ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 2, pp. 155–163. © Pleiades Publishing, Ltd., 2021.
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Tetra-, Penta-, and Hexacoordinate Stereoisomers of the Bis(ligand) Complexes of Zn(II) and Cd(II) Based on (N,O,S(Se))-Tridentate Azomethines. A Quantum Chemical Study

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Received July 9, 2020; revised August 5, 2020; accepted August 7, 2020

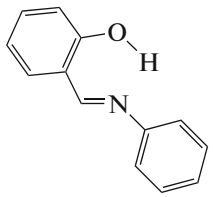
Abstract—The molecular structures and relative energies of tetra-, penta-, and hexacoordinate stereoisomers of the Zn(II) and Cd(II) bis(ligand) complexes based on (N,O,Y (Y = S, Se))-tridentate azomethines (coordination nodes of the competing stereoisomers are MN_2O_2, MN_2O_2Y, and $MN_2O_2Y_2$, respectively) are calculated by the density functional theory and nonempirical Hartree–Fock method. The simulation of the mechanism for the formation of the tetra-, penta-, and hexacoordinate stereoisomers with allowance for the subsequent stereoisomerization makes it possible to establish the preferable tetracoordination (as a pseudotetrahedron) for the zinc complexes and penta- or hexacoordination for the cadmium complex depending on the specific features of the ligand structure.

Keywords: quantum chemical simulation, coordination compounds, polydentate ligands, stereoisomerization, azomethines

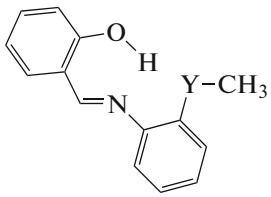
DOI: 10.1134/S1070328421020020

INTRODUCTION

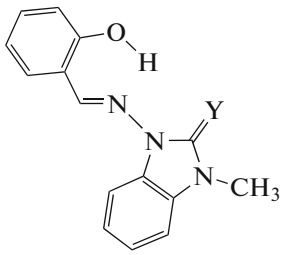
The bis(ligand) tetracoordinate complexes of transition 3*d* metals based on aromatic azomethines of the chelate type were studied in detail [1–3]. Their structures and spectral, magnetic, and other physical properties were found to be mainly determined by the composition and configuration of the coordination node MN_2X_2 (X = NR, O, S, Se). The formation of one of possible pseudotetrahedral and *cis*- or *trans*-planar configuration of the MN_2X_2 coordination node depends on the type of the central ion, nature of ligating atoms, and structural features of the ligands, which was found experimentally [1–3] and interpreted theoretically (on the basis of quantum chemical studies) [4, 5]. The situation becomes substantially more complicated in the case of the bis(ligand) complexes ML_2 based on azomethines including additional coordinatively active Y-donor centers (**II**, **III**), since the possibility of forming additional coordination bonds Y→ M transforms the bidentate ligands of the (N,O)-chelate type **I** into potentially (N,O,Y)-tridentate ligands **II** and **III**.



I: LH

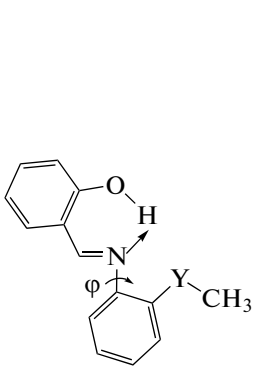


II: LH (Y = S, Se)

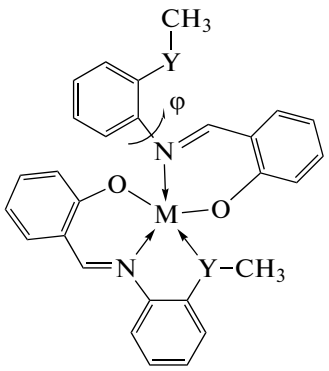


III: LH (Y = S, Se)

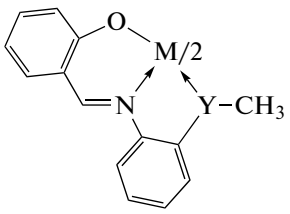
For potentially tridentate azomethines **II** and **III**, the ML_2 complexes based on the latter are polyvariant in composition and configuration of the coordination node (MN_2O_2, MN_2O_2Y, $MN_2O_2Y_2$ (Y = S, Se)), which is manifested in the series of competing tetra-, penta-, and hexacoordinate stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc**. (The coordination number (CN) is given in parentheses.)



