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Quantum-Chemical DFT Model for the Formation of the MN_2O_2, MN_2O_2X, or $MN_2O_2X_2$ (X = S, Se) Coordination Mode in the Bis(ligand) Ni(II), Zn(II), and Cd(II) Azomethine Complexes

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Abstract—The molecular structures and relative energies of tetra-, penta-, and hexacoordinated stereoisomers of the bis(ligand) complexes ML_2 (M = Ni(II), Zn(II), Cd(II)) with bi- and tridentate heterocyclic azomethine derivatives (coordination modes MN_2O_2, MN_2O_2X, or $MN_2O_2X_2$ (X = S, Se)) are calculated using the density functional theory. The dependences of the relative stabilities of the stereoisomers of the complexes with the coordination numbers 4, 5, and 6 on the electronic configuration of the central metal atom and structural features of the ligands are established.

Keywords: quantum chemistry, DFT simulation, coordination compounds, polydentate ligands, azomethines

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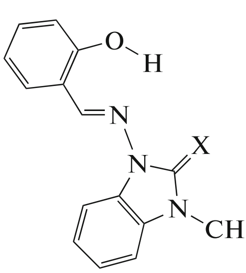
INTRODUCTION

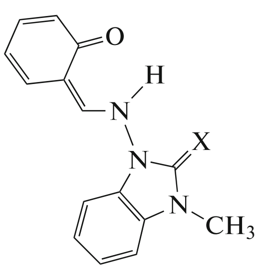
The molecular structures and spectral, magnetic, and other physical properties of the bis(chelate) azomethine complexes of tetracoordinated transition metals were studied in detail [1–4]. Their structures were established to be predominantly determined by the configuration of the coordination mode MN_2X_2 (X = NR, O, S, Se) and to depend on the type of the central ion, ligating atoms, and structural features of the ligand. The transition from the O-containing (X = O) to the S- or Se-containing (X = S, Se) tetracoordinated Ni(II) azomethine complexes is accompanied, as a rule, by a principal change in the configuration of the coordination mode from *trans*-planar NiN_2O_2 to *cis*-planar NiN_2S_2 or NiN_2Se_2. The influence of specific features of the ligand structure on the configuration of the coordination mode is most pronounced in the Ni(II) azomethine bis(chelates) as a transition from the planar to *pseudo*-tetrahedral configuration. The transition is related to the annelation of five-membered carbo- or heterocycles to metallocycles [1, 5, 6].

If the chelating ligand contains an additional donor center capable of forming a coordination bond with the central metal atom, the possibility appears to form not only tetra- but also penta- and hexacoordinated structures of Ni(II) [7–14], Zn(II) [15–18], and Cd(II) [18–20] in bis(ligand) metallocomplexes.

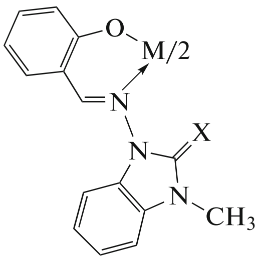
The purpose of this work is the theoretical (on the basis of quantum-chemical calculations using the density functional theory) simulation of the structures of all possible stereoisomers of the bis(ligand) complexes ML_2 and the evaluation of their relative stabilities using as examples the Ni(II), Zn(II), and Cd(II) complexes with the heterocyclic azomethine derivatives (**Ic** and **IIc**, Scheme 1), which are potentially capable of forming tetra- (MN_2O_2, coordination number (CN) 4), penta- (MN_2O_2X, CN 5), and hexacoordinated structures ($MN_2O_2X_2$, CN 6):



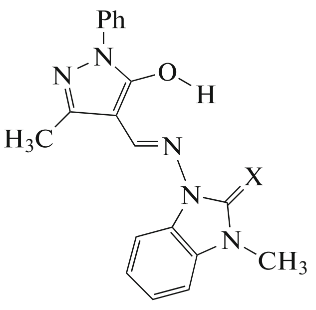
(Ia)



