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Quantum Chemical Modeling of the Mechanism of Formation of Bis-Ligand Co(II) Complexes Based on Polydentate Heterocyclic Azomethine Derivatives: Competition between Four-, Five-, and Six-Coordination

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Abstract—The molecular structures and relative energies of four-, five-, and six-coordinate stereoisomers of bis-ligand Co(II) complexes based on polydentate heterocyclic azomethine derivatives (CoN_2O_2, CoN_2O_2Y, and $CoN_2O_2Y_2$ coordination units of the isomers (Y = S, Se)) were calculated using density functional theory. In terms of the proposed quantum chemical model for the mechanism of CoL_2 complex formation, the five-coordinate structure of complexes with non-equivalent ligands, one being tridentate and the other being bidentate is most probable; this result is in line with experimental data.

Keywords: quantum chemical modeling, coordination compounds, stereoisomerization, polydentate ligands, heterocyclic azomethine derivatives

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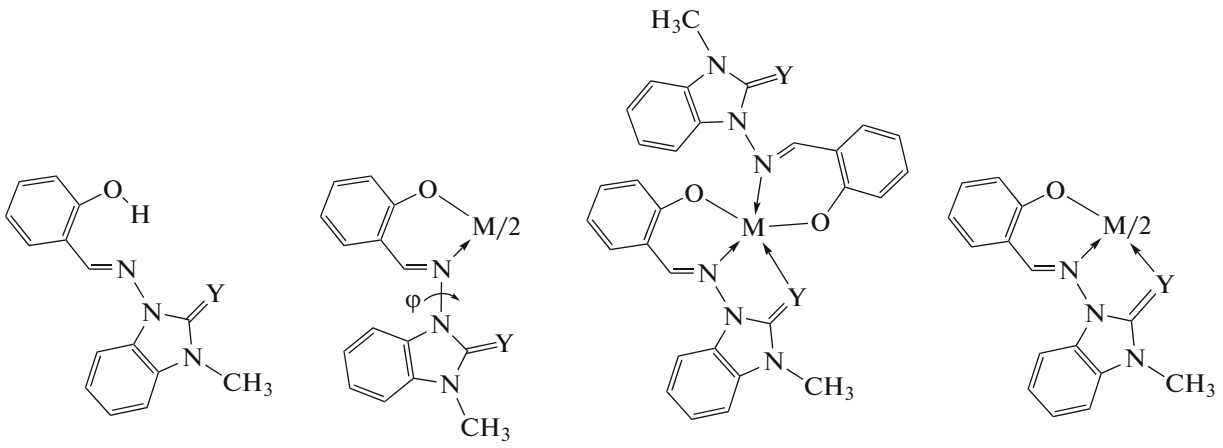
INTRODUCTION

The molecular structure and spectral, magnetic, and other physical properties of bis-chelate 3*d*-transition metal complexes with azomethine ligands are determined, most of all, by the composition and configuration of the MN_2X_2 coordination unit (X = NR, O, S, Se) [1–3]. The experimentally established dependences of the configuration of four-coordinate azomethine metal complexes on the type of the central metal ion, the nature of the ligating atoms, and the ligand structural features [1–3] have been previously theoretically substantiated by quantum chemical modeling of the stereochemical effects observed in the series of bis-chelate metal complexes with MN_2X_2 coordination units (X = O, S, Se) [4]. A more intricate case is represented by metal complexes with (N,O)-chelating azomethine ligands with coordinatively active Y-containing substituents at the azomethine nitrogen (Y = N, O, S, Se). These ligands can be not only bidentate, but also tridentate, which expands the coordination unit and results in the formation of complexes with not only four-, but also five- and six-coordinate central metal atom via the additional Y → M interaction. The variability of the coordination unit arising in this case (MN_2X_2, MN_2X_2Y, or $MN_2X_2Y_2$) for azomethine metal complexes with these ligands L brings about the issue of determination of the most probable configuration for the ML_2 complexes. A theoretical study of the competition of four-, five-, and six-coordinate stereoisomers of azomethine ML_2 complexes during the formation of their structure has been previously carried out for Ni(II), Zn(II), and Cd(II) compounds [5]. In this paper, the study is continued for Co(II) complexes with heterocyclic azomethine derivatives (LH), which are able to exhibit both bi- and tridentate behavior [6–9] owing to additional Y → Co coordination (Y = S, Se).

In the absence of additional Y → Co bonds (Y = S, Se), the CoN_2O_2 coordination unit (**Ia**) occurs in CoL_2 complexes, while with participation of the additional Y → Co bond involving the Y atom of one ligand, the coordination unit is CoN_2O_2Y (**Ib**). The involvement of additional Y → Co bonds formed by the Y atoms of both ligands results in the $CoN_2O_2Y_2$ coordination unit (**Ic**).