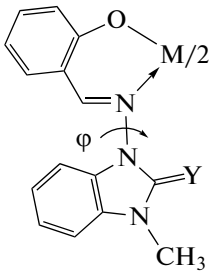
IIa: ML_2 (CN 4)



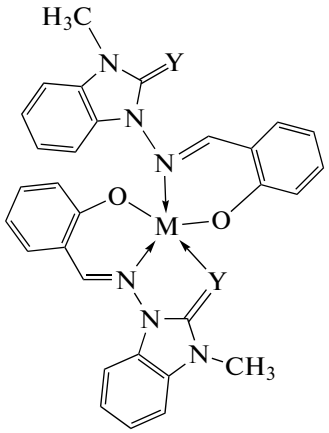
IIb: ML_2 (CN 5)



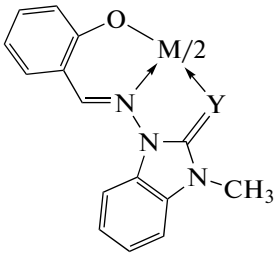
IIc: ML_2 (CN 6)



IIIa: ML_2 (CN 4)



IIIb: ML_2 (CN 5)



IIIc: ML_2 (CN 6)

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

The role of the electronic configuration of the central metal atom in the competition of tetra-, penta-, and hexacoordinate stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc** of the ML_2 complexes based on azomethines **II** and **III**, respectively, was studied [6] for the cobalt ($d^7(Co^{2+})$) and nickel ($d^8(Ni^{2+})$) complexes. To determine the role and influence of the central ion size on the competition of tetra-, penta-, and hexacoordination during the formation of the ML_2 complexes, we continued the quantum chemical study of the relative stability of stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc** for the complexes of d^{10} metals: zinc(II) and cadmium(II). By analogy to [6], we also studied the influence of specific features of the structures of the ligands of the type **II** (containing phenylthio(seleno)ester fragments with the Y atom in the thiol form) and ligands of the type **III** (containing thio(seleno)benzimidazole fragments with the Y atom in the thione form) on the competition of tetra-, penta-, and hexacoordination in the ZnL_2 and CdL_2 complexes.

It should be mentioned that, according to the X-ray diffraction analysis results, the bis(ligand) complexes of the d^{10} metals (Zn^{2+}, Cd^2) based on azomethines of the chelate type **I** are characterized by the pseudotetrahedral configuration [1] and the d^{10}-metal complexes with the ligands having additional donor centers are characterized by the extension of the composition of the coordination node (from tetra- to penta- and hexacoordination) in both the Zn(II) complexes [7–13] and Cd(II) complexes [8, 12, 14–16].

CALCULATION PROCEDURE

The quantum chemical calculations of the molecular structures of the Zn(II) and Cd(II) complexes (as of similar Co(II) and Ni(II) complexes in the previous study [6]) were performed using the Gaussian09 program [17] by the density functional theory (DFT) method [18] with the B3LYP hybrid functional [19, 20]. At the same time, taking into account the known influence of the type of the chosen density functional

Table 1. Relative energies ignoring (ΔE, kcal/mol) and taking into account zero-point vibrations (ΔE_{ZPE}, kcal/mol) of stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc** for complexes ZnL_2 (Y = S, Se)

Stereoisomers **IIa**, **IIb**, and **IIc** (Y)					Stereoisomers **IIIa**, **IIIb**, and **IIIc** (Y)				
ZnL_2 (Y) Y = S, Se	DFT/B3LYP		RHF		ZnL_2 (Y) Y = S, Se	DFT/B3LYP		RHF	
	kcal/mol					kcal/mol			
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}		ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
IIa (S)	0.0	0.0	0.0	0.0	**IIIa** (S)	0.0	0.0	0.0	0.0
IIb (S)	1.3	1.1	1.0	0.7	**IIIb** (S)	2.2	1.7	2.2	1.8
IIc (S)	1.2	0.9	1.7	1.6	**IIIc** (S)	7.1	6.3	11.1	10.5
IIa (Se)	0.0	0.0	0.0	0.0	**IIIa** (Se)	0.0	0.0	0.0	0.0
IIb (Se)	1.8	1.5	0.6	0.3	**IIIb** (Se)	1.8	1.5	2.2	1.8
IIc (Se)	2.1	1.8	3.6	3.5	**IIIc** (Se)	7.3	6.8	12.2	11.5

on results of the DFT studies [21, 22], the DFT/B3LYP calculations in this work were duplicated by the calculations of the stereoisomers of the Zn(II) and Cd(II) complexes by the nonempirical Hartree–Fock method for molecular systems with the closed shell (RHF). The 6-311++G(d,p) basis set for the Zn(II) complexes and the SDD basis set for the Cd(II) complexes were used in the DFT and RHF calculations. Stationary points on the potential energy surface were localized and analyzed using the complete geometry optimization of the molecules accompanied by the calculation of vibrational spectra for the ground states of the stereoisomers of the Zn(II) and Cd(II) complexes and transition states in the stereoisomerization reaction in the Zn(II) complexes. It was taken into account in the calculations that the low-spin electron state is the ground state for the tetra-, penta-, and hexacoordinate stereoisomers of the Zn(II) and Cd(II) complexes. The graphical images of the molecular structures were drawn using the ChemCraft program [23].

