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Quantum Chemical Simulation of Hexa-, Penta-, and Tetracoordination Modes in Stereoisomers of the Co(II) and Ni(II) Bis(ligand) Complexes Based on (N,O,S(Se))-Tridentate Azomethines

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Abstract—The molecular structures and relative energies of hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) and Ni(II) bis(ligand) complexes based on (N,O,Y)-tridentate azomethines with the phenyl thio(seleno) ether substituent at the azomethine nitrogen atom (coordination modes of the competing stereoisomers $MN_2O_2Y_2$, MN_2O_2Y, or MN_2O_2 (Y = S, Se)) are calculated using the density functional theory. Hexacoordination is predominant in the Co(II) and Ni(II) complexes (combined with tetracoordination for the Co(II) complexes), unlike pentacoordination prevailing in similar Co(II) and Ni(II) complexes based on azomethines with thio(seleno)benzimidazole fragments (with Y atoms in the thione form). The quantum chemical simulation is performed for possible stereoisomerization reactions in the CoL_2 complexes to take into account the role of interconfiguration transitions in the competition of the hexa-, penta-, and tetracoordinated stereoisomers.

Keywords: quantum chemical simulation, coordination compounds, stereoisomerization, tridentate azomethines

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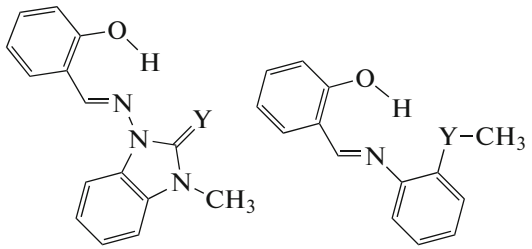
INTRODUCTION

The molecular structures and spectral, magnetic, and other physical properties of the bis(chelate) complexes of transition 3*d* metals with azomethine ligands have been studied earlier [1–3]. On the one hand, their properties are mainly determined by the composition and configuration of the MN_2X_2 coordination mode (X = O, S, Se). On the other hand, the configuration (*trans*- or *cis*-planar, or pseudotetrahedral) of the MN_2X_2 coordination mode depends on the type of the central atom, nature of ligating atoms, and structural features of the ligands. This dependence was especially distinctly observed in experimental studies of the Ni(II) azomethine complexes [1–3] and has theoretically been interpreted previously [4–6] on the basis of the quantum chemical simulation of stereoeffects in a series of the tetracoordinated metal complexes with the aromatic and heterocyclic azomethine derivatives as ligands of the (N,O)-, (N,S)-, and (N,Se)-chelate type [4–6]. A more complicated case is presented by metal complexes with azomethines, including coordinately active Y-donating centers in substituents at the azomethine nitrogen atom (**I**, **II**), which transforms bidentate azomethine ligands of the chelate type into potentially tridentate ligands due to the possibility of formation of additional coordination bonds Y→M. For the ML_2 bis(ligand) complexes based on (N,O,Y)-tridentate azomethines (**I**, **II**) and taking into account possible interconfiguration transitions with the Y→M bond cleavage, polyvariance appears by both the composition of the coordination mode ($MN_2O_2Y_2$, MN_2O_2Y, or MN_2O_2) and, correspondingly, the configuration of the complexes. Therefore, the problem of establishing the most probable composition and configuration of the coordination mode becomes primary.



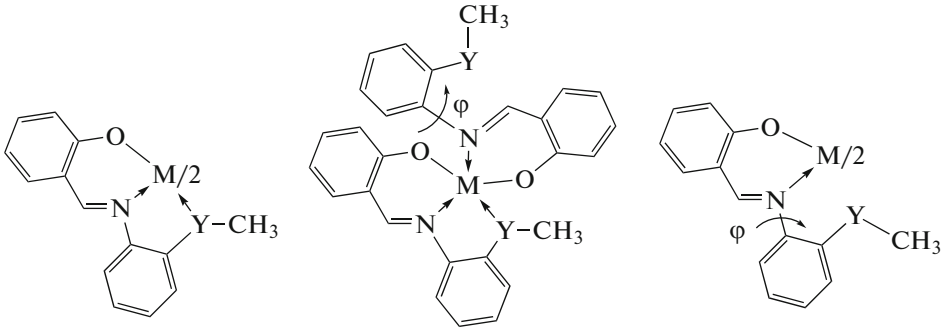
I: LH (Y = S, Se) **II**: LH (Y = S, Se)

The experimental studies (X-ray diffraction analysis) show that the cobalt [7–13] and nickel [13–19] complexes based on polydentate azomethines are

characterized by the extension of the coordination mode (from tetra- to hexacoordination of the central metal atom).

Our previous studies (in the framework of quantum chemical simulation) concerned the regularities of the formation and competition of the hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) and Ni(II) bis(ligand) complexes based on tridentate azomethines **I** with the coordinately active thio(seleno)benzimidazole fragments (with the Y atom in the thione form) [20–22]. In this work, the study is continued for the Co(II) and Ni(II) bis(ligand) complexes based on tridentate azomethines (**II**) with the phenyl thio(seleno) ether substituent at the azomethine nitrogen atom with the sulfur(selenium) atom in the thiol form involved in the formation of Y→M coordination bonds.

The competition between the hexa-, penta-, and tetracoordinated isomers of the Co(II) and Ni(II) complexes with tridentate azomethines **II** (i.e., competition between isomers **IIa** (coordination number (C.N.) 6), **IIb** (C.N. 5), and **IIc** (C.N. 4)) was considered by a combination of the quantum chemical calculations of the relative energies of the stereoisomers of the complexes and simulation of possible interconfiguration transitions between them with the estimation of the barriers and, correspondingly, the possibility of these transitions by analogy to the earlier studies [21, 22] of the bis(ligand) Co(II) and Ni(II) complexes with tridentate azomethines **I**.



IIa: ML_2 (C.N. 6)

IIb: ML_2 (C.N. 5)
M = Co(II), Ni(II); Y = S, Se

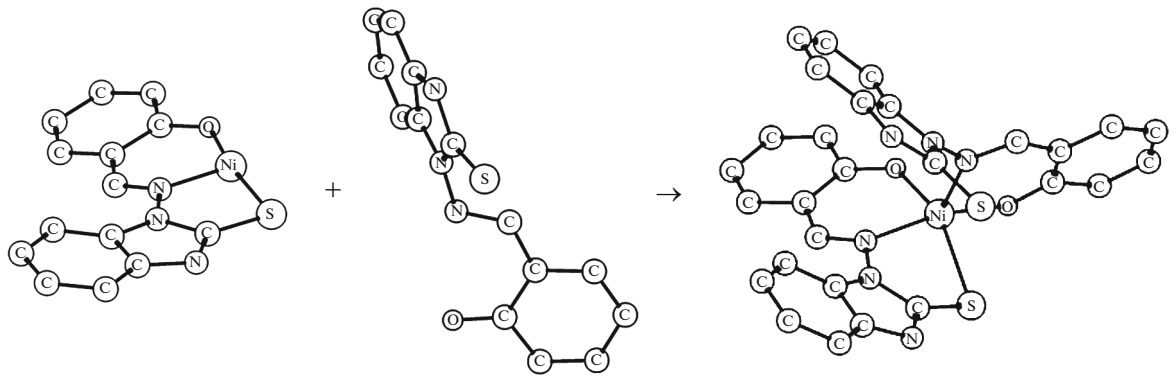
IIc: ML_2 (C.N. 4)