The bis-ligand Co(II) complexes based on (N,O)-chelating hydroxyazomethine ligands typically have a *pseudo*-tetrahedral configuration of the CoN_2O_2 coordination unit, which is typical, according to numerous X-ray diffraction studies, of cobalt complexes with both cyclic [10–12] and acyclic [13–18] azomethines. In some cases, four-coordination in Co(II) azomethine complexes occurs as a *trans*-planar CoN_2O_2 coordination unit [19–22]. The possibility of expansion of the CoN_2O_2 unit in bis-ligand Co(II) complexes by coordinatively active Y-containing substituents at the azomethine nitrogen atoms has also been established in a series of X-ray diffraction studies of complexes containing additional Y → Co coordination bonds (Y = N [23, 24], O [25–30], S or Se [3, 31–35]).



(LH) (**Ia**; ML_2 (C.N. 4)) (**Ib**; ML_2 (C.N. 5)) (**Ic**; ML_2 (C.N. 6))

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

(C.N. 4 (MN_2O_2), C.N. 5 (MN_2O_2Y), C.N. 6 ($MN_2O_2Y_2$))

The bi- or tridentate behavior of ligands L in the formation of the CoL_2 bis-ligand complexes, which determines four- (**Ia**), five- (**Ib**), or six-coordination (**Ic**) of the central metal atom, is considered in this work based on quantum chemical study of the relative stabilities of four-, five-, and six-coordinate stereoisomers of Co(II) complexes with allowance for the possible configuration transitions **Ia** $\rightleftharpoons$ **Ib** or **Ib** $\rightleftharpoons$ **Ic**.

CALCULATION PROCEDURE

Quantum chemical calculations were carried out by the Gaussian09 program [36]. Density functional theory (DFT) was chosen as the calculation method [37]. In view of the known dependence of the results of DFT calculations on the type of the used functional [38–40], calculations were carried out for three hybrid functionals, PBE0 [41], TPSSh [42], and B3LYP [43, 44], in combination with the 6-311++G(d,p) basis set. Furthermore, calculations of the molecular structures of four-, five-, and six-coordinate stereoisomers of Co(II) bis-ligand complexes took into account the possibility of both low-spin (S = 1/2) and high-spin (S = 3/2) ground states of complexes. The stationary points in the potential energy surface were located by full optimization of the molecular geometry. The graphical images of the molecular structures were constructed by the ChemCraft program [45].

RESULTS AND DISCUSSION

According to the results of calculations of the relative energies (ΔE) of four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** for CoL_2 bis-ligand complexes (Y = S, Se), the *pseudo*-tetrahedral **Ia** (*tt*) and five-coordinate **Ib** structures are most competitive (Table 1). Comparative calculations for low-spin (S = 1/2) and high-spin (S = 3/2) states showed that only for the planar configuration of the CoN_2O_2 coordination unit, the doublet electronic state determining the low-spin form of the complexes is the ground state, while for the *pseudo*-tetrahedral and five- and six-coordinate configurations, the quartet electronic state determining the high-spin form is the ground state.

It is noteworthy that the competition between four-, five-, and six-coordinate stereoisomers as possible complex formation products may be studied using the thermodynamic approach alone (for evaluation of the relative stability of stereoisomers) only provided that the transitions between competing stereoisomers have low barriers and the molecular system can spontaneously roll down to the energy minimum. In a different case (to which the present system belongs, as will be shown below), there is a need, first, to construct a model mechanism for the formation of ML_2 bis-ligand complexes in order to identify the most probable initial isomer for the subsequent possible stereoisomerization (for example, in this case, for configuration transitions **Ia** $\rightleftharpoons$ **Ib** or **Ib** $\rightleftharpoons$ **Ic**) and, second, to model the stereoisomerization mechanism in order to determine the energy barriers and, hence, the probability of these reactions. The construction of these models is the key objective of our study.

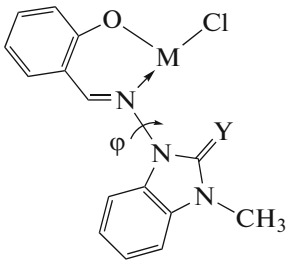
Since four-, five-, or six-coordination of the central metal atom is dictated by either bi- or tridentate behavior of the ligands (L), the search for the most probable initial stereoisomer (**Ia**, **Ib**, or **Ic**) was carried out in terms of the stepwise model of formation of the

Table 1. Calculated relative energies (ΔE, kcal/mol) of four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of the CoL_2 complexes (Y = S, Se)