RESULTS AND DISCUSSION

According to the results of the quantum chemical DFT calculations duplicated by the RHF method, the relative energies of the tetra-, penta-, and hexacoordinate stereoisomers of the Zn(II) bis(ligand) complexes based on potentially tridentate azomethines **II** and **III** (Y = S, Se) indicate that the tetracoordinate isomers (Table 1) in the form of pseudotetrahedra (Table 2) are more favorable. The results of the RHF and DFT calculations are consistent at the qualitative level (Table 1).

The calculated (DFT method) geometric parameters of the coordination nodes of tetra-, penta-, and hexacoordinate stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, IIIc for the complexes ZnL_2 (Y = S, Se) based on azomethines of the types **II** and **III** are presented in Table 2 (numerical values in parentheses are given for the ligands manifested bidenticity during the formation of the pentacoordinate stereoisomers).

The possibility of forming tetracoordinate stereoisomers **IIa** and **IIIa** of the ZnL_2 complexes (Y = S, Se) as the most favorable compounds from the viewpoint of total energy (Table 1) was evaluated using the earlier proposed [24, 25] stepwise model for the mechanism of forming bis(ligand) complexes ML_2. The first step in this model is $M^{++} + (L)^- \rightarrow (ML)^+$, i.e., binding of the first ligand by the metal ion. The second step is $(ML)^+ + (L)^- \rightarrow ML_2$, i.e., binding of the second ligand by the $(ML)^+$ ion and the formation of the starting stereoisomer of the ML_2 complex. The third step is the stereoisomerization from the initial to the energetically most favorable isomer of the ML_2 complex. The estimate for the barrier of this step characterizes the possibility of forming the final structure. If the initial stereoisomer of complex ML_2, as the product of the reaction $(ML)^+ + (L)^- \rightarrow ML_2$, is simultaneously the most energetically favorable, then this isomer is predicted to be preferable.

The quantum chemical calculations of the molecular structures of cations $(ZnL)^+$ were performed for the first step of the model reaction (formation of the $(ZnL)^+$ cations based on azomethines **II**). The calculations showed that the additional Y-donor center of the first ligand (Y = S, Se) was involved in the formation of the Y→Zn coordination bond and the first ligand manifested tridenticity during the formation of the $(ZnL)^+$ cations (Fig. 1). This was used for the construction of the model for the second step: binding of the second ligand $(L)^-$ by the $(ZnL)^+$ cation and formation of the initial (for the possible subsequent stereoisomerization) isomer of the ZnL_2 complex (Fig. 1).

Pentacoordinate structure **IIb** of the ZnL_2 complexes (Y = S, Se) in which the tridenticity of the first ligand is combined with the bidenticity of the second

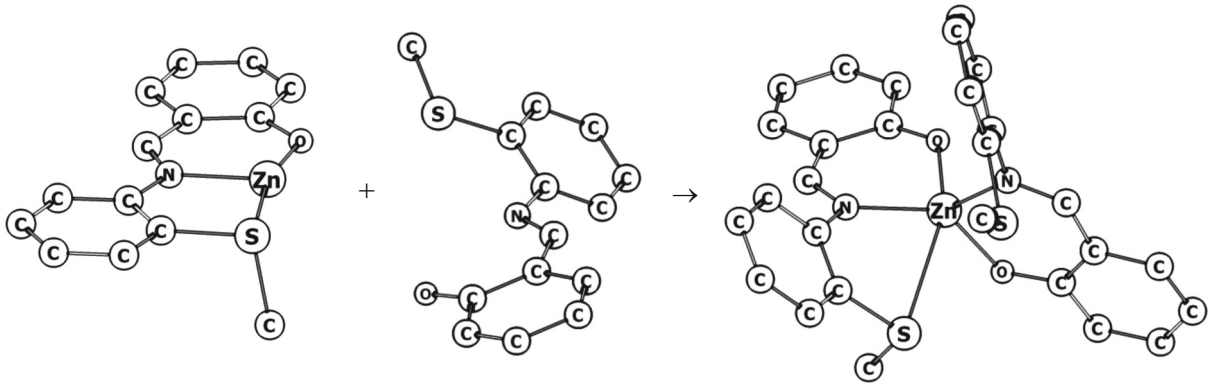
Table 2. Calculated (DFT method) geometric parameters of the coordination nodes ZnN_2O_2, ZnN_2O_2Y, and $ZnN_2O_2Y_2$ of stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc** for complexes ZnL_2 based on azomethines **II** and **III** (Y = S, Se)