CALCULATION PROCEDURE

Quantum chemical calculations were performed by the density functional theory [23] using the Gaussian 09 program [24]. According to the known dependence of the DFT calculation results on the type of the used functional [25–27], the calculations were performed for three variants of hybrid functionals: B3LYP [28, 29], PBE0 [30], and TPSSh [31] in combination with the 6-311++G(d,p) basis set. The possibility of both the low-spin and high-spin states as the ground one was taken into account in the calculations of the stereoisomers of the Co(II) and Ni(II) complexes. The stationary points on the potential energy surface were localized and analyzed by the full geometry optimization of the molecules of the stereoisomers of the Co(II) and Ni(II) complexes accompanied by the calculation of vibrational spectra for the ground states of the stereoisomers and transition states between them. The graphical images of the molecular structures were drawn using the ChemCraft program [32].

RESULTS AND DISCUSSION

The previous quantum chemical simulation of the hexa-, penta-, and tetracoordinated stereoisomers and possible transitions between them for the Co(II) and Ni(II) bis(ligand) complexes based on (N,O,Y)-tridentate azomethines **I** established that the pentacoordination mode of the central metal atom was preferential [21, 22]. In particular, it is the pentacoordinated stereoisomer of complexes ML_2 (M = Co(II), Ni(II); Y = S, Se) based on azomethines **I** that was the starting one for possible subsequent interconfiguration transitions in the framework of the step model for the formation of complexes ML_2 ($M^{++} + (L)^- \rightarrow (ML)^+$, $(ML)^+ + (L)^- \rightarrow ML_2$ [21, 22]). As shown by the calculations [21, 22], the barrier for interconfiguration transitions in the Co(II) and Ni(II) complexes based on azomethines **I** turned out to be fairly high, which caused the preferable character of the pentacoordinated stereoisomers also in the cases where these isomers were not most favorable by the total energy. The nature of the obtained result (preference of pentacoordination for the formation of stereoisomers of the CoL_2 and NiL_2 bis(ligand) complexes based on azomethines **I**) was attributed mainly to the specific feature of the structure of the L^- anion, mainly, its acoplanarity with the dihedral angle φ of turning the benzimidazole fragment about the N–N bond by 140°



$(NiL)^+$
(**I**, Y = S)

L^-
(**I**, Y = S)
φ(N–N) = 140°

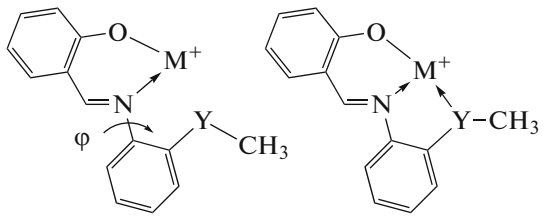
NiL_2 (C.N. 5)
(**I**, Y = S)

Fig. 1. Cyclic fragments of the calculated (DFT/B3LYP/6-311++G(d,p)) structures of cation $(NiL)^+$, anion L^-, and pentacoordinated stereoisomer of the NiL_2 complex based on tridentate azomethines **I** (Y = S).

(Fig. 1). Owing to this turn, the Y donor atom (Y = S, Se) was shifted from the reaction space of the L^- anion in **I**, whose structure takes the distinct (N,O)-chelate form, which results in the bidentate character of the second ligand and, correspondingly, in the formation of the pentacoordinated stereoisomer of complexes CoL_2 [21] and NiL_2 [22]. Note that the conclusion about the pentacoordination mode in the Co(II) bis(ligand) complexes based on tridentate azomethines **I** was made on the basis of the experimental studies of the physicochemical properties of these compounds [33–35]. This is exemplified in Fig. 1 by the scheme of formation of the starting (in terms of the step model for the formation of the bis(ligand) metal complexes [22]) pentacoordinated stereoisomer of complex NiL_2 based on azomethines **I** (Y = S).

As compared to the structure of the L^- anion of azomethines **I** (φ(N–N) = 140°, Fig. 1), the L^- anion of azomethines **II** is much more flattened (φ(C–N) = 37° (Figs. 2, 3)). In this case, the donor Y atom (Y = S, Se) is located together with the N and O atoms in the reaction space of the L^- anion, whose donor center gains the (N,O,Y)-tridentate form (Figs. 2, 3). This structure of the L^- anion of azomethines **II** allows the manifestation of both the bi- (as in the case of azomethines **I**) and tridentate character by the L^- anion for the formation of the penta- or hexacoordinated stereoisomer (as the starting one for the subsequent interconfiguration transitions), respectively. The quantum chemical model for binding the L^- anion by the $(ML)^+$ cation for azomethines **II** at the starting distance (equal to 5 Å) between the nickel or cobalt atom of the $(ML)^+$ cation and the donor nitrogen atom of the L^- anion shows that both variants of denticity manifestation by the second ligand take place in fact. This occurs, on the one hand, when the hexacoordinated isomer of the NiL_2 complexes (Fig. 2) and, on the other hand, the pentacoordinated isomer of the CoL_2 complexes (Fig. 3) are formed as the initial isomers for possible subsequent interconfiguration transitions.

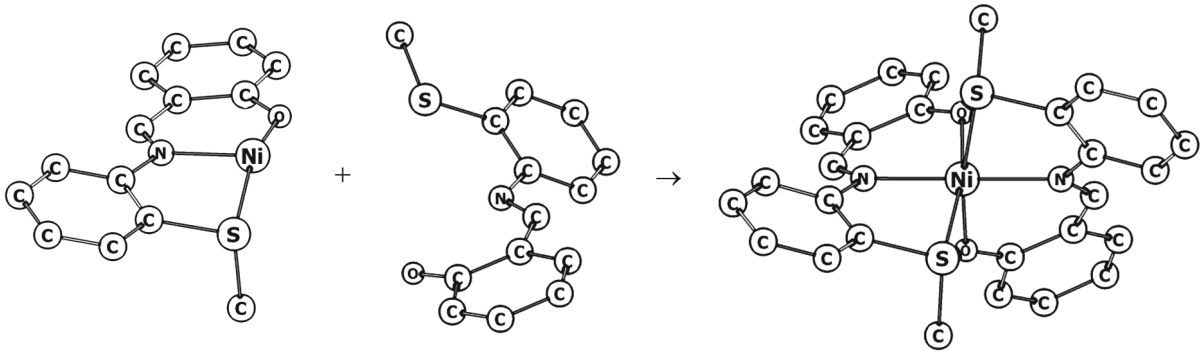
Note that the preferentially tridentate character of the first ligand (**II**) during the formation of the $(ML)^+$ cation (for M = Ni, Co; Y = S, Se) follows from the quantum chemical calculations of two models. The first model is the representation of the isomer of the $(ML)^+$ cation with C.N. 2 (without Y→M bond formation). The second model is the representation of the isomer of the $(ML)^+$ cation with C.N. 3 (with the formation of the additional Y→M coordination bond).



