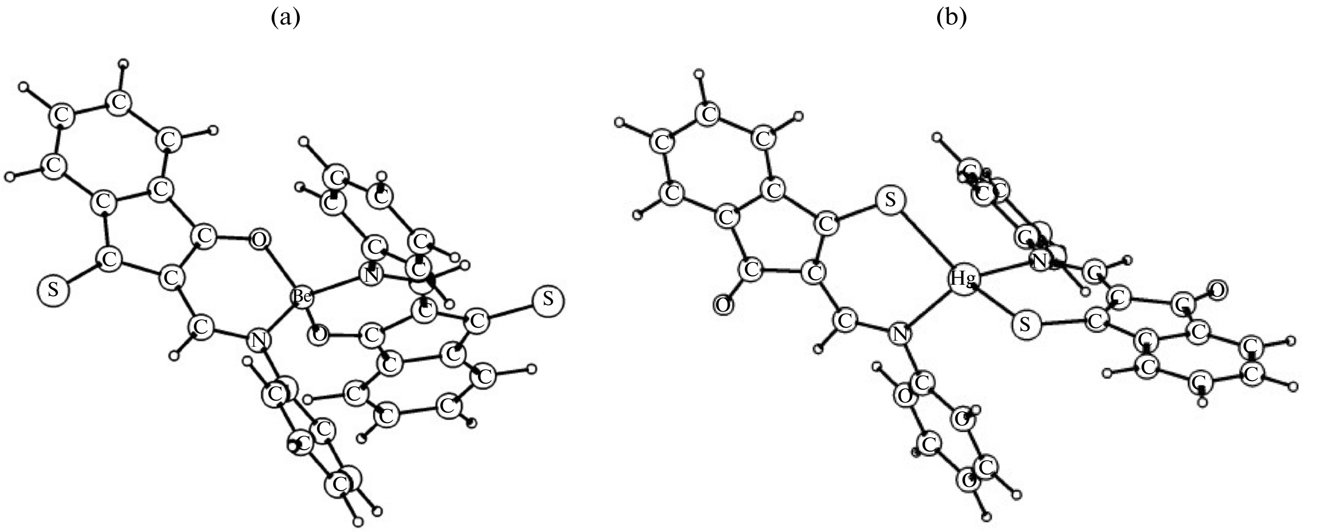


Fig. 1. Calculated (DFT/B3LYP) molecular structures of the energetically favorable (a) a(MN_2O_2)) isomer of the Be(II) complex and (b) b(MN_2S_2) isomer of the Hg(II) complex.

Pd^{2+} and Pt^{2+} are soft Lewis acids, which allow one to expect that the b(MN_2S_2) isomer would be preferable compared to the a(MN_2O_2) isomer for complexes **I** (M = Pd(II), Pt(II)). Unlike the above considered beryllium and mercury complexes, the palladium and platinum complexes are polyvariant by the composition (MN_2O_2 or MN_2S_2) and configuration (*trans*- or *cis*-planar) of the coordination mode. Taking this into

Table 2. Calculated (DFT/B3LYP) geometric parameters of the coordination modes MN_2O_2 and MN_2S_2 (lengths (Å) of the M–N and M–Y (Y = O, S) bonds and angles (deg) between them) for the isomers of complexes **I** (M = Be(II), Ni(II), Pd(II), Pt(II), and Hg(II)) (*ps-tt* is *pseudo*-tetrahedral, *trans* is *trans*-planar, and *cis* is *cis*-planar configuration)