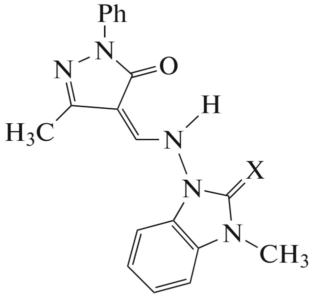
(Ib)



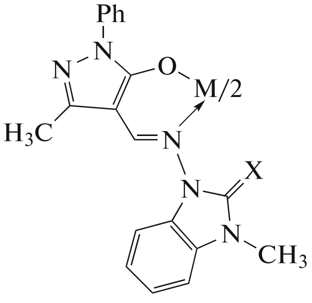
(Ic)



(IIa)



(IIb)

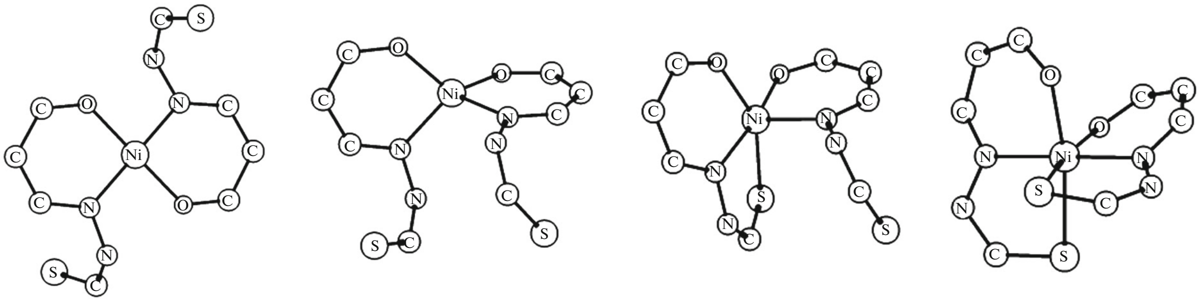


(IIc)

The presence in donor molecules of an additional chelating donor center X (X = S, Se) of the (N,O) type (**Ia**, **Ib** and **IIa**, **IIb**) capable of forming the coordination bond X → M is a reason for the competition of the tetra-, penta-, and hexacoordinated stereoisomers of the studied complexes with the coordination mode MN_2O_2, MN_2O_2X, or $MN_2O_2X_2$ (Fig. 1) controlled by their relative energies.

The molecular fragments of the calculated structures of stereoisomers **Ic** (X = S) of the nickel complexes constructed using the ChemCraft program [21] are shown in Fig. 1 for the clear presentation of possible variants of the tetra-, penta-, and hexacoordination modes of the central metal atom in stereoisomers **Ic** and **IIc**.

Donor molecules **Ia**, **Ib** and **IIa**, **IIb** were chosen as objects of the study, because a comparison of related complexes **Ic** and **IIc** makes it possible to evaluate the influence of the structural features of the ligands on the relative stabilities of the stereoisomers of complexes ML_2 associated with the number of units of the molecular fragments annelated to the metallocycles (six-membered rings are annelated in complexes **Ic**, and five-membered rings are annelated in complexes **IIc**). A comparison of the relative stabilities of the stereoisomers of bis(ligand) complexes ML_2 in the series of metals Ni(II), Zn(II), and Cd(II) allows one to analyze the dependences of the relative stability on the electronic configuration of the metal atom (for the



Ic, **IIc** (CN 4) (MN_2O_2)-*tr-pl*

Ic, **IIc** (CN 4) (MN_2O_2)-*ps-tt*

Ic, **IIc** (CN 5) (MN_2O_2X)

Ic, **IIc** (CN 6) $(MN_2O_2X_2)$

Fig. 1. Tetra-, penta-, and hexacoordination states in complexes **Ic** and **IIc** using the molecular fragments of calculated isomers **Ic** (CN 4, 5, 6; X = S) of the Ni(II) complexes as examples (*tr-pl* and *ps-tt* are *trans*-planar and *pseudo*-tetrahedral configurations, respectively, of the MN_2O_2 mode).