ZnL_2 (Y, CN) Y = S, Se	Zn–N, Å	Zn–O, Å	∠NZnO, deg	∠NZnN, deg	∠OZnO, deg	Zn–Y, Å
Stereoisomers **IIa**, **IIb**, and **IIc** for complexes ZnL_2 (Y = S, Se)						
IIa (S, CN 4)	2.031	1.947	95.0	124.8	120.7	
IIb (S, CN 5)	2.078 (2.035)	1.987 (1.958)	91.1 (95.7)	121.3	103.1	3.019
IIc (S, CN 6)	2.128	2.030	88.1	166.4	94.8	2.757
IIa (Se, CN 4)	2.032	1.950	94.9	128.6	121.6	
IIb (Se, CN 5)	2.078 (2.037)	1.993 (1.961)	90.8 (95.5)	124.1	102.1	3.100
IIc (Se, CN 6)	2.134	2.031	88.0	167.5	93.9	2.871
Stereoisomers **IIIa**, **IIIb**, and **IIIc** for complexes ZnL_2 (Y = S, Se)						
IIIa (S, CN 4)	2.042	1.936	93.6	117.1	115.4	
IIIb (S, CN 5)	2.181 (2.102)	1.988 (1.976)	84.4 (90.1)	101.9	100.0	2.613
IIIc (S, CN 6)	2.165	2.044	83.6	169.5	91.3	2.684
IIIa (Se, CN 4)	2.039	1.937	93.5	118.0	115.2	
IIIb (Se, CN 5)	2.204 (2.109)	1.990 (1.984)	83.9 (89.6)	100.9	99.3	2.685
IIIc (Se, CN 6)	2.184	2.049	82.8	169.1	89.9	2.786

ligand was localized (DFT method) for the second step of the model reaction (Fig. 1) at a starting distance of 5 Å between the zinc cation $(ZnL)^+$ and nitrogen atom of the second ligand $(L)^-$.

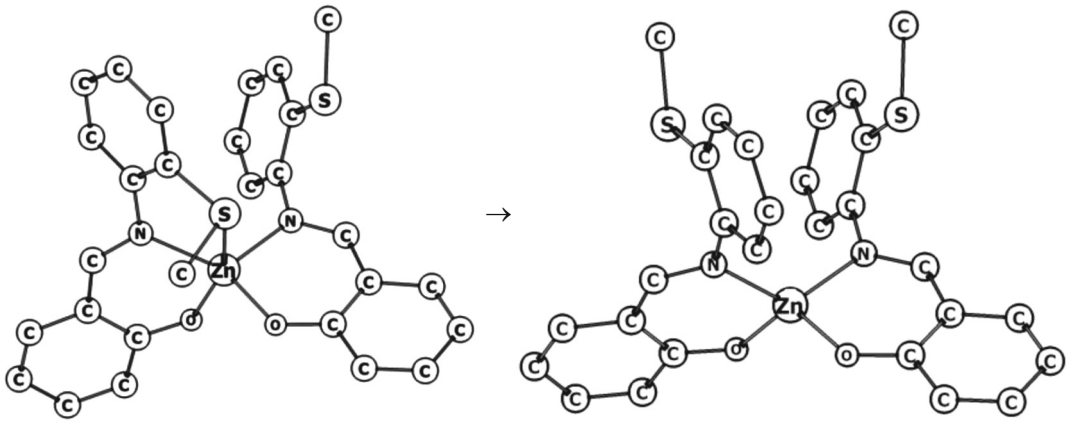
Since pentacoordinate isomer **IIb** for complexes ZnL_2 (Y = S, Se) formed in the first step of the model reaction (Fig. 1) is not most favorable in total energy (Table 1), this isomer cannot be considered as the initial isomer for the subsequent interconfigurational transition **IIb** → **IIa** toward energetically more favorable tetracoordinate isomer **IIa** (Fig. 2).