Mode MN_2Y_2	Configuration	Bond, Å		Angle, deg			
		M–N	M–Y	NMY	NMY'*	NMN	YMY
BeN_2O_2	*ps-tt*	1.738	1.643	106.8	111.8	112.9	106.7
BeN_2S_2	*ps-tt*	1.717	2.162	108.8	110.7	114.1	103.2
HgN_2O_2	*ps-tt*	2.124	2.467	88.4	100.2	164.7	112.0
HgN_2S_2	*ps-tt*	2.313	2.592	95.4	121.8	105.8	117.9
PdN_2O_2	*trans*	2.070	2.027	92.7	87.3	180.0	174.7
PdN_2O_2	*cis*	2.057	2.049	91.9	168.0	95.3	82.7
PdN_2S_2	*trans*	2.075	2.426	93.2	87.3	176.5	163.9
PdN_2S_2	*cis*	2.097	2.396	93.4	168.7	92.4	82.6
PtN_2O_2	*trans*	2.068	2.033	93.0	87.0	179.8	176.0
PtN_2O_2	*cis*	2.054	2.059	92.0	169.5	95.2	82.0
PtN_2S_2	*trans*	2.078	2.432	93.5	86.8	177.4	167.0
PtN_2S_2	*cis*	2.091	2.410	93.7	170.0	91.7	82.3
NiN_2O_2	*ps-tt*	1.996	1.969	95.2	110.1 137.4**	111.8	106.0
NiN_2O_2	*trans*	1.955	1.876	93.9	86.5	175.3	179.2
NiN_2O_2	*cis*	1.935	1.902	93.8	162.0	95.0	82.3
NiN_2S_2	*ps-tt*	2.007	2.313	98.9	103.9 108.1**	139.2	103.7
NiN_2S_2	*trans*	1.945	2.263	95.6	87.6	166.9	151.8
NiN_2S_2	*cis*	1.963	2.235	96.0	156.7	92.4	84.7

* The NMY' angle, unlike the NMY angle, is the angle between the bonds of the central M atom and the donor centers of two ligands of the complex.

** In the a(MN_2O_2) and b(MN_2S_2) isomers of the Ni(II) complexes in the *pseudo*-tetrahedral configuration, two NMY' angles differ for each isomer.

Table 3. Calculated (DFT/B3LYP/SDD) total E (au), relative ΔE (kcal/mol), and relative with allowance for zero-point vibrations ΔE_{ZPE} (kcal/mol) energies for the a(MN_2O_2) and b(MN_2S_2) isomers of complexes **I** (M = Pd(II), Pt(II))

Mode	*trans*-Configuration			*cis*-Configuration		
	E	ΔE	ΔE_{ZPE}	E	ΔE	ΔE_{ZPE}
PdN_2O_2	–2415.527314	1.7	2.3	–2415.518655	6.6	7.2
PdN_2S_2	–2415.529954	0.0	0.0	–2415.529092	0.0	0.0
PtN_2O_2	–2406.995140	3.6	4.2	–2406.986219	7.8	8.5
PtN_2S_2	–2407.000875	0.0	0.0	–2406.998622	0.0	0.0

Table 4. Relative ΔE (kcal/mol) and relative with allowance for zero-point vibrations ΔE_{ZPE} (kcal/mol) energies for the *trans*- and *cis*-planar configurations of the a(MN_2O_2) and b(MN_2S_2) isomers of complexes **I** (M = Pd(II), Pt(II))

Configuration	Mode							
	PdN_2O_2		PdN_2S_2		PtN_2O_2		PtN_2S_2	
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
trans-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cis-	5.4	5.4	0.5	0.5	5.6	5.7	1.4	1.4

account, the calculations of the a(MN_2O_2) and b(MN_2S_2) isomers of the Pd(II) and Pt(II) complexes were performed for the *trans*- and *cis*-configurations of the coordination mode (Tables 2, 3).

The obtained results (Table 3) show that the b(MN_2S_2) isomer is more preferable than a(MN_2O_2) for both the *trans*- and *cis*-configurations of the coordination mode of the Pd(II) and Pt(II) complexes in full agreement with the thermodynamic representation of the HBAS principle.

The comparison of the results of calculations of the *trans*- and *cis*-planar configurations of the **a** and **b** isomers of complexes **I** (M = Pd(II), Pt(II)) makes it possible to draw two main conclusions. The first conclusion concerns the a(MN_2O_2) isomer: the *trans*-planar conformation of this isomer is noticeably more preferable than the *cis*-planar conformation of the coordination mode MN_2O_2 (Table 4). The second conclusion refers to the b(MN_2S_2) isomer and can be reduced to the fact that the *cis*-planar configuration for this isomer becomes energetically competitive with respect to the *trans*-planar configuration of the coordination mode MN_2S_2 (Table 4).