Table 1. DFT-Calculated total energies (E, au), relative energies (ΔE, kcal/mol), and relative zero-point vibration energies (ΔE_{ZPE}, kcal/mol) of the **a** and **b** forms of prototropic tautomers **I** and **II** (X = S, Se)

Form	**I** (X = S)			**I** (X = Se)		
	E	ΔE	ΔE_{ZPE}	E	ΔE	ΔE_{ZPE}
a	–1217.32509	0.0	0.0	–3220.65501	0.0	0.0
b	–1217.31327	7.4	6.9	–3220.64281	7.7	7.1
Form	**II** (X = S)			**II** (X = Se)		
	E	ΔE	ΔE_{ZPE}	E	ΔE	ΔE_{ZPE}
a	–1481.71758	5.1	4.9	–3485.05154	2.2	2.3
b	–1481.72564	0.0	0.0	–3485.05507	0.0	0.0

pair d^8(Ni^{2+}) and d^{10}(Zn^{2+})) and on the size of the latter (for the pair Zn(II) and Cd(II)).

CALCULATION PROCEDURE

Quantum-chemical calculations were performed using the Gaussian09 program [22]. The method of the density functional theory (DFT) [23] using the B3LYP hybrid functional [24, 25] was chosen as a calculation scheme. The scheme is based on the results of methodical works on the applicability of the DFT methods to the investigation of the molecular structures [26–28], including those of the coordination compounds [28]. The 6-311++G(d, p) basis set was used for tautomers of the donor molecules (**Ia** and **Ib**, **IIa** and **IIb**) and the Ni(II) and Zn(II) complexes, whereas the SDD basis set was used for the Cd(II) complexes. The molecular structures were determined by the full optimization of the molecular geometries, and the images of the molecules were constructed using the ChemCraft program [21].

RESULTS AND DISCUSSION

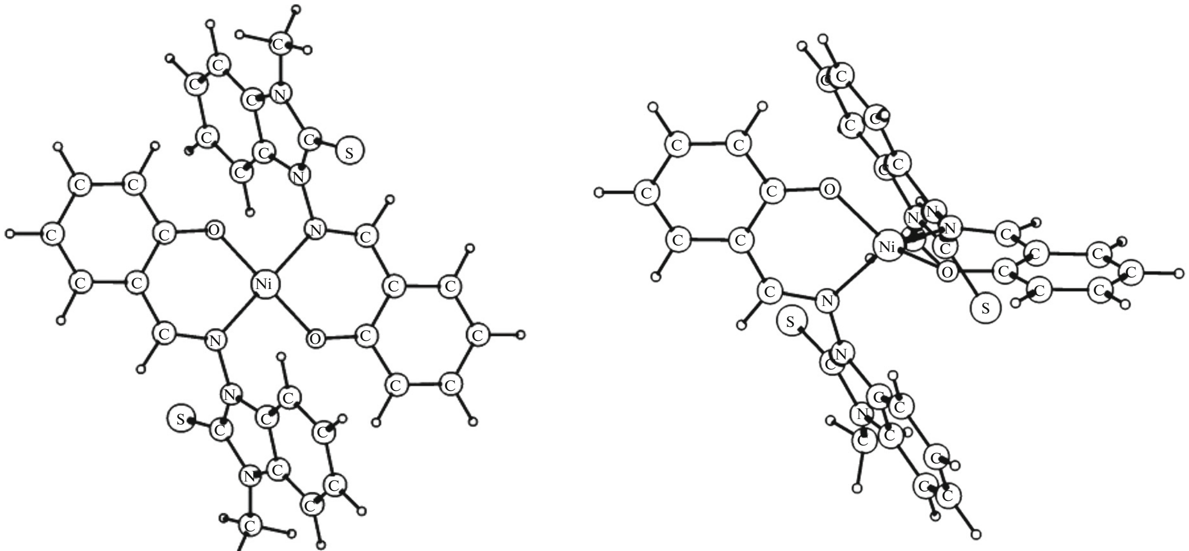
π-Conjugated (N,O)-prototropic tautomers. According to the data of the DFT calculations of the relative energies of the **a** and **b** forms of the π-conjugated (N,O)-prototropic tautomers based on heterocyclic azomethine derivatives **I** and **II** (X = S, Se) given in Table 1, the **a** form with proton localization at the oxygen atom is most favorable for ligands **I** (X = S, Se), whereas, on the contrary, the **b** form with proton localization at the nitrogen atom is most favorable for molecules **II** (X = S, Se).