The mechanism of stereoisomerization **IIb** → **IIa** in the ZnL_2 complexes is reduced to the cleavage of the coordination bond Y→Zn (Y = S, Se) due to the turn about the C–N bond of the phenyl fragment of the first ligand (Fig. 2). Stereoisomer **IIa** can be formed from the initial **IIb** due to both the clockwise and anticlockwise turns of the phenyl fragment. The transition



$(ZnL)^+$ (**II**, Y = S) $(L)^-$ (**II**, Y = S) ZnL_2 (**IIb**, Y = S)

Fig. 1. Cyclic fragments of the calculated (DFT method) structures of the $(ZnL)^+$ cation, $(L)^-$ anion, and pentacoordinate isomer of the **IIb** type for complex ZnL_2 (Y = S).



IIb: ZnL_2 (CN 5, Y = S) **IIa**: ZnL_2 (CN 4, Y = S)

Fig. 2. Cyclic fragments of the calculated (DFT method) molecular structures of tetra- and pentacoordinate isomers **IIa** (CN 4) and **IIb** (CN 5) for complex ZnL_2 (Y = S).

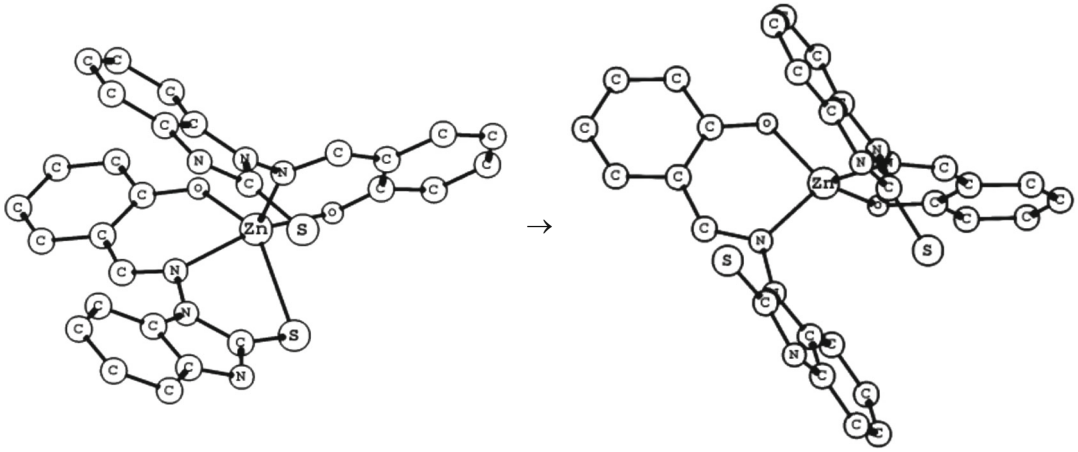
state for the stereoisomerization **IIb** → **IIa** (as shown by the quantum chemical calculations) is achieved by the clockwise turn by 124° and 121° for the S- and Se-containing ZnL_2 complexes, respectively, and the barrier of the reaction **IIb** → **IIa** is 6.9 (Y = S) and 7.3 kcal/mol (Y = Se), respectively. For the anticlockwise turn about the C–N bond of the phenyl fragment of the first ligand, the transition state is attained for the S- and Se-containing ZnL_2 complexes at the turn by 51° and 55°, respectively, and the barrier of the reaction **IIb** → **IIa** is 2.8 and 2.9 kcal/mol. These values of the barrier of the stereoisomerization **IIb** → **IIa** from the initial **IIb** to the energetically most favorable tetracoordinate isomer **IIa** (pseudotetrahedron (Table 2)) suggest that the barrier is accessible for the formation of the ZnL_2 complexes based on azomethines **II** (Y = S, Se).

For the energetically most favorable tetracoordinate isomer **IIIa** (Table 1), its accessibility in the formation of the ZnL_2 complexes based on azomethines **III** (Y = S, Se) was studied in terms of the stepwise model of the mechanism for forming bis(ligand) complexes ML_2 [24] and provided the same conclusions as those made above for the ZnL_2 complexes based on azomethines **II** (Y = S, Se). First, the quantum chemical calculations for the step of formation of the $(ZnL)^+$ cations based on azomethines **III** (Y = S, Se) established the involvement of the Y-donor center of the first ligand in the formation of the additional coordination bond Y→Zn. Second, pentacoordinate structure **IIIb** for the ZnL_2 complexes was also localized (DFT method) in the model of binding of the anion of the second ligand $(L)^-$ by the $(ZnL)^+$ cation (Fig. 3). Third, pentacoordinate isomer **IIIb** is not energetically most favorable (Table 1) and can also be considered as the starting one for the subsequent interconfigurational transition toward more favorable tetracoordinate isomer **IIIa** (Fig. 3).