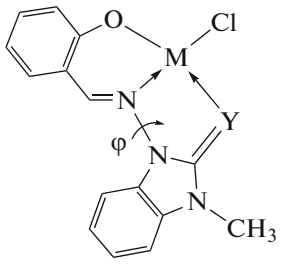
Stereoisomers	Spin	CoL_2 (Y = S)			CoL_2 (Y = Se)		
		DFT functionals					
		PBE0	TPSSh	B3LYP	PBE0	TPSSh	B3LYP
Ia (*tt*)*	3/2	0.0	0.0	0.0	0.0	0.0	0.0
Ia (*pl*)*	1/2	11.3	3.7	6.6	11.3	3.8	6.4
Ib	3/2	–0.5	0.2	2.2	–0.7	0.0	1.9
Ic	3/2	3.9	2.6	6.8	4.6	3.2	7.6

* *tt* is *pseudo*-tetrahedral and *pl* is *trans*-planar configurations of the CoN_2O_2 unit.

CoL_2 bis-ligand complexes, with the first step being binding of one ligand to the metal cation to give an intermediate complex (**IIa** or **IIb)** and determination of the denticity of the first ligand and the second step being binding of the second ligand to this intermediate complex to form one of the possible stereoisomers with four- (**Ia**), five- (**Ib**), or six-coordination (**Ic**) of the metal depending on the denticity of the second ligand.

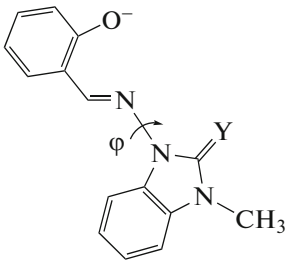


(IIa)

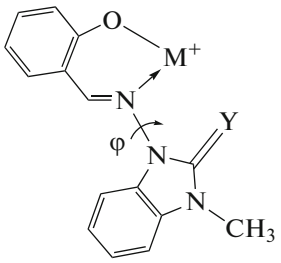


(IIb)

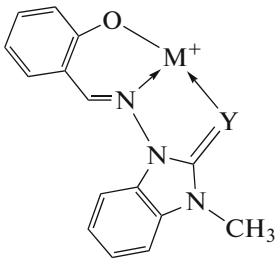
According to quantum chemical calculations for isomers **IIa** (without additional Y → Co coordination (φ(N–N) ≈ 90°)) and **IIb** (with additional Y → Co coordination (φ(N–N) ≈ 0°)) as possible products of the first step in terms of the stepwise model for the CoL_2 formation, isomers **IIb** are more preferable than **IIa** by 18.1 (PBE0), 19.5 (TPSSh), or 9.2 (B3LYP) kcal/mol for Y = S and by 12.2 (PBE0), 12.9 (TPSSh), and 10.3 (B3LYP) kcal/mol for Y = Se. Hence, within the framework of this model, the first ligand L tends to exhibit tridentate behavior, with the additional Y → Co coordination bond (Y = S, Se) being present in the coordination unit. A similar conclusion about the tridentate function of the first ligand towards the metal ion in the stepwise model of formation of CoL_2 complexes (Y = S, Se) also follows from quantum chemical calculations (DFT/PBE0, TPSSh, B3LYP/6-311++G(d,p)) carried out for isomer pairs **IIIa** and **IIIb** (Y = S, Se); according to the results, only form **IIIb** with an additional Y → Co coordination bond is detected (Fig. 1; structure **IIIb**; Y = S).



(L^-)



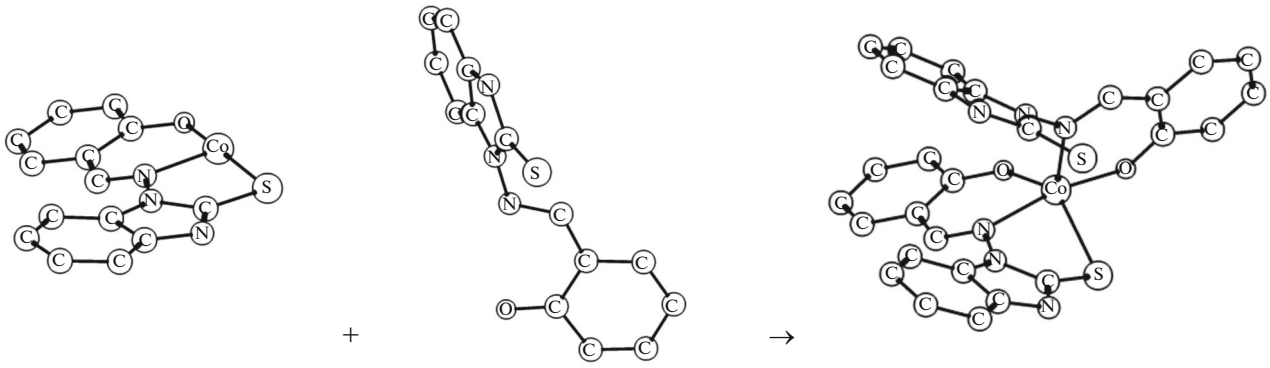
(IIIa $(ML)^+$)