The obtained reversal of the relative stability of the **a** and **b** forms in the pair of π-conjugated (N,O)-prototropic tautomers **I** and **II** with the phenyl ring (tautomer **I**) and five-membered heterocycle (tautomer **II**) annelated to the H cycle is completely consistent with the earlier determined ratio of the relative stabilities of the enol–imine **a** form and keto–enimine **b** form in structurally similar pairs of the π-conjugated (N,O)-prototropic tautomers based on the hydroxyphenyl and, correspondingly, indanedione derivatives of the cyclic azomethine analogs [29].

Complexes of Ni(II), Zn(II), and Cd(II). The calculations of the molecular structures of stereoisomers **Ic** and **IIc** (CN 4, 5, 6; X = S, Se) of the Ni(II), Zn(II), and Cd(II) bis(ligand) complexes with the tetra-, penta-, and hexacoordination modes of the central metal atom (Fig. 2, Tables 2, 3) were performed taking into account the fact that, unlike the Zn(II) and Cd(II) complexes, both low-spin (S = 0) and high-spin (S = 1) electronic states are possible for the Ni(II) complexes.

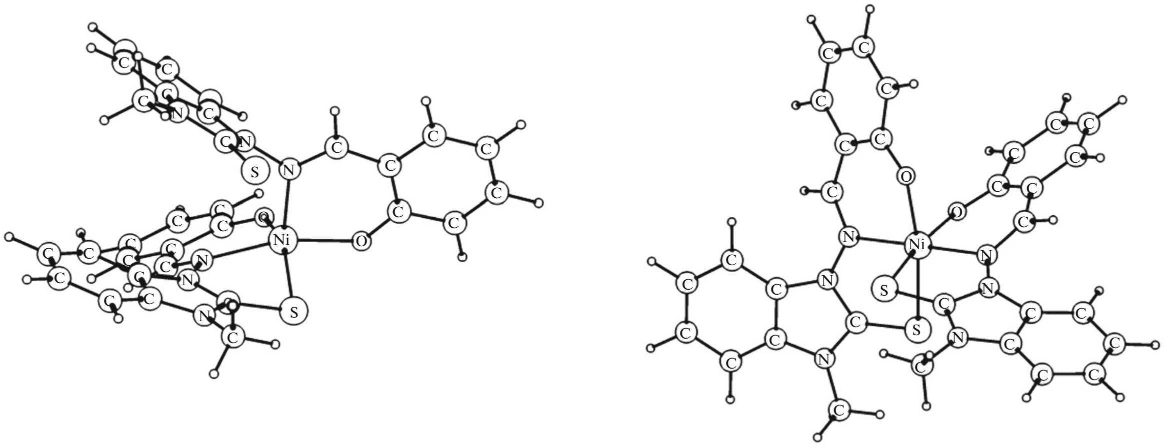
The calculated molecular structures of tetra-, penta-, and hexacoordinated stereoisomers **Ic** (CN 4, 5, 6; X = S) of the nickel complexes are exemplified in Fig. 2. The geometric parameters of the coordination modes of all calculated stereoisomers **Ic** and **IIc** (CN 4, 5, 6; X = S, Se) of the Ni(II), Zn(II), and Cd(II) complexes are collected in Tables 2 (stereoisomers **Ic**) and 3 (stereoisomers **IIc**). The numerical values presented in parentheses in Tables 2 and 3 for the complexes with the pentacoordination mode of the metals concern the ligands manifesting bidenticity in the formation of the MN_2O_2X coordination mode.