The conclusions about the stability of the *trans*- and *cis*-planar configurations of the coordination modes MN_2O_2 or MN_2S_2 of the Pd(II) and Pt(II) complexes can be assigned to the conformational features of the O- and S-containing metallocycles.

According to the stereochemical model of the tetracoordinated metal chelates [6], the S-containing metallocycles are characterized, as a rule, by a significant inflection along the line of the donor atoms N–S, unlike the flattened O-containing metallocycles. The mentioned conformational differences in the O- and S-containing metallocycles appeared completely in the results of the quantum-chemical calculations of complexes **I** (M = Pd(II), Pt(II)). For the most favorable *trans*-planar configuration of the Pd(II) and Pt(II) azomethine complexes, the inflection angles of the metallocycles along the lines of the N–O atoms in the a(MN_2O_2) isomers are 8.6° (M = Pd(II)) and 7.2° (M = Pt(II)), whereas the inflection angles along the line of the N–S atoms in the b(MN_2S_2) isomers are 28.2° (M = Pd(II)) and 35.9° (M = Pt(II)). In other words, interligand interactions of the substituents at the donor nitrogen atoms of the azomethine group for the flattened structures of the O-containing metallocycles result in steric hindrances for the formation of the *cis*-planar configuration and favor, according to the calculations (Table 4), the formation of the *trans*-planar configuration of the coordination mode MN_2O_2 in the Pd(II) and Pt(II) complexes. At the same time, for the S-containing complexes of these metals, a considerable inflection of the metallocycles along the line of the N–S donor atoms (Fig. 2) decreases the corresponding interligand interactions, which aligns (Table 4) the differences in the total energy of the *trans*- and *cis*-isomers of the Pd(II) and Pt(II) complexes. The *trans*-configuration of complexes **I** (M = Pd(II), Pt(II); Y = O, S) is characterized by an “umbrella” conformation (Fig. 2a), whereas the *cis*-conformation is typical of a “step” conformation (Fig. 2b).

The comparison of the results of calculations of the relative energy (ΔE) and the relative with allowance for zero-point vibration energy (ΔE_{ZPE}) of the isomers of the complexes presented in Tables 1, 3, and 4 shows that the allowance for the zero-point vibration energy exerts almost no effect on the discussed results and, hence, only the value of ΔE was used further for the

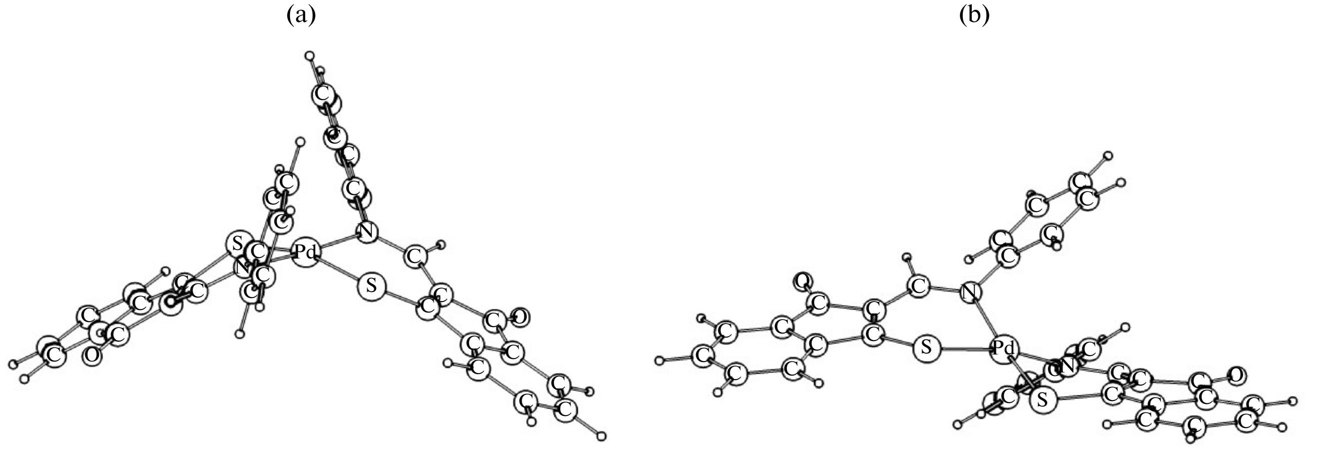


Fig. 2. Calculated molecular structures of the (a) *trans*- and (b) *cis*-configurations of the b(MN_2S_2) isomer of complex **I** (M = Pd(II)).

estimation of the relative energy of the isomers of the complexes.