$(ML)^+$, C.N. 2 $(ML)^+$, C.N. 3

M = Co(II), Ni(II); Y = S, Se

According to the calculation results (using the B3LYP, PBE0, and TPSSh potentials), the isomers of the $(ML)^+$ cations with C.N. 3 are preferable than the isomers of the $(ML)^+$ cations with C.N. 2 more than by 30 kcal/mol for the $(NiL)^+$ cations, while only the isomers with C.N. 3 can be localized for the $(CoL)^+$ cations. This result was used for the construction of the model for binding the L^- anion of azomethines **II** by the $(ML)^+$ cations (Figs. 2, 3).



$(NiL)^+$
(**II**, Y = S)

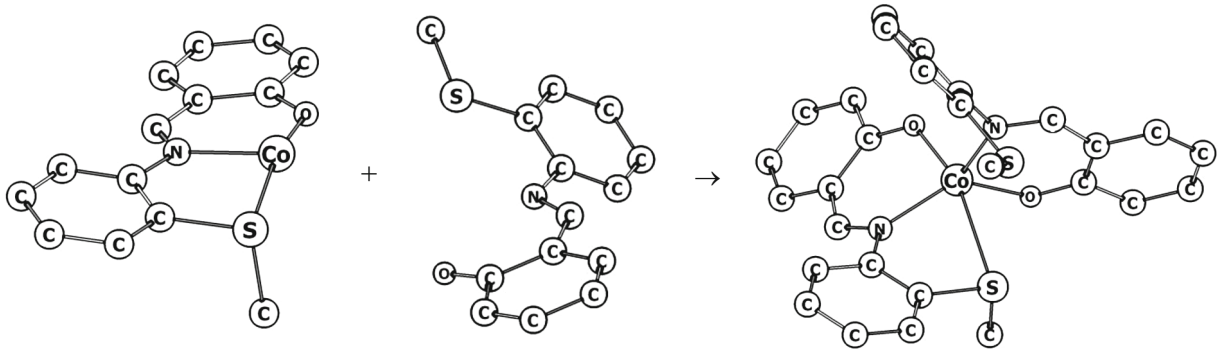
+

L^-
(**II**, Y = S)
φ(C–N) = 37°

→

NiL_2 (C.N. 6)
(**II**, Y = S)

Fig. 2. Cyclic fragments of the calculated (DFT/B3LYP/6-311++G(d,p)) structures of cation $(NiL)^+$, anion L^-, and hexacoordinated stereoisomer **IIa** of the NiL_2 complex (Y = S).



$(CoL)^+$
(**II**, Y = S)

+

L^-
(**II**, Y = S)
φ(C–N) = 37°

→

CoL_2 (C.N. 5)
(**II**, Y = S)

Fig. 3. Cyclic fragments of the calculated (DFT/B3LYP/6-311++G(d,p)) structures of cation $(CoL)^+$, anion L^-, pentacoordinated stereoisomer **IIb** of the CoL_2 complex (Y = S).

In the framework of the step model for the mechanism of the formation of the ML_2 bis(ligand) complexes [21, 22], the determined hexacoordinated stereoisomers of the Ni(II) complexes and pentacoordinated stereoisomers of the Co(II) complexes based on azomethines **II** (Y = S, Se) are the starting isomers for possible subsequent interconfiguration transitions from the hexa- to penta- and then from the penta- to tetracoordinated state of the central metal atom in the NiL_2 complexes (Y = S, Se), i.e., transitions **IIa** → **IIb** and **IIb** → **IIc**, as well as from the penta- to hexa- and from penta- to tetracoordinated state of the central metal atom in the CoL_2 complexes (Y = S, Se), i.e., transitions **IIb** → **IIa** and **IIb** → **IIc**.

It should be noted for the tetracoordinated state of the Co(II) and Ni(II) complexes (according to the numerous experimental studies of the Co(II) and Ni(II) bis(chelates) [1]) that the pseudoterahedral and *trans*-planar configurations of the MN_2O_2 coordination mode are the most characteristic of the complexes based on hydroxyazomethine ligands of the (N,O)-chelate type. These configuration variants were taken into account during the simulation of tetracoordinated stereoisomers **IIc** of the Co(II) and Ni(II) complexes based on tridentate azomethines **II** (Y = S, Se).

The Ni(II) complexes. The following subsequent interconfiguration transitions (Fig. 4) are possible if accepting the hexacoordinated stereoisomers of the Ni(II) bis(ligand) complexes based on tridentate azomethines **II** as the starting ones (Fig. 2): (1) transition from hexa- to pentacoordination due to the cleavage of the Y→Ni coordination bond involving the Y atom (Y = S, Se) of the second ligand accompanying the turn of its phenyl fragment about the C–N bond;

Table 1. Calculated relative energies ignoring (ΔE, kcal/mol) and taking into account zero-point vibrations (ΔE_{ZPE}, kcal/mol) of stereoisomers **IIa**, **IIb**, and **IIc** of complexes NiL_2 (Y = S, Se)

NiL_2	Isomers **IIa**, **IIb**, **IIc**	Coordination mode of isomers **IIa**, **IIb**, **IIc**	Spin	DFT functionals					
				B3LYP		PBE0		TPSSh	
				ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
NiL_2 (Y = S)	**IIa**	$NiN_2O_2S_2$	1	0.0	0.0	0.0	0.0	0.0	0.0
	IIb	NiN_2O_2S	1	6.0	5.7	8.2	7.9	8.7	8.5
	IIc (*tt*-1)*	NiN_2O_2	1	8.9	8.7	13.8	13.7	14.2	14.1
	IIc (*pl*-1)*	NiN_2O_2	0	6.2	7.0	14.0	14.9	7.7	8.5
	IIc (*tt*-2)	NiN_2O_2	1	9.1	9.0	13.7	13.7	14.0	14.0
	IIc (*pl*-2)	NiN_2O_2	0	6.4	7.3	14.3	15.2	8.0	8.9
NiL_2 (Y = Se)	**IIa**	$NiN_2O_2Se_2$	1	0.0	0.0	0.0	0.0	0.0	0.0
	IIb	NiN_2O_2Se	1	5.2	4.8	7.4	7.2	8.2	7.9
	IIc (*tt*-1)	NiN_2O_2	1	8.2	8.0	13.5	13.4	14.0	13.9
	IIc (*pl*-1)	NiN_2O_2	0	5.0	5.8	13.2	14.1	6.9	7.8
	IIc (*tt*-2)	NiN_2O_2	1	8.5	8.3	13.4	13.5	14.0	14.0
	IIc (*pl*-2)	NiN_2O_2	0	5.3	6.1	13.7	14.5	7.5	8.3

* *tt* and *pl* are the pseudotetrahedral and *trans*-planar configurations, respectively, of the NiN_2O_2 mode.