The interconfigurational transition from the starting pentacoordinate isomer **IIIb** to the most favorable tetracoordinate isomer **IIIa** of the ZnL_2 complexes based on azomethines **III** is reduced to the cleavage of the coordination bond Y→Zn (Y = S, Se) due to the turn of the benzimidazole fragment involved in the additional coordination about the N–N bond, as in the case of the ZnL_2 complexes based on azomethines **II** (Fig. 3). When this fragment turns clockwise, the barrier of the reaction **IIIb** → **IIIa** for the complexes ZnL_2 (Y = S) and ZnL_2 (Y = Se) is 2.0 and 2.5 kcal/mol, respectively [24]. This suggests the possibility of the formation of the most favorable tetracoordinate isomer **IIIa** (Table 1), as for the considered above tetracoordinate isomer **IIa** of the ZnL_2 complexes based on azomethines **II** (Y = S, Se).

Thus, according to the quantum chemical study of the tetra-, penta-, and hexacoordinate stereoisomers of the ZnL_2 complexes based on potentially tridentate azomethines **III** (Y = S, Se) with allowance for possible interconfigurational transitions, tetracoordinate stereoisomer **IIIa** is more preferable.

According to the results of the quantum chemical calculations of the molecular structures and relative energies of the tetra-, penta-, and hexacoordinate stereoisomers of the Cd(II) bis(ligand) complexes based on tridentate azomethines **II** and **III** (Tables 3, 4), the most favorable are, on the one hand, hexacoordinate isomer **IIc** of the CdL_2 complexes based on azomethines **II** and, on the other hand, pentacoordinate isomer **IIIb** of the CdL_2 complexes based on azomethines **III**. An agreement of the results of the RHF and DFT calculations at the qualitative level can be mentioned for the CdL_2 complexes (Table 3).



IIIb: ZnL_2 (CN 5, Y = S) **IIIa**: ZnL_2 (CN 4, Y = S)

Fig. 3. Cyclic fragments of the calculated (DFT method) molecular structures of tetra- and pentacoordinate isomers **IIIa** (CN 4) and **IIIb** (CN 5) for complex ZnL_2 (Y = S).

The calculated (DFT method) geometric parameters of the coordination nodes of the tetra-, penta-, and hexacoordinate stereoisomers of the CdL_2 complexes based on azomethines **II** and **III** (Y = S, Se) are presented in Table 4.

To evaluate the possibility of forming most favorable in energy hexacoordinate isomer **IIc** for the CdL_2 complexes based on azomethines **II** and pentacoordinate isomer **IIIb** for the CdL_2 complexes based on azomethines **III** in the framework of the stepwise model for the mechanism of forming bis(ligand) complexes ML_2 [24, 25], we performed the quantum chemical calculations of the molecular structures of the $(CdL)^+$ cations as a result of binding of the anion of the first ligand by the metal ion. The calculation results show that the Y-donor center of the first ligand is involved in the additional coordination Y→Cd (Y = S, Se) during the formation of the $(CdL)^+$ cations based on azomethines **II** and **III**. This was taken into account in the model of the second step of forming complexes ML_2 (Figs. 4, 5) in which hexacoordinate isomer **IIc**, on the one hand, and pentacoordinate isomer **IIIb**, on the other hand, are localized at the starting distance (5 Å) between the cadmium atom of the $(CdL)^+$ cation and nitrogen atom of the $(L)^-$ anion of the second ligand.

Thus, hexacoordinate isomer **IIc** of the Cd(II) complexes based on azomethines **II** and pentacoordinate isomer **IIIb** of the Cd(II) complexes based on azomethines **III**, on the one hand, are the starting isomers for the subsequent interconfigurational transitions (as the products of the reaction $(CdL)^+ + (L)^- \rightarrow CdL_2$ (Figs. 4, 5)). On the other hand, the same isomers are most favorable in total energy (Table 3), which suggests that the hexacoordination is preferable in the CdL_2 complexes based on azomethines **II** and

Table 3. Relative energies ignoring (ΔE, kcal/mol) and taking into account zero-point vibrations (ΔE_{ZPE}, kcal/mol) of stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc** for complexes CdL_2 (Y = S, Se)