(IIIb $(ML)^+$)

In the second step of CoL_2 formation, that is, binding of the second ligand (L^-) to intermediate complex **IIIb**, the ligand is bidentate as a result of non-planarity of L^-, with the dihedral angle φ of rotation of the benzimidazole moiety around the N–N bond being ~140° (Fig. 1). As a result of this rotation, the donor Y atom (Y = S, Se) is almost removed from the reaction space of the L^- anion and the donor center of the second ligand has a clear-cut (N,O)-chelating type, which determines the bidentate function of the second ligand in the interaction with the intermediate complex **IIIb** (Fig. 1).

Within the considered stepwise model for the formation of the CoL_2 bis-ligand complexes, the combination of spatial structures of the interacting cation **IIIb** ($(CoL)^+$) and the anion L^- that is shown in Fig. 1



IIIb $(CoL)^+$ (Y = S) + $(L)^-$ (Y = S, φ(N–N) = 140°) → **Ib** (Y = S)

Fig. 1. Cyclic moieties of calculated (DFT/B3LYP/6-311++G(d,p)) structures of intermediates **IIIb** ($(CoL)^+$) and L^- of the formation of five-coordinate stereoisomer **Ib** of CoL_2 (Y = S).

predetermines five-coordination (structure **Ib**) as the most probable initial CoL_2 configuration (Y = S, Se) for the subsequent configuration transitions, **Ib** (C.N. 5) → **Ia** (C.N. 4) or **Ib** (C.N. 5) → **Ic** (C.N. 6). The probability of these transitions at the final step of structure formation of CoL_2 is determined, first of all, by the relative energies of stereoisomers **Ia**, **Ib**, and **Ic** and, second, the height of barrier for these configuration transitions.

The configuration transition **Ib** (C.N. 5) → **Ic** (C.N. 6) is the formation of the additional Y → Co coordination bond involving the Y atom (Y = S, Se) of the second ligand via rotation around the N–N bond of the benzimidazole moiety (Fig. 2).

The configuration transition **Ib** (C.N. 5) → **Ia** (C.N. 4 (*tt*)) is cleavage of the additional Y → Co bond involving the Y atom (Y = S, Se) of the first ligand via rotation around the N–N bond of the benzimidazole moiety (Fig. 3).

It is noteworthy that the rotation of the benzimidazole moiety of the first ligand around the N–N bond, which accompanies the Y → Co bond cleavage, can occur in two ways, either clockwise (to give the *pseudo*-tetrahedral isomer **Ia** (*tt*-1)) or counter-clockwise (to give isomer **Ia** (*tt*-2)), as shown in Fig. 3. The subsequent flattening of *pseudo*-tetrahedral configuration **Ia** (*tt*-1) gives rise to *trans*-planar stereoisomer **Ia** (*pl*-1) with antiparallel benzimidazole moieties (Fig. 3), while flattening of configuration **Ia** (*tt*-2) leads to energetically less favorable *trans*-planar stereoisomer **Ia** (*pl*-2) with parallel benzimidazole moieties (Fig. 3, Tables 2 and 3).

Thus, rotation (around the N–N bond) of benzimidazole moieties of the first and second ligands of CoL_2 complexes (Y = S, Se) gives rise to three sorts of stereoisomerization:

(1) CoL_2 (C.N. 5) → CoL_2 (C.N. 6);

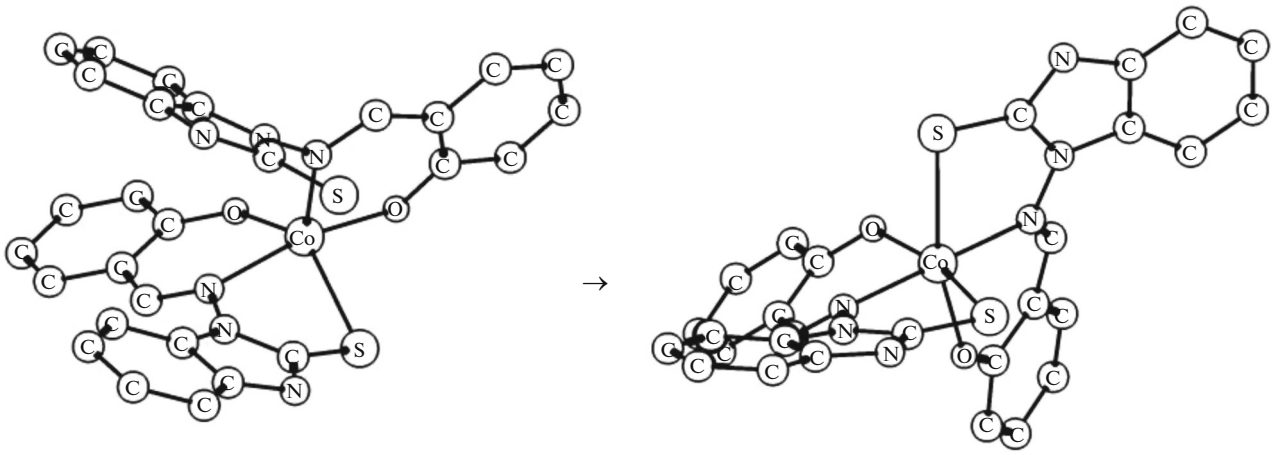
(2) CoL_2 (C.N. 5) → CoL_2 (C.N. 4 (*tt*-1));