(2) transition from penta- to tetracoordination due to the cleavage of the Y→Ni coordination bond involving the Y atom (Y = S, Se) of the first ligand accompanying the turn of its phenyl fragment about the C–N bond, and this turn can be accomplished in two variants (both clockwise with the formation of pseudotetrahedron **IIc** (*tt*-1) and counterclockwise with the formation of pseudotetrahedron **IIc** (*tt*-2)); and (3) subsequent flattening of the pseudotetrahedral **IIc** (*tt*-1) to *trans*-planar **IIc** (*pl*-1) isomer with the antiparallel phenyl fragments and, correspondingly, flattening of the pseudotetrahedral **IIc** (*tt*-2) to *trans*-planar **IIc** (*pl*-2) isomer with the parallel phenyl substituents.

The cyclic fragments of the calculated (DFT/B3LYP/6-311++G(d,p)) molecular structures of the hexa-, penta-, and tetracoordinated (including pseudotetrahedral (*tt*-1), (*tt*-2) and *trans*-planar (*pl*-1), (*pl*-2)) stereoisomers of the Ni(II) bis(ligand) complexes based on tridentate azomethines **II** (Y = S, Se) are presented in Fig. 4. The relative energies of these stereoisomers calculated both ignoring (ΔE) and taking into account the zero-point vibration energy (ΔE_{ZPE}) are given in Table 1.

It should be mentioned that the comparative quantum chemical calculations of the low-spin ($S = 0$) and high-spin ($S = 1$) states of the tetracoordinated stereoisomers of the Ni(II) complexes show (in full accord with the known concept about spin states of the Ni(II) bis(chelates) [1]) that the singlet electronic state determining the low-spin form is the ground state for the planar configuration of the complexes with the NiN_2O_2 coordination mode, whereas the triplet state determining the high-spin form is the ground state for the pseudotetrahedral configuration of the complexes with the NiN_2O_2 mode. According to the calculations for the penta- and hexacoordinated stereoisomers of the Ni(II) bis(ligand) complexes, their ground state is the triplet electronic state determining their high-spin form, which is seen from the data in Table 1.

The calculated (DFT/B3LYP/6-311++G(d,p)) geometric parameters of the coordination modes of the hexa-, penta-, and tetracoordinated stereoisomers of the Ni(II) bis(ligand) complexes based on azomethines **II** (Y = S, Se) are presented in Table 2 (numerical values in parentheses for the pentacoordinated isomers concern the bidentate ligands, whereas numerical values in parentheses for isomers **IIc** (*tt*-1) show that the structures of two ligands L in these isomers are not equivalent).

According to the obtained DFT calculations (Table 1) of the relative energies of the hexa-, penta-, and tetracoordinated stereoisomers of the Ni(II) bis(ligand) complexes based on tridentate azomethines **II** (Y = S, Se), the hexacoordinated stereoisomer is most energetically favorable (when using the B3LYP, PBE0, and TPSSh potentials). It is the hexacoordinated stereoisomer (according to the model of binding the L^- anion by the $(NiL)^+$ cation (Fig. 2)) that is the starting one for possible subsequent interconfiguration transitions. This suggests that the hexacoordination mode is preferable in the Ni(II) bis(ligand) complexes based on tridentate azomethines **II** (Y = S, Se) with the *N*-phenyl thio(seleno) ether substituent. Note that the result obtained in terms of the theoretical model (preferable hexacoordi-