A comparison of the calculated molecular structures of tetracoordinated stereoisomers **Ic** and **IIc** of the complexes (Tables 2, 3) shows a distinct increase in the intraligand angles (NMO) on going from complexes **Ic** to complexes **IIc**, thus reflecting the earlier mentioned [30] increase in the size of the ligand “claw” caused by the five-membered heterocycles annelated to the metallocycles in complexes **IIc**. According to the stereomodel of metallochelates ML_2 [30], this structural effect leads to a change in the relative stabilities of the planar and tetrahedral configurations of the nickel complexes in favor of the latter. This result was detected by the quantum-chemical calculations of the total energy (E, Table 4) and relative energies (Table 5), which were determined both ignoring (ΔE) and taking into account (ΔE_{ZPE}) the zero-point vibration energy for the tetracoordinated stereoisomers of nickel complexes **Ic** and **IIc**.



Ic (M = Ni, X = S, CN 4 (*tr-pl*))

Ic (M = Ni, X = S, CN 4 (*ps-tt*))



Ic (M = Ni, X = S, CN 5)

Ic (M = Ni, X = S, CN 6)

Fig. 2. Calculated molecular structures of stereoisomers **Ic** (CN 4, 5, 6; X = S) of the Ni(II) complexes for the tetra-, penta-, and hexacoordinated states of the metal atom (*tr-pl* and *ps-tt* are *trans*-planar and *pseudo*-tetrahedral configurations, respectively, of the MN_2O_2 mode).

It should be noted that the correction to taking into account zero-point vibrations in the estimation of the relative stabilities of stereoisomers **Ic** and **IIc** (CN 4, 5, 6) of the Ni(II), Zn(II), and Cd(II) bis(ligand) complexes does not exceed, as a rule, 1 kcal/mol (Table 5), which quite corresponds to the earlier mentioned similar conclusion drawn on the basis of the quantum-chemical calculations of the relative stabilities of the configuration isomers in the series of the bis(chelate) metal complexes [5, 6, 29]. Nevertheless, in some of the cases considered in the present work (stereoisomers **Ic** and **IIc** of the nickel complexes, stereoisomers **IIc** of the zinc and cadmium complexes (X = S)), the correction to the zero-point vibration energy is comparable with the relative stabilities of the compared stereoisomers (Table 5), which required to take into account this correction in the discussion of the obtained results.

The reversal of the relative stabilities of the *trans*-planar and *pseudo*-tetrahedral configurations of the tetracoordinated stereoisomers of the Ni(II) complexes on going from compounds **Ic** (CN 4) to compounds **IIc** (CN 4) determined by the quantum-chemical calculations (Table 5) agrees completely with the experimentally established [1] and theoretically interpreted [5, 6] effect of the tetrahedral distortion of the coordination mode caused by the five-membered hetero- or carbocycles annelated to the metallocycles.

The mentioned structural distinction in the ligands of tetracoordinated nickel complexes **Ic** and **IIc** (X = S, Se) was also manifested in the results of calculations of the relative stabilities of tetra-, penta-, and hexacoordinated stereoisomers **Ic** and **IIc** (X = S, Se) of the

Table 2. Calculated geometric parameters of the coordination modes MN_2O_2, MN_2O_2X, and $MN_2O_2X_2$ in stereoisomers **Ic** of complexes ML_2 (M = Ni(II), Zn(II), Cd(II); X = S, Se)

Stereoisomers **Ic** of complexes ML_2 (M = Ni(II), Zn(II), Cd(II); X = S)