(3) CoL_2 (C.N. 5) → CoL_2 (C.N. 4 (*tt*-2)).

Out of these reactions, of most interest is the stereoisomerization of the initial five-coordinate **Ib** to four-coordinate **Ia** (*tt*-2), which is the isomer competing most successfully with **Ib** from the energy standpoint (Tables 2, 3). Tables 2 and 3, which summarize the calculated total (E) and relative (ΔE) energies of four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of CoL_2 (Y = S, Se), were composed in view of the considered model, which implies five-coordination as the initial configuration taken as the reference point.

Table 4 summarizes the calculated geometric parameters of the coordination units of four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of CoL_2 (the numerical values in parentheses for five-coordinate isomers refer to ligands with bidentate behavior, while numerical values in parentheses for isomers **Ia** (*tt*-1) reflect the structural non-equivalence of the two ligands L in these isomers).

According to the results of calculations of the relative stabilities of four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of S- and Se-containing CoL_2 bis-ligand complexes (Tables 2, 3), the four-coordination giving *pseudo*-tetrahedral isomer **Ia** (*tt*-2) is quite competitive relative to five-coordination (isomer **Ib**), which is included in the stepwise model of complex formation as the initial structure for the subsequent possible configuration transitions. This competition between four-coordination and the initial five-coordination was manifested most clearly in the calculations of stereoisomeric Co(II) complexes using the B3LYP functional both without (ΔE) and with (ΔE_{ZPE}) zero-point vibration correction (Table 3). This accounted for the use of particularly B3LYP potential for the DFT modeling of the mechanism of



Ib (Y = S) **Ic** (Y = S)

Fig. 2. Cyclic moieties of calculated (DFT/B3LYP/6-311++G(d,p)) structures of five- and six-coordinate stereoisomers **Ib** and **Ic** of CoL_2 (Y = S).

stereoisomerization between competing structures from the initial (five-coordinate (**Ib**)) structure to four-coordinate (**Ia** (*tt*-2)) one and for subsequent estimation of the height δ of the barrier for this reaction (Table 5).

As the reaction coordinate for stereoisomerization **Ib** → **Ia** (*tt*-2), we used the φ(N–N) rotation angle of the benzimidazole moiety of the first ligand around the N–N bond (Fig. 3), because this rotation determines cleavage of the Y → Co bond (Y = S, Se) and transition from five- to four-coordination in the CoL_2 complexes (Y = S, Se). Having taken the φ(N–N) angle in the initial five-coordinate isomers of CoL_2 (Y = S, Se) as the reference starting point, we carried out quantum chemical calculations for a number of intermediate structures on the **Ib** → **Ia** (*tt*-2) pathway with fixing the φ angles (φ = 0°, 60°, 70°, 80°, ...) and optimization of all other geometric parameters of the molecules (Table 5).

Note that the rotation of the benzimidazole moiety of the first ligand around the N–N bond, which underlies the configuration transition **Ib** → **Ia** (*tt*-2), is

Table 2. Calculated total energies without (*E*, at.u.) and with (E_{ZPE}, at.u.) inclusion of zero-point vibrations for four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of CoL_2 (Y = S, Se)