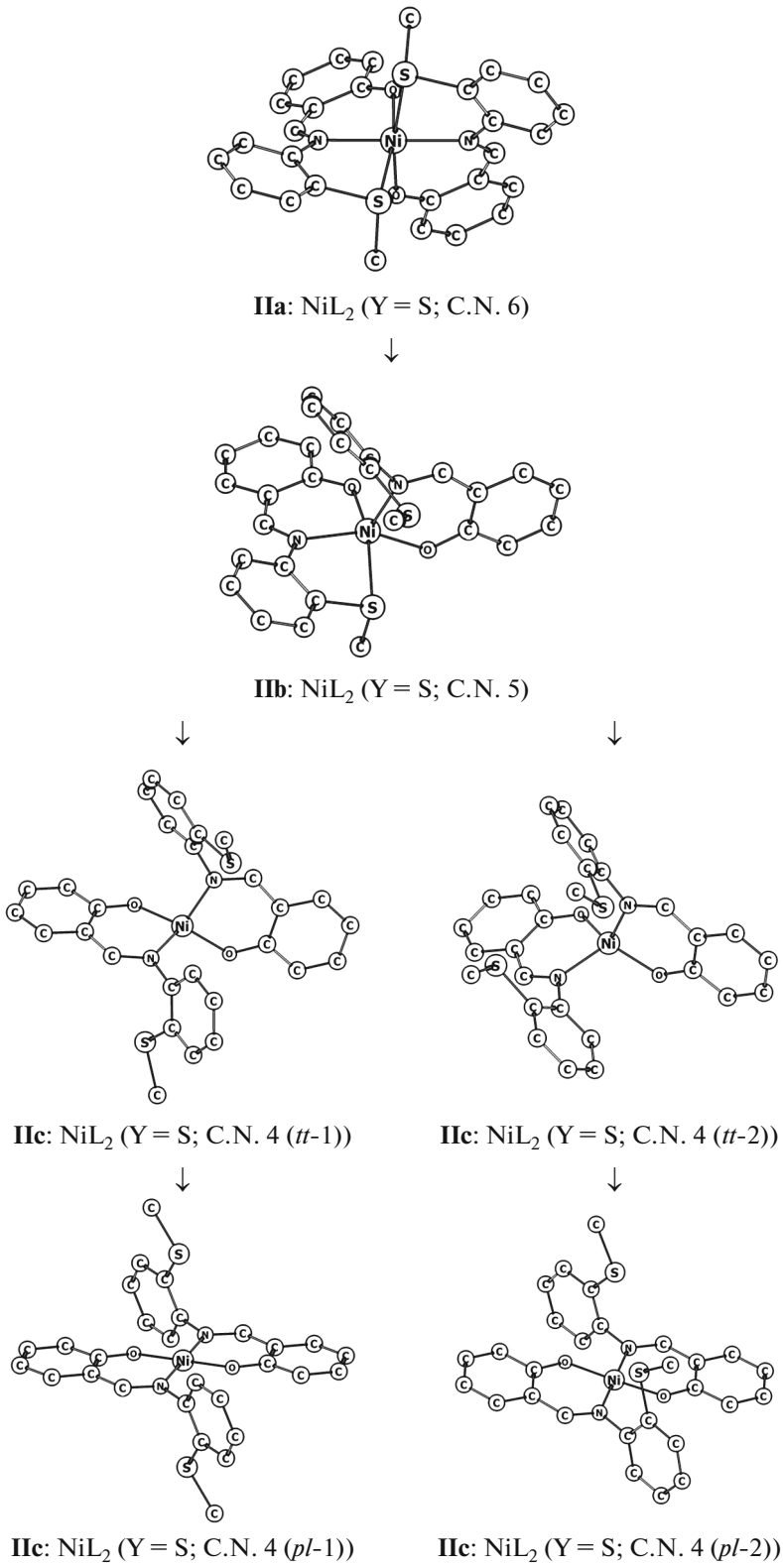


Fig. 4. Cyclic fragments of the calculated (DFT/B3LYP/6-311++G(d,p)) molecular structures of the stereoisomers of the NiL_2 complexes based on tridentate azomethines **II** (Y = S).

Table 2. Calculated (DFT/B3LYP/6-311++G(d,p)) bond lengths and bond angles in the coordination modes $NiN_2O_2Y_2$, NiN_2O_2Y, and NiN_2O_2 of stereoisomers **IIa**, **IIb**, and **IIc** of complexes NiL_2 (Y = S, Se)

NiL_2	Isomers **IIa**, **IIb**, **IIc**	Coordination mode	Ni–N, Å	Ni–O, Å	∠NNiO, deg	∠NNiN, deg	∠ONiO, deg	Ni–Y, Å
NiL_2 (Y = S)	**IIa**	$NiN_2O_2S_2$	2.072	2.017	89.6	177.4	91.6	2.568
	IIb	NiN_2O_2S	2.064	1.979	90.8	111.3	93.9	2.538
			(2.022)	(1.960)	(93.4)			
	IIc (*tt*-1)*	NiN_2O_2	2.001	1.925	92.5	115.1	136.9	
			(2.019)	(1.914)	(93.1)			
	IIc (*pl*-1)*	NiN_2O_2	1.941	1.851	92.6	180.0	180.0	
	IIc (*tt*-2)	NiN_2O_2	2.004	1.921	92.9	115.7	130.8	
	IIc (*pl*-2)	NiN_2O_2	1.941	1.850	92.7	179.1	177.2	
NiL_2 (Y = Se)	**IIa**	$NiN_2O_2Se_2$	2.080	2.017	89.4	177.4	91.0	2.685
	IIb	NiN_2O_2Se	2.047	1.978	91.3	106.1	92.8	2.666
			(2.049)	(1.953)	(91.9)			
	IIc (*tt*-1)	NiN_2O_2	2.003	1.926	92.5	116.6	138.4	
			(2.020)	(1.914)	(92.9)			
	IIc (*pl*-1)	NiN_2O_2	1.940	1.851	92.7	180.0	180.0	
	IIc (*tt*-2)	NiN_2O_2	2.005	1.921	92.8	117.0	130.2	
	IIc (*pl*-2)	NiN_2O_2	1.940	1.850	92.8	179.3	177.4	

* *tt* and *pl* are the pseudotetrahedral and *trans*-planar configurations, respectively, of the NiN_2O_2 mode.

nation) is consistent with the X-ray diffraction analysis data [13–19].

The Co(II) complexes. The following subsequent interconfiguration transitions (Fig. 5) are possible if accepting the pentacoordinated stereoisomers of the Co(II) bis(ligand) complexes based on tridentate azomethines **II** (Y = S, Se) as the starting ones (Fig. 3): (1) transition from penta- to hexacoordination due to the formation of the Y→Co coordination bond involving the Y atom (Y = S, Se) of the second ligand accompanying the turn of its phenyl fragment about the C–N bond; (2) transition from penta- to tetracoordination due to the cleavage of the Y→Co coordination bond involving the Y atom Y (Y = S, Se) of the first ligand accompanying the turn of its phenyl fragment about the C–N bond both clockwise to form pseudotetrahedron **IIc** (*tt*-1) and counterclockwise with the formation of pseudotetrahedron **IIc** (*tt*-2); and (3) subsequent flattening of pseudotetrahedral **IIc** (*tt*-1) to the *trans*-planar isomer **IIc** (*pl*-1) with antiparallel phenyl fragments and, correspondingly, flattening of the pseudotetrahedral **IIc** (*tt*-2) to *trans*-planar isomer **IIc** (*pl*-2) with parallel phenyl fragments.

The cyclic fragments of the calculated molecular structures of the hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) bis(ligand) complexes based on tridentate azomethines **II** (Y = S, Se) are presented in Fig. 5. The relative energies of these stereoisomers calculated both ignoring ΔE and taking into account the zero-point vibration energy ΔE_{ZPE} are given in Table 3. The comparative quantum chemical calculations of the low-spin ($S = 1/2$) and high-spin ($S = 3/2$) states of the hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) complexes based on azomethines **II** (Y = S, Se) show that the doublet electronic state determining the low-spin form is the ground state for the *trans*-planar configuration of the complexes with the CoN_2O_2 coordination mode, whereas the quartet electronic state determining the high-spin form of the CoL_2 complexes is the ground state for the pseudotetrahedral configuration of the complexes with the CoN_2O_2 mode, as well as for the penta- and hexacoordinated stereoisomers, which is seen from the data in Table 3.

The calculated (DFT/B3LYP/6-311++G(d,p)) geometric parameters of the coordination modes of the hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) bis(ligand) complexes based on azomethines **II** (Y = S, Se) are given in Table 4 (numerical values in parentheses for the pentacoordinated isomers are referred to the ligands manifesting bidentate denticity, and numerical values in parentheses for isomers **IIc** (*tt*-1) show the nonequivalence of the structures of two ligands L in these isomers).