Coordination mode	Spin	M–N, Å	M–O, Å	Angle NMO, deg	Angle NMN, deg	Angle OMO, deg	M–X, Å
NiN_2O_2 (*tr-pl*)*	0	1.928	1.853	91.8	180.0	180.0	
NiN_2O_2 (*ps-tt*)*	1	2.009	1.910	91.4	111.1	121.2	
NiN_2O_2X	1	2.062	1.993	87.4	102.9	93.7	2.523
		(2.035)	(1.959)	(91.3)			
$NiN_2O_2X_2$	1	2.064	2.025	87.5	179.5	89.6	2.574
ZnN_2O_2 (*ps-tt*)	0	2.042	1.936	93.6	117.1	115.4	
ZnN_2O_2X	0	2.181	1.988	84.4	101.9	100.0	2.613
		(2.102)	(1.976)	(90.1)			
$ZnN_2O_2X_2$	0	2.165	2.044	83.6	169.5	91.3	2.684
CdN_2O_2 (*ps-tt*)	0	2.248	2.134	85.9	114.9	120.2	
CdN_2O_2X	0	2.342	2.187	79.1	102.0	107.1	2.811
		(2.298)	(2.155)	(83.9)			
$CdN_2O_2X_2$	0	2.368	2.226	77.3	164.6	90.7	2.835
Stereoisomers **Ic** of complexes ML_2 (M = Ni(II), Zn(II), Cd(II); X = Se)							
NiN_2O_2 (*tr-pl*)*	0	1.927	1.853	91.8	180.0	180.0	
NiN_2O_2 (*ps-tt*)*	1	2.007	1.911	91.3	112.1	120.9	
NiN_2O_2X	1	2.069	1.997	87.2	102.7	93.7	2.633
		(2.037)	(1.961)	(91.2)			
$NiN_2O_2X_2$	1	2.068	2.031	87.0	179.3	88.5	2.694
ZnN_2O_2 (*ps-tt*)	0	2.039	1.937	93.5	118.0	115.2	
ZnN_2O_2X	0	2.204	1.990	83.9	100.9	99.3	2.685
		(2.109)	(1.974)	(89.6)			
$ZnN_2O_2X_2$	0	2.184	2.049	82.8	169.1	89.9	2.786
CdN_2O_2 (*ps-tt*)	0	2.242	2.134	86.1	116.0	119.4	
CdN_2O_2X	0	2.357	2.191	78.8	101.1	106.1	2.854
		(2.301)	(2.165)	(83.4)			
$CdN_2O_2X_2$	0	2.387	2.233	76.6	166.7	89.5	2.903

* *tr-pl* and *ps-tt* are *trans*-planar and *pseudo*-tetrahedral configurations, respectively, of the MN_2O_2 mode.

Ni(II) complexes. According to the calculations (Table 5), the pentacoordination mode (especially taking into account the zero-point vibration energy) is most favorable for these complexes. This is valid for complexes **Ic** (X = S, Se) in combination with the *trans*-planar configuration of the coordination mode NiN_2O_2 (i.e., without the formation of additional coordination bonds X→Ni), while for complexes **IIc** (X = S, Se) this is combined with the hexacoordination mode, i.e., the formation of the coordination mode $NiN_2O_2X_2$ due to the inclusion of two additional coordination bonds X → Ni into the mode.

Unlike nickel complexes ($d^8(Ni^{2+})$) **Ic** and **IIc** (X = S, Se) for which only the *pseudo*-tetrahedral configuration turned out to be unfavorable in all cases considered, in the zinc complexes ($d^{10}(Zn^{2+})$), on the contrary, the *pseudo*-tetrahedral configuration of the coordination mode ZnN_2O_2 turned out (according to the electronic configuration of the central atom $d^{10}(Zn^{2+})$) to be preferable. For complexes **IIc** (X = S, Se), this configuration is preferable in combination with the pentacoordination mode, i.e., with the formation of the coordination mode ZnN_2O_2X due to the inclusion of the additional coordination bond X → Zn (Table 5).

The calculation of the relative stabilities of the tetra-, penta-, and hexacoordinated stereoisomers of cadmium complexes **Ic** and **IIc** (X = S, Se) showed that the pentacoordination mode, i.e., the formation of the coordination mode CdN_2O_2X with one additional coordination bond X → Cd, is preferable in all cases considered. According to the calculation results, a combination of the hexacoordination and pentacoordination modes with the formation of the

Table 3. Calculated geometric parameters of the coordination modes MN_2O_2, MN_2O_2X, and $MN_2O_2X_2$ in stereoisomers **IIc** of complexes ML_2 (M = Ni(II), Zn(II), Cd(II); X = S, Se)