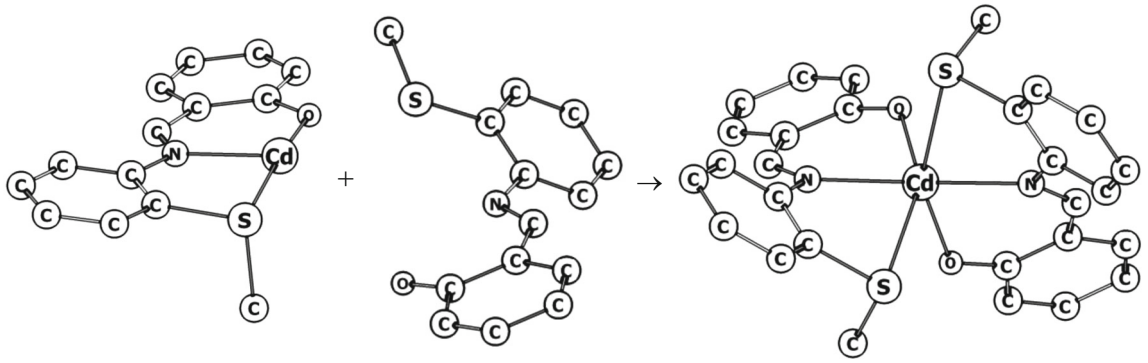
Stereoisomers **IIa**, **IIb**, and **IIc** (Y)					Stereoisomers **IIIa**, **IIIb**, and **IIIc** (Y)				
CdL_2 (Y) Y = S, Se	DFT/B3LYP		RHF		CdL_2 (Y) Y = S, Se	DFT/B3LYP		RHF	
	kcal/mol					kcal/mol			
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}		ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
IIa (S)	5.6	5.8	5.4	5.4	**IIIa** (S)	3.1	3.4	1.4	1.7
IIb (S)	3.4	3.6	3.0	2.9	**IIIb** (S)	0.0	0.0	0.0	0.0
IIc (S)	0.0	0.0	0.0	0.0	**IIIc** (S)	2.9	2.4	6.1	5.8
IIa (Se)	4.5	4.7	2.3	2.4	**IIIa** (Se)	3.0	3.1	2.0	2.4
IIb (Se)	2.6	2.6	0.5	0.5	**IIIb** (Se)	0.0	0.0	0.0	0.0
IIc (Se)	0.0	0.0	0.0	0.0	**IIIc** (Se)	2.4	1.9	6.6	6.2

Table 4. Calculated (DFT method) geometric parameters of the coordination nodes CdN_2O_2, CdN_2O_2Y, and $CdN_2O_2Y_2$ of stereoisomers **IIa**, **IIb**, **IIc** and **IIIa**, **IIIb**, **IIIc** for complexes CdL_2 based on azomethines **II** and **III** (Y = S, Se)

CdL_2 (Y, CN) Y = S, Se	Cd–N, Å	Cd–O, Å	∠NCdO, deg	∠NCdN, deg	∠OCdO, deg	Cd–Y, Å
Stereoisomers **IIa**, **IIb**, and **IIc** for complexes CdL_2 (Y = S, Se)						
IIa (S, CN 4)	2.226	2.154	88.2	136.6	129.597.2	
IIb (S, CN 5)	2.294 (2.232)	2.201 (2.176)	83.5 (88.1)	136.2	109.0	2.913
IIc (S, CN 6)	2.319	2.219	82.5	159.5	97.2	2.911
IIa (Se, CN 4)	2.220	2.156	87.9	137.1	128.2	
IIb (Se, CN 5)	2.296 (2.237)	2.197 (1.183)	83.9 (87.4)	134.3	107.2	2.977
IIc (Se, CN 6)	2.318	2.227	82.4	171.1	94.2	2.968
Stereoisomers **IIIa**, **IIIb**, and **IIIc** for complexes CdL_2 (Y = S, Se)						
IIIa (S, CN 4)	2.248	2.134	85.9	114.9	115.4	
IIIb (S, CN 5)	2.342 (2.298)	2.187 (2.155)	79.1 (83.9)	102.0	100.0	2.811
IIIc (S, CN 6)	2.368	2.226	77.3	164.6	90.7	2.835
IIIa (Se, CN 4)	2.242	2.134	86.1	116.0	119.4	
IIIb (Se, CN 5)	2.357 (2.301)	1.191 (2.165)	78.8 (83.4)	101.1	106.1	2.854
IIIc (Se, CN 6)	2.387	2.233	76.6	166.7	89.5	2.903