According to the obtained DFT calculations (Table 3) of the relative energies of the hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) bis(ligand) complexes based on tridentate azome-

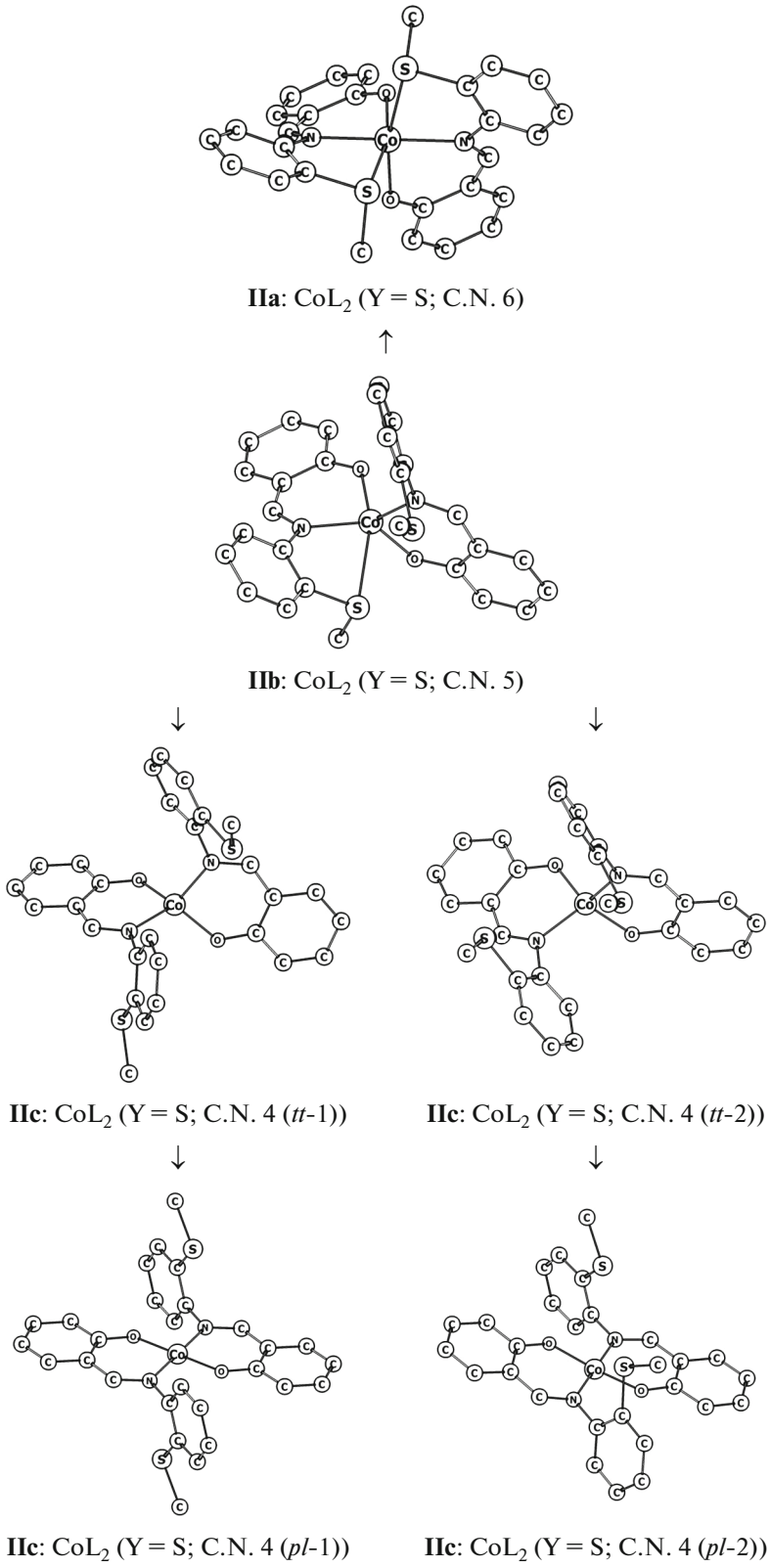


Fig. 5. Cyclic fragments of the calculated (DFT/B3LYP/6-311++G(d,p)) structures of the stereoisomers of the CoL_2 complexes based on tridentate azomethines **II** (Y = S).

Table 3. Calculated relative energies ignoring (ΔE, kcal/mol) and taking into account zero-point vibrations (ΔE_{ZPE}, kcal/mol) of stereoisomers **IIa**, **IIb**, and **IIc** of complexes CoL_2 (Y = S, Se)

CoL_2	Isomers **IIa**, **IIb**, **IIc**	Coordination mode of isomers **IIa**, **IIb**, **IIc**	Spin	DFT functionals					
				B3LYP		PBE0		TPSSh	
				ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
CoL_2 (Y = S)	**IIa**	$CoN_2O_2S_2$	3/2	0.0	0.0	0.0	0.0	0.0	0.0
	IIb	CoN_2O_2S	3/2	2.2	2.2	4.6	4.5	4.6	4.5
	IIc (*tt*-1)*	CoN_2O_2	3/2	1.5	1.5	6.0	6.0	5.9	5.9
	IIc (*pl*-1)*	CoN_2O_2	1/2	7.2	8.1	13.2	14.0	7.8	8.7
	IIc (*tt*-2)	CoN_2O_2	3/2	0.8	0.9	5.1	5.2	5.0	5.2
	IIc (*pl*-2)	CoN_2O_2	1/2	7.2	8.2	15.2	15.9	7.7	8.6
CoL_2 (Y = Se)	**IIa**	$CoN_2O_2Se_2$	3/2	0.0	0.0	0.0	0.0	0.0	0.0
	IIb	CoN_2O_2Se	3/2	1.6	1.6	4.3	4.2	4.4	4.3
	IIc (*tt*-1)	CoN_2O_2	3/2	0.6	0.7	5.6	5.6	5.6	5.7
	IIc (*pl*-1)	CoN_2O_2	1/2	6.0	6.9	11.9	12.6	7.1	8.1
	IIc (*tt*-2)	CoN_2O_2	3/2	–0.1	0.0	4.7	4.9	4.8	5.0
	IIc (*pl*-2)	CoN_2O_2	1/2	6.1	7.1	14.6	15.5	7.0	8.0

* *tt* and *pl* are the pseudotetrahedral and *trans*-planar configurations, respectively, of the CoN_2O_2 mode.

Table 4. Calculated (DFT/B3LYP/6-311++G(d,p)) geometric parameters of the coordination modes CoN_2O_2, CoN_2O_2Y, and $CoN_2O_2Y_2$ of stereoisomers **IIa**, **IIb**, and **IIc** of complexes CoL_2 based on tridentate azomethines **II** (Y = S, Se)

CoL_2	Isomers **IIa**, **IIb**, **IIc**	Coordination mode	Co–N, Å	Co–O, Å	∠NCoO, deg	∠NCoN, deg	∠OCoO, deg	Co–Y, Å
CoL_2 (Y = S)	**IIa**	$CoN_2O_2S_2$	2.117	2.024	87.4	178.8	94.9	2.621
	IIb	CoN_2O_2S	2.075	1.964	91.1	123.1	104.6	2.894
			(2.035)	(1.943)	(94.7)			
	IIc (*tt*-1)*	CoN_2O_2	2.019	1.936	94.3	123.1	122.5	
			(2.027)	(1.925)	(94.5)			
	IIc (*pl*-1)*	CoN_2O_2	1.959	1.857	91.9	180.0	180.0	
	IIc (*tt*-2)	CoN_2O_2	2.016	1.931	94.7	123.8	121.4	
	IIc (*pl*-2)	CoN_2O_2	1.960	1.858	91.9	178.6	173.9	
CoL_2 (Y = Se)	**IIa**	$CoN_2O_2Se_2$	2.125	2.024	87.4	178.9	94.0	2.732
	IIb	CoN_2O_2Se	2.080	1.965	90.8	123.8	103.7	2.987
			(2.037)	(1.945)	(94.5)			
	IIc (*tt*-1)	CoN_2O_2	2.021	1.935	94.3	124.5	122.6	
			(2.028)	(1.925)	(94.5)			
	IIc (*pl*-1)	CoN_2O_2	1.959	1.856	91.9	180.0	180.0	
	IIc (*tt*-2)	CoN_2O_2	2.017	1.932	94.7	125.9	121.9	
	IIc (*pl*-2)	CoN_2O_2	1.959	1.857	92.0	178.3	173.1	

* *tt* and *pl* are the pseudotetrahedral and *trans*-planar configurations, respectively, of the CoN_2O_2 mode.