Stereoisomers	Spin	DFT-functionals			
		PBE0	TPSSh	B3LYP	
		E	*E*	*E*	E_{ZPE}
Stereoisomers of CoL_2 complexes (Y = S)					
Ib (C.N. 5)	3/2	–3813.84959	–3816.40559	–3816.31191	–3815.82424
Ic (C.N. 6)	3/2	–3813.84259	–3816.40174	–3816.30453	–3815.81707
Ia (C.N. 4 (*tt*-1))*	3/2	–3813.84045	–3816.39815	–3816.30836	–3815.82075
Ia (C.N. 4 (*pl*-1))*	1/2	–3813.83080	–3816.40004	–3816.30489	–3815.81533
Ia (C.N. 4 (*tt*-2))	3/2	–3813.84873	–3816.40585	–3816.31536	–3815.82708
Ia (C.N. 4 (*pl*-2))	1/2	–3813.82878	–3816.39869	–3816.30321	–3815.81365
Stereoisomers of CoL_2 complexes (Y = Se)					
Ib (C.N. 5)	3/2	–7820.18319	–7822.86224	–7822.97223	–7822.48605
Ic (C.N. 6)	3/2	–7820.17472	–7822.85708	–7822.96314	–7822.47759
Ia (C.N. 4 (*tt*-1))	3/2	–7820.17301	–7822.85382	–7822.96769	–7822.48157
Ia (C.N. 4 (*pl*-1))	1/2	–7820.16402	–7822.85624	–7822.96502	–7822.47704
Ia (C.N. 4 (*tt*-2))	3/2	–7820.18214	–7822.86225	–7822.97526	–7822.48884
Ia (C.N. 4 (*pl*-2))	1/2	–7820.16148	–7822.85448	–7822.96285	–7822.47467

* *tt* is *pseudo*-tetrahedral and *pl* is *trans*-planar configuration of the CoN_2O_2 unit.