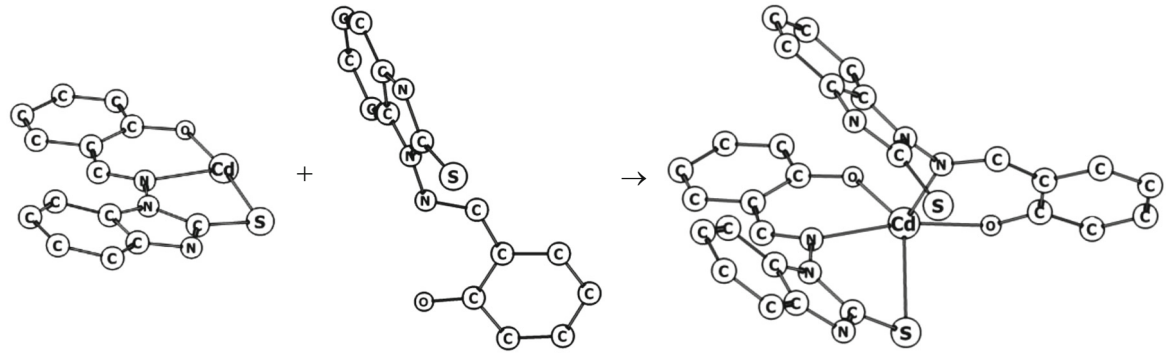
the pentacoordination is preferable in the CdL_2 complexes based on azomethines **III**.

It should be mentioned that the revealed (in the case of the CdL_2 complexes based on azomethines **II** and **III**) dependence of the structure of the preferable stereoisomer (with hexa- and pentacoordination, respectively) on specific features of the ligand structure is analogous to that analyzed earlier for the Ni(II) bis(ligand) complexes based on azomethines **II** and **III** [6]. Taking into account this dependence, we can assign the formation of cadmium pentacoordination in the starting isomers of the CdL_2 complexes based on azomethines **III** (Fig. 5) to a high degree of acoplanarity of the $(L)^-$ anion (the dihedral turning angle φ of the benzimidazole fragment about the N–N bond is 140°). As a result, the donor Y atom is withdrawn from the reaction space of the $(L)^-$ anion, which imparts it the pronounced (N,O)-chelate type. This structure of



$(CdL)^+$ (**II**, Y = S) $(L)^-$ (**II**, Y = S) φ(C–N) = 37° CdL_2 (**IIc**, Y = S)

Fig. 4. Cyclic fragments of the calculated (DFT method) structures of the $(CdL)^+$ cation, $(L)^-$ anion, and hexacoordinate isomer **IIc** for complex CdL_2 (Y = S).



$(CdL)^+$ (**III**, Y = S) $(L)^-$ (**III**, Y = S) CdL_2 (**IIIb**, Y = S)
φ(N–N) = 140°

Fig. 5. Cyclic fragments of the calculated (DFT method) structures of the $(CdL)^+$ cation, $(L)^-$ anion, and pentacoordinate isomer **IIIb** for complex CdL_2 (Y = S).

the $(L)^-$ anion of azomethines **III** favors the manifestation of bidenticity by the second ligand during the formation of the starting (pentacoordinate) isomer of the CdL_2 complex (Fig. 5). Unlike azomethines **III**, the structure of the $(L)^-$ anion for azomethines **II** is more flattened (the dihedral angle φ of the phenyl fragment about the C–N bond is 37°). In this case, the Y atom is located together with other donor atoms N and O in the reaction space of the $(L)^-$ anion, favoring the manifestation of tridenticity by this atom during the formation of the starting (hexacoordinate) isomer of the CdL_2 complex (Fig. 4).

To conclude, the quantum chemical study of the mechanism for the formation of the Zn(II) and Cd(II) bis(ligand) complexes based on (N,O,S(Se))-tridentate azomethines with allowance for interconfigurational transitions for the tetra-, penta-, and hexacoordinate stereoisomers made it possible to establish that the tetracoordination (in the form of a pseudotetrahedron) is preferable for the zinc complexes and the penta- or hexacoordination is preferable for the cadmium complexes depending on specific features of the structures of the ligands. The hexacoordination is preferable for the azomethine ligands with the *N*-phenylthio(seleno)ester substituent in the CdL_2 complexes, unlike the pentacoordination preferable for the CdL_2 complexes based on azomethines with the thio-(seleno)benzimidazole fragments.

ACKNOWLEDGMENTS

The author is sincerely grateful to Academician of the Russian Academy of Sciences V.I. Minkin for fruitful consultations made in the course of this study.

FUNDING

This study was supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of state assignment in the sphere of scientific activities (project no. 0852-2020-0019).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Yablonskaya