Table 5. Calculated turning angle of the phenyl fragments (φ(C–N), deg) and relative energies (Δ*E*, kcal/mol) of the competing stereoisomers and transition states (*ts*) between them in complexes CoL_2 based on azomethines **II** (Y = S, Se)

Stereoisomerization (method)		Coordination mode	Y = S		Y = Se	
			φ(C–N)	Δ*E*	φ(C–N)	Δ*E*
IIb → **IIa** (DFT/B3LYP)	**IIb**	CoN_2O_2Y	0.0	0.0	0.0	0.0
	ts		69.0	2.5	63.0	3.0
	IIa	$CoN_2O_2Y_2$	135.0	–2.2	137.0	–1.6
IIb → **IIa** (DFT/PBE0)	**IIb**	CoN_2O_2Y	0.0	0.0	0.0	0.0
	ts		70.0	1.2	63.0	1.4
	IIa	$CoN_2O_2Y_2$	134.5	–4.6	137.0	–4.3
IIb → **IIa** (DFT/TPSSh)	**IIb**	CoN_2O_2Y	0.0	0.0	0.0	0.0
	ts		70.0	1.4	66.0	1.8
	IIa	$CoN_2O_2Y_2$	138.0	–4.6	139.0	–4.4
IIb → **IIc** (*tt*-1) (DFT/B3LYP)	**IIb**	CoN_2O_2Y	0.0	0.0	0.0	0.0
	ts		47.0	1.4	32.0	0.9
	IIc (*tt*-1)	CoN_2O_2	70.0	–0.7	69.0	–1.0
IIc (*tt*-1) → **IIc** (*tt*-2) (DFT/B3LYP)	**IIc** (*tt*-1)	CoN_2O_2	0.0	0.0	0.0	0.0
	ts		73.0	6.8	71.0	7.2
	IIc (*tt*-2)	CoN_2O_2	138.5	–0.7	136.0	–0.7
IIb → **IIc** (*tt*-2) (DFT/B3LYP)	**IIb**	CoN_2O_2Y	0.0	0.0	0.0	0.0
	ts		42.0	5.4	48.0	6.8
	IIc (*tt*-2)	CoN_2O_2	151.5	–1.4	154.0	–1.7

thines **II** (Y = S, Se), the initial (for possible subsequent interconfiguration transitions) stereoisomer (pentacoordinated (Fig. 3)) is not most energetically favorable, unlike the above considered stereoisomers of the NiL_2 complexes (Y = S, Se). The hexa- (**IIa**) and tetracoordinated (**IIc** (*tt*-1), **IIc** (*tt*-2)) stereoisomers successfully compete with pentacoordinated stereoisomer **IIb**. This competition is most pronounced in the DFT calculations with the B3LYP functional of the stereoisomers of the Co(II) complexes (Table 3). In the DFT calculations using the PBE0 and TPSSh functionals, the main competitor for the initial pentacoordinated stereoisomer is energetically much more favorable hexacoordinated stereoisomer **IIa** (Table 3). The probability of interconfiguration transitions from the starting (pentacoordinated) isomer to the isomers competitive with it was evaluated by the quantum chemical calculations of the barriers of the corresponding stereoisomerization reactions (Table 5).

Note that all considered variants of stereoisomerization are based on turns of the phenyl fragments about the C–N bond (at the φ(C–N) angle) accompanying the formation or cleavage of the Y→Co coordination bond involving the Y atom (Y = S, Se) of the first and second ligands (Fig. 5). Tetracoordinated stereoisomer **IIc** (*tt*-2) can be formed from the starting (pentacoordinated) stereoisomer via two routes (Fig. 5): clockwise turn of the phenyl fragment of the first ligand, i.e., via route **IIb** → **IIc** (*tt*-2), and its counterclockwise turn passing through intermediate stereoisomer **IIc** (*tt*-1), i.e., via route **IIb** → **IIc** (*tt*-1) → **IIc** (*tt*-2). Therefore, the barrier for the reaction **IIc** (*tt*-1) → **IIc** (*tt*-2) is also presented in Table 5 together with the barriers of the reactions **IIb** → **IIa**, **IIb** → **IIc** (*tt*-1), and **IIb** → **IIc** (*tt*-2).

Taking into account the calculated (DFT/B3LYP, PBE0, TPSSh/6-311++G(d,p)) barriers of stereoisomerization (Table 5) from the starting isomer **IIb** (pentacoordinated) to the most favorable (by the total energy (Table 3)) hexacoordinated stereoisomer **IIa**, one may conclude that the latter is preferable for the formation of the coordination mode of the CoL_2 bis(ligand) complexes (Y = S, Se) based on tridentate azomethines **II** with the *N*-phenyl thio(seleno) ether substituent (with the Y atom in the thiol form). The result obtained in terms of the theoretical model (preference of hexacoordination) is consistent with the aforementioned X-ray diffraction studies [7–13].

Pseudotetrahedral stereoisomers **IIc** (*tt*-1) and **IIc** (*tt*-2) are also competitive toward the initial pentacoordinated isomer along with the hexacoordinated one. However, the calculated barriers of interconfiguration transitions from the starting pentacoordination mode to tetracoordination (Table 5) show that more favorable by the total energy isomer **IIc** (*tt*-2) with geomet-

rically equivalent ligands (Fig. 5, Table 4) is poorly accessible via both the direct transition route **IIb** → **IIc** (*tt*-2) and the route passing through intermediate isomer **IIc** (*tt*-1), i.e., route **IIb** → **IIc** (*tt*-1) → **IIc** (*tt*-2). At the same time, pseudotetrahedral isomer **IIc** (*tt*-1) with geometrically nonequivalent ligands (Fig. 5, Table 4), on the one hand, is more favorable by the total energy than the starting pentacoordinated isomer **IIb** (Table 3). On the other hand, isomer **IIc** (*tt*-1) is easily accessible due to the low barrier (Table 5) of the interconfiguration transition **IIb** → **IIc** (*tt*-1).