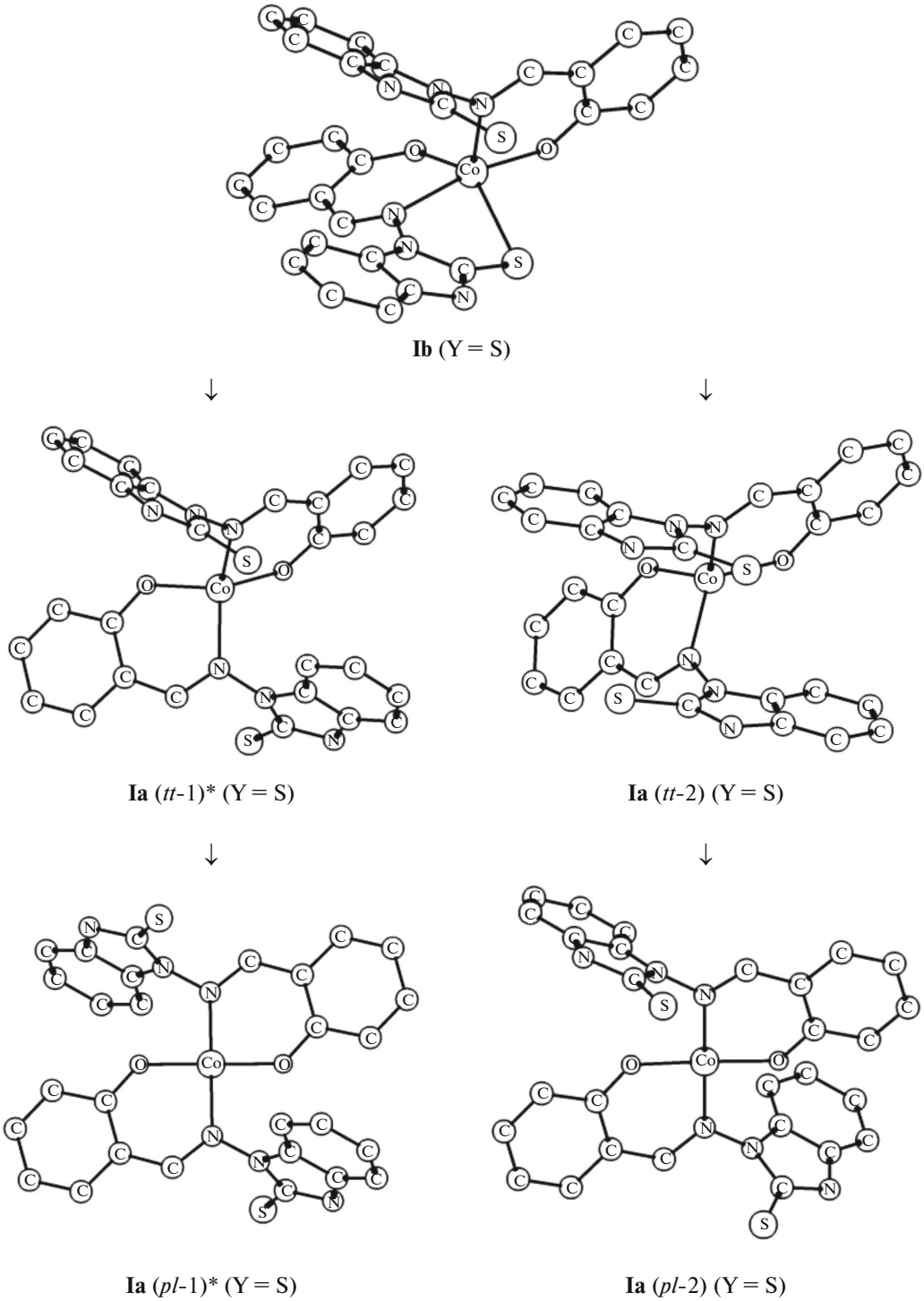


Fig. 3. Cyclic moieties of calculated (DFT/B3LYP/6-311++G(d,p)) structures of four- and five-coordinate stereoisomers **Ia** and **Ib** of CoL_2 (Y = S). * *tt* is *pseudo*-tetrahedral and *pl* is *trans*-planar configuration of the CoN_2O_2 unit.

sterically hindered, as during this transition the Y_1 heteroatom (Y_1 = S, Se) of this ligand crosses the space of the Y_2 atom (Y_2 = S, Se) of the second ligand (Fig. 3). This steric restriction is largely removed through the accompanying increase (by more than 70° (Table 5)) in the bond angle α(NCoN) between the ligands, which separates the Y_1 and Y_2 atoms of the two ligands in space (Fig. 3). The configuration transition **Ib** → **Ia** (*tt*-2), which reflects cleavage of the $Y_1 \rightarrow$ Co coordination bond (Y_1 = S, Se), is accompanied, according

Table 3. Calculated relative energies without (ΔE, kcal/mol) and with (ΔE_{ZPE}, kcal/mol) inclusion of zero-point vibrations for four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of CoL_2 (Y = S, Se)

Stereoisomers	Spin	CoL_2 (Y = S)				CoL_2 (Y = Se)			
		DFT-functionals				DFT-functionals			
		PBE0	TPSSh	B3LYP		PBE0	TPSSh	B3LYP	
		ΔE	ΔE	ΔE	ΔE_{ZPE}	ΔE	ΔE	ΔE	ΔE_{ZPE}
Ib (C.N. 5)	3/2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ic (C.N. 6)	3/2	4.4	2.4	4.6	4.5	5.3	3.2	5.7	5.3
Ia (C.N. 4 (*tt*-1))*	3/2	5.7	4.1	2.2	2.2	6.4	5.3	2.9	2.8
Ia (C.N. 4 (*pl*-1))*	1/2	11.8	3.5	4.4	5.6	12.0	3.8	4.5	5.7
Ia (C.N. 4 (*tt*-2))	3/2	0.5	−0.2	−2.2	−1.8	0.7	−0.0	−1.9	−1.7
Ia (C.N. 4 (*pl*-2))	1/2	13.1	4.3	5.5	6.6	13.6	4.9	5.9	7.1

* *tt* is *pseudo*-tetrahedral and *pl* is *trans*-planar configuration of the CoN_2O_2 unit.

Table 4. Calculated (DFT/B3LYP/6-311++G(d,p)) geometric parameters of the CoN_2O_2, CoN_2O_2Y, and $CoN_2O_2Y_2$ coordination units in four-, five-, and six-coordinate stereoisomers **Ia**, **Ib**, and **Ic** of CoL_2 (Y = S, Se)

Stereoisomers of CoL_2 (Y = S)							
Stereoisomers	Spin	Co–N, Å	Co–O, Å	∠ NCoO, deg	∠ NCoN, deg	∠ OCoO, deg	Co–Y, Å
Ib (C.N. 5)	3/2	2.197 (2.072)	1.974 (1.959)	83.4 (90.6)	97.5	100.4	2.531
Ic (C.N. 6)	3/2	2.113	2.029	85.6	177.9	93.3	2.627
Ia (C.N. 4 (*tt*-1))*	3/2	2.032 (2.034)	1.925 (1.932)	93.0 (92.2)	133.1	133.5	
Ia (C.N. 4 (*pl*-1))*	1/2	1.945	1.860	91.1	180.0	180.0	
Ia (C.N. 4 (*tt*-2))	3/2	2.019	1.923	93.5	117.0	116.6	
Ia (C.N. 4 (*pl*-2))	1/2	1.947	1.858	91.1	179.1	176.3	
Stereoisomers of CoL_2 complexes (Y = Se)							
Ib (C.N. 5)	3/2	2.207 (2.077)	1.975 (1.962)	83.2 (90.4)	97.4	100.1	2.637
Ic (C.N. 6)	3/2	2.113	2.035	85.3	178.4	91.4	2.751
Ia (C.N. 4 (*tt*-1))	3/2	2.033 (2.037)	1.926 (1.932)	92.9 (92.0)	134.5	135.3	
Ia (C.N. 4 (*pl*-1))	1/2	1.944	1.861	91.1	180.0	180.0	
Ia (C.N. 4 (*tt*-2))	3/2	2.018	1.924	93.5	117.1	117.1	
Ia (C.N. 4 (*pl*-2))	1/2	1.946	1.858	91.1	179.5	177.7	