The Ni(II) complexes. In the classification series of Pearson's chemical hardness, Ni^{2+} is assigned to an intermediate type of Lewis acids capable of manifesting the properties of both hard and soft acids [7–9]. In addition, as the above considered Pd(II) and Pt(II) complexes, the nickel complex is polyvariant by both the composition (MN_2O_2 or MN_2S_2) and configuration (*pseudo*-tetrahedral, *trans*- and *cis*-planar) of the coordination mode [1–4]. Taking this into account, we performed calculations (Tables 2 and 5) for the *pseudo*-tetrahedral configuration corresponding to the triplet electron state and for the *trans*- and *cis*-planar configurations corresponding to the singlet electron state of the a(MN_2O_2) and b(MN_2S_2) isomers of complex **I** (M = Ni(II)).

An analysis of the total energies of the considered configurations of the coordination mode shows that the b(MN_2S_2) isomer is preferable compared to the a(MN_2O_2) isomer (Table 5). This means that Ni^{2+} manifests the properties of a soft Lewis acid according to the HSAB principle. In complete accordance with the experimental regularities indicating the tetrahedral distortion of the coordination mode in the Ni(II) bis(chelates) including annelated five-membered hetero- or carbocycles [1], the calculations showed the preference of the *pseudo*-tetrahedral configuration (Fig. 3) compared to the *trans*- and *cis*-planar configurations for both the a(NiN_2O_2) (Fig. 3a) and b(NiN_2S_2) (Fig. 3b) isomers of complex **I** (M = Ni(II)).

The energy preference of the *pseudo*-tetrahedral configuration of the a(NiN_2O_2) isomer over the *trans*-planar configuration is 3.1 kcal/mol, whereas that over the *cis*-planar configuration is 7.7 kcal/mol. For the b(NiN_2S_2) isomer, the *pseudo*-tetrahedral configuration is more favorable by 5.4 kcal/mol compared to the *trans*-planar configuration and by 5.3 kcal/mol compared to the *cis*-planar configuration.

The comparison of the total energies of the *trans*- and *cis*-planar configurations of the a(NiN_2O_2) and b(NiN_2S_2) isomers of the nickel complex shows that, as in the case of the above considered Pd(II) and Pt(II) complexes, the *trans*-configuration of the coordination mode NiN_2O_2 is more favorable (by 4.6 kcal/mol) than the *cis*-configuration. For the coordination mode NiN_2S_2, the *trans*- and *cis*-configurations are characterized by nearly equal total energies (the difference is 0.1 kcal/mol).

As for the Pd(II) and Pt(II) complexes, this result can be ascribed to the mentioned above conformational features of the O- and S-containing metallocycles that determine the degree of steric interligand

Table 5. Calculated (DFT/B3LYP/6-311++G(d,p)) total *E* (au) and relative Δ*E* (kcal/mol) energies for the a(MN_2O_2) and b(MN_2S_2) isomers of complex **I** (M = Ni(II)) in the *pseudo*-tetrahedral and *trans*- and *cis*-planar configurations

Mode	Configuration					
	pseudo-tetrahedron		*trans*-planar		*cis*-planar	
	E	Δ*E*	*E*	Δ*E*	*E*	Δ*E*
NiN_2O_2	–3796.621774	4.5	–3796.616888	2.2	–3796.609491	6.9
NiN_2S_2	–3796.628995	0.0	–3796.620397	0.0	–3796.620536	0.0