Therefore, along with the hexacoordinated isomer (**IIa**), tetracoordinated isomer **IIc** (*tt*-1) can also be assigned to the most probable stereoisomers of the CoL_2 bis(ligand) complexes (Y = S, Se) based on tridentate azomethines **II** with the *N*-phenylthio-(seleno) ether substituent (with the Y atom in the thiol form).

To conclude, it is found by the quantum chemical study of the regularities of formation of the coordination mode ($MN_2O_2Y_2$, MN_2O_2Y, or M_2O_2 (M = Co(II), Ni(II); Y = S, Se)) in the bis(ligand) metal complexes with (N,O,Y)-tridentate azomethines with the *N*-phenyl thio(seleno) ether substituent (with the Y atom in the thiol form) that hexacoordination is preferable in the Co(II) and Ni(II) complexes (hexacoordination combined with tetracoordination in the Co(II) complexes), unlike the predomination of pentacoordination in similar Co(II) and Ni(II) complexes based on azomethines with the *N*-thio(seleno)benzimidazole substituent (with the Y atom in the thione form). The role of structural features of the (N,O,Y)-tridentate azomethine ligands (degree of acoplanarity) in the formation of the coordination mode ($MN_2O_2Y_2$, MN_2O_2Y, or MN_2O_2 (Y = S, Se)) in the Co(II) and Ni(II) bis(ligand) complexes was revealed. The theoretical description of the competition of the hexa-, penta-, and tetracoordinated stereoisomers of the Co(II) and Ni(II) bis(ligand) complexes with (N,O,Y)-tridentate azomethines along with the quantum chemical calculations of the relative stability of the competing stereoisomers also requires the construction of the model of the reaction mechanism for the formation of the ML_2 bis(ligand) complexes, including the quantum chemical study of possible interconfiguration transitions with the estimation of their barriers.

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REFERENCES

1. Garnovskii, A.D., Nivorozhkin, A.L., and Minkin, V.I., *Coord. Chem. Rev.*, 1993, vol. 126, no. 1, p. 1.
2. Bourget-Merle, L., Lappert, M.F., and Severn, J.R., *Chem. Rev.*, 2002, vol. 102, no. 6, p. 3031.
3. Garnovskii, A.D., Vasilchenko, I.S., Garnovskii, D.A., and Kharisov, B.I., *J. Coord. Chem.*, 2009, vol. 62, no. 2, p. 151.
4. Kharabaev, N.N., Starikov, A.G., and Minkin, V.I., *Dokl. Ross. Akad. Nauk*, 2014, vol. 458. no. 5, p. 555.
5. Kharabayev, N.N., Starikov, A.G., and Minkin, V.I., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 7, p. 421. https://doi.org/10.1134/S1070328415070039
6. Kharabaev, N.N., Starikov, A.G., and Minkin, V.I., *J. Struct. Chem.*, 2016, vol. 57. no. 3, p. 431.
7. Pal, S., Sengupta, P., Ghosh, S., et al., *J. Coord. Chem.*, 2002, vol. 55, p. 271.
8. Rajsekhar, G., Rao, C.P., Saarenketo, P., et al., *Inorg. Chem. Commun.*, 2002, vol. 5, p. 649.
9. Rajsekhar, G., Rao, C.P., Saarenketo, P., et al., *New J. Chem.*, 2004, vol. 28, p. 75.
10. Roy, N., Sproules, S., Bothe, E., et al., *Eur. J. Inorg. Chem.*, 2009, p. 2655.
11. Lucas, C.R., Byrne, J.M.D., Collins, J.L., et al., *Can. J. Chem.*, 2011, vol. 89, p. 1174.
12. Manikandan, R., Vijayan, P., Anitha, P., et al., *Inorg. Chim. Acta*, 2014, vol. 421, p. 80.
13. Pattanayak, P., Pratihar, J.L., Patra, D., et al., *Polyhedron*, 2013, vol. 51, p. 275.
14. Kalita, M., Bhattacharjee, T., Gogoi, P., et al., *Polyhedron*, 2013, vol. 60, p. 47.
15. Kalita, M., Gogoi, P., Barman, P., and Sarma, B., *J. Coord. Chem.*, 2014, vol. 67, p. 2445.
16. Pattanayak, P., Pratihar, J.L., Patra, D., et al., *Inorg. Chim. Acta*, 2014, vol. 418, p. 171.
17. Kalita, M., Tamuli, K.J., Barman, P., et al., *Polyhedron*, 2015, vol. 97, p. 140.
18. Sarma, K., Devi, N., Kalita, M., et al., *J. Coord. Chem.*, 2015, vol. 68, p. 3685.
19. Roebuck, J.W., Turkington, J.R., Rogers, D.M., et al., *Dalton Trans.*, 2016, vol. 45, p. 3734.
20. Kharabayev, N.N. and Minkin, V.I., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 3, p. 139. https://doi.org/10.1134/S1070328417030022
21. Kharabayev, N.N., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 12, p. 807. https://doi.org/10.1134/S107032841712003X
22. Kharabaev N.N., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 8, p. 1663.
23. Parr, R. and Yang, W., *Density-Functional Theory of Atoms and Molecules*, New York: Oxford Univ., 1989.
24. Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., *Gaussian 09, Revision D.01*, Wallingford: Gaussian, Inc., 2013.

25. Sousa, S.F., Fernandes, P.A., and Ramos, M.J., *J. Phys. Chem. A*, 2007, vol. 111, no. 42, p. 10439.

26. Burke, K. and Wagner, L.O., *Int. J. Quantum Chem.*, 2013, vol. 113, no. 2, p. 96.

27. Tsipis, A.C., *Coord. Chem. Rev.*, 2014, vol. 272, p. 1.

28. Becke, A.D., *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, vol. 38, p. 3098.

29. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev., B*: *Solid State*, 1988, vol. 37, p. 785.

30. Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett.*, 1996, vol. 77, p. 3865.

31. Tao, J., Perdew, J.P., Staroverov, V.N., and Scuseria, G.E., *Phys. Rev. Lett.*, 2003, vol. 91, p. 146401.

32. Zhurko, G.A. and Zhurko, D.A., Chemcraft. Version 1.6. http://www.chemcraftprog.com

33. Vasil'chenko, I.S., Kuz'menko, T.A., Shestakova, T.E., et al., *Russ. J. Coord. Chem.*, 2005, vol. 31, no. 10, p. 747. https://doi.org/10.1007/s11173-005-0163-6

34. Vasil'chenko, I.S., Shestakova, T.E., Ikorskii, V.N., et al., *Russ. J. Coord. Chem.*, 2007, vol. 33, no. 3, p. 176. https://doi.org/10.1134/s1070328407030049

35. Garnovskii, A.D., Burlov, A.S., Vasil'chenko, I.S., et al., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 2, p. 81. https://doi.org/10.1134/s1070328410020016

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