* *tt* is *pseudo*-tetrahedral and *pl* is *trans*-planar configuration of the CoN_2O_2 unit.

to calculations (Table 5), by increasing $r(Y_1–Co)$ interatomic distance from 2.5 to 4.6 Å in CoL_2 (Y = S) and from 2.6 to 4.7 Å in CoL_2 (Y = Se). Meanwhile, the $r(Y_1–Y_2)$ interatomic distance is maintained at no less than 4.3 Å throughout the whole stereoisomerization **Ib** → **Ia** (*tt*-2) pathway. The completion of the benzimidazole rotation (after the sterically stressed segment has been passed) is accompanied by a decrease in the α(NCoN) inter-ligand angle by more than 50° (Table 5). This forced structural rearrangement of the coordination unit (increase in the α(NCoN) inter-ligand angle, cleavage of the $Y_1 \rightarrow Co$ coordination bond (Y_1 = S, Se)) during the configuration transition **Ib** → **Ia** (*tt*-2) is ultimately reflected in the barrier δ for this reaction (Table 5).

The quantum chemical estimate of the barrier δ for the stereoisomerization **Ib** → **Ia** (*tt*-2) gave 6.1 and 7.3 kcal/mol for CoL_2 (Y = S) and CoL_2 (Y = Se), respectively (Table 5). Hence, according to the obtained results, the possible intramolecular configuration transitions **Ib** → **Ia** (*tt*-2) in the CoL_2 complexes (Y = S, Se) have relatively high barriers; therefore, the considered model of CoL_2 formation predicts the five-coordinate structure **Ib** containing non-equivalent ligands, one being bidentate and the other being tridentate, as the initial structure for the subsequent possible configuration transitions.

Table 5. Calculated (DFT/B3LYP/6-311++G(d,p)) inter-ligand α(NCoN) bond angles, $r(Y_1–Co)$ distances, and relative energies ΔE for the intermediate structures of CoL_2 (Y = S, Se) along the φ(N–N) reaction coordinate of the stereoisomerization **Ib** → **Ia** (*tt*-2)

φ (N–N), deg	Y = S			Y = Se		
	α(NCoN), deg	$r(Y_1–Co)$, Å	ΔE, kcal/mol	α(NCoN), deg	$r(Y_1–Co)$, Å	ΔE, kcal/mol
0 (**Ib**)	97.5	2.53	0.0	97.4	2.64	0.0
60	173.0	2.54	0.6	175.1	2.63	0.5
70	171.3	2.62	1.9	173.8	2.68	1.1
80	169.0	2.72	4.1	171.1	2.76	2.7
87 (*ts*)*	163.0	2.99	6.1			
90	135.1	3.87	2.6	168.2	2.93	5.5
97 (*ts*)				163.2	3.27	7.3
100	127.1	4.12	0.3	132.5	4.07	1.9
110	122.8	4.29	–1.0	123.7	4.35	–0.1
120	120.9	4.44	–1.6	121.2	4.51	–1.2
132.0 **Ia** (*tt*-2)	117.0	4.64	–2.2			
135.9 **Ia** (*tt*-2)				117.1	4.72	–1.9

* *ts* is transition state.

In conclusion, we would like to note that experimental studies of the physicochemical properties of these compounds [6–8], as well as studies of analogous Cu(II) bis-ligand complexes [6–9], also lead to the conclusion of five-coordination in bis-ligand Co(II) complexes with S- and Se-containing heterocyclic derivatives of azomethines (L) capable of both bi- and tridentate behavior.

Thus, a theoretical model was proposed for the mechanism of formation of Co(II) bis-ligand complexes with heterocyclic azomethine derivatives (capable of both bi- and tridentate coordination), as a combination of quantum chemical calculations of the relative stabilities of competing four-, five-, and six-coordinate stereoisomers of Co(II) complexes and quantum chemical modeling of the mechanisms of the possible intramolecular stereoisomerization reactions. Using the model, it was ascertained that the five-coordinate structure of the CoL_2 complexes is the most probable (out of competing ones) initial structure for the subsequent possible, but high-barrier configuration transitions. The preferred formation of the five-coordinate structure for the CoL_2 complexes with non-equivalent ligands L, one being tridentate and the other being bidentate, corresponds to experimental data, whose theoretical interpretation required, apart from considering the thermodynamic aspect of the competition of four-, five-, and six-coordination, also the construction of stepwise model for the mechanism of formation of CoL_2 complexes with polydentate ligands.

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