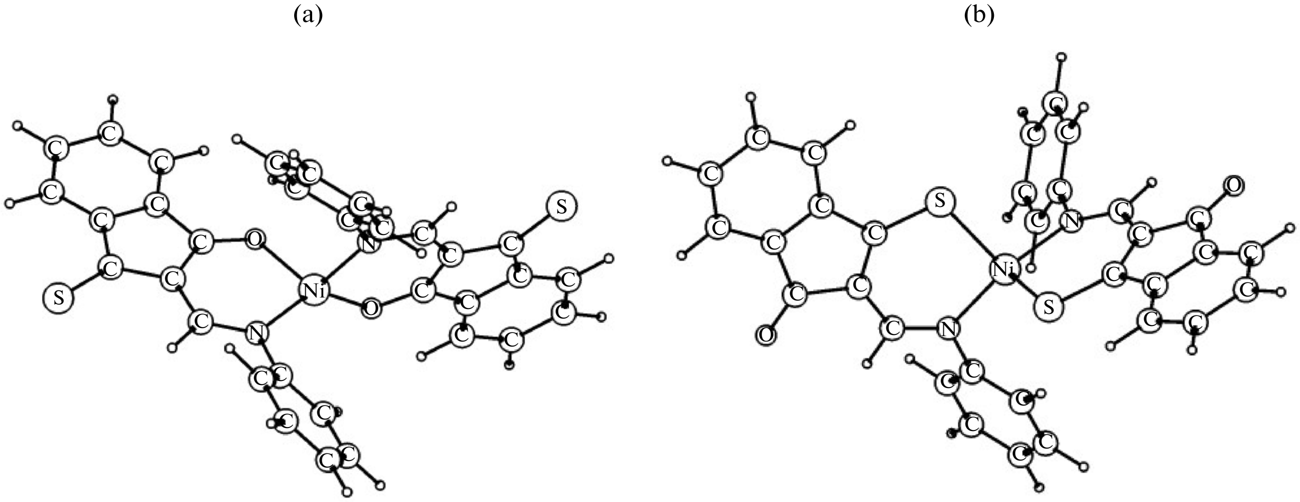


Fig. 3. Calculated molecular structures of the (a) a(NiN_2O_2) and (b) b(NiN_2S_2) isomers of complex **I** (M = Ni(II)) in the *pseudo*-tetrahedral configuration.

interactions. The calculations of the molecular structures of the Ni(II) complexes revealed characteristic of the S-containing metallocycles inflections along the line of the donor atoms N–S (27.6° for the more favorable *cis*-configuration) and flattened O-containing metallocycles (the inflection along the line of the N–O atoms was 13.3° for the more favorable *trans*-configuration). It should be mentioned that, as for the Pd(II) and Pt(II) compounds, the *trans*-configuration of the Ni(II) complexes is characterized by the "umbrella" conformation, whereas the *cis*-configuration is characterized by the "step" conformation similarly to the structures presented in Figs. 2a and 2b, respectively.

Thus, the quantum-chemical DFT study of the competitive coordination during the formation of the molecular structure of the bis(chelate) metal complexes with the polydentate ligands shows that Pearson's HSAB concept is a useful tool for an analysis of intramolecular acid–base interactions and allows the prediction of the relative stability of the complexes at the qualitative level based on the properties of the complexing central atom and ligating donor atoms. The DFT simulation of the spatial structure of the bis(chelate) azomethine complexes of d^8 metals (Ni^{2+}, Pd^{2+}, and Pt^{2+}) shows that the B3LYP functional makes it possible to theoretically substantiate the dependences of the coordination mode on the nature of the metal atom, the composition of the donor atoms, and specific features of the ligand structure.

The quantum-chemical calculations were performed using the Gaussian09 program [22] by the DFT method. In the calculations of the Be(II) and Hg(II) complexes, the B3LYP, PBE0, and TPSSh hybrid functionals were used in combination with the 6-311++G(d,p) basis set for the Be(II) complexes and the SDD basis set for the Hg(II) complexes. The B3LYP/6-311++G(d,p) approximation was used in the calculations of the Ni(II) complexes, whereas the Pd(II) and Pt(II) complexes were calculated in the B3LYP/SDD approximation. The stationary points were localized on the potential energy surface by the full geometry optimization of the molecular structures. The graphical images of the molecular structures (Figs. 1–3) were constructed using the ChemCraft program [23] in which the Cartesian coordinates of atoms obtained in the quantum-chemical calculations served as input parameters.

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