Coordination mode	Spin	M–N, Å	M–O, Å	Angle NMO, deg	Angle NMN, deg	Angle OMO, deg	M–X, Å
Stereoisomers **IIc** of complexes ML_2 (M = Ni(II), Zn(II), Cd(II); X = S)							
NiN_2O_2 (*tr-pl*)*	0	1.944	1.891	92.9	179.0	179.0	–
NiN_2O_2 (*ps-tt*)*	1	2.009	1.954	94.1	112.2	117.4	
NiN_2O_2X	1	2.076	2.032	90.2	101.8	89.7	2.466
		(2.045)	(2.011)	(93.7)			
$NiN_2O_2X_2$	1	2.080	2.084	89.7	178.0	86.8	2.540
ZnN_2O_2 (*ps-tt*)	0	2.026	1.982	96.7	120.2	108.2	
ZnN_2O_2X	0	2.180	2.035	87.4	102.3	92.6	2.539
		(2.085)	(2.043)	(93.0)			
$ZnN_2O_2X_2$	0	2.151	2.115	86.7	171.7	86.5	2.655
CdN_2O_2 (*ps-tt*)	0	2.220	2.186	89.6	120.6	110.5	
CdN_2O_2X	0	2.333	2.231	83.0	102.6	98.9	2.767
		(2.276)	(2.212)	(87.3)			
$CdN_2O_2X_2$	0	2.341	2.286	81.9	169.3	84.7	2.819
Stereoisomers **IIc** of complexes ML_2 (M = Ni(II), Zn(II), Cd(II); X = Se)							
NiN_2O_2 (*tr-pl*)	0	1.944	1.891	92.9	180.0	180.0	
NiN_2O_2 (*ps-tt*)	1	2.009	1.954	94.0	113.1	116.8	
NiN_2O_2X	1	2.082	2.037	90.0	101.6	89.3	2.578
		(2.049)	(2.014)	(93.6)			
$NiN_2O_2X_2$	1	2.085	2.092	89.2	179.0	86.2	2.659
ZnN_2O_2 (*ps-tt*)	0	2.026	1.981	96.7	121.1	108.0	
ZnN_2O_2X	0	2.203	2.035	87.0	100.7	92.2	2.628
		(2.092)	(2.051)	(92.5)			
$ZnN_2O_2X_2$	0	2.161	2.123	86.1	172.4	85.2	2.766
CdN_2O_2 (*ps-tt*)	0	2.218	2.189	89.5	122.4	109.1	
CdN_2O_2X	0	2.351	2.236	82.5	101.9	97.4	2.816
		(2.279)	(2.224)	(87.5)			
$CdN_2O_2X_2$	0	2.360	2.294	81.2	171.7	83.7	2.892

* *tr-pl* and *ps-tt* are *trans*-planar and *pseudo*-tetrahedral configurations, respectively.

Table 4. Calculated total energies (*E*, au) of stereoisomers **Ic** and **IIc** of the Ni(II), Zn(II), and Cd(II) complexes with the coordination mode MN_2O_2, MN_2O_2X, or $MN_2O_2X_2$ (X = S, Se)

Coordination mode	Spin	**Ic** (X = S)	**Ic** (X = Se)	**IIc** (X = S)	**IIc** (X = Se)
NiN_2O_2 (*tr-pl*)*	0	–3941.84460	–7948.50467	–4470.64273	–8477.30313
NiN_2O_2 (*ps-tt*)*	1	–3941.84148	–7948.50102	–4470.65156	–8477.31117
NiN_2O_2X	1	–3941.84405	–7948.50398	–4470.66162	–8477.32170
$NiN_2O_2X_2$	1	–3941.84209	–7948.50113	–4470.66113	–8477.32069
ZnN_2O_2 (*ps-tt*)	0	–4212.88291	–8219.54270	–4741.69886	–8748.35890
ZnN_2O_2X	0	–4212.87937	–8219.53991	–4741.69797	–8748.35876
$ZnN_2O_2X_2$	0	–4212.87164	–8219.53099	–4741.69123	–8748.35104
CdN_2O_2 (*ps-tt*)	0	–2600.52499	–1822.87391	–3129.11254	–2351.46169
CdN_2O_2X	0	–2600.52846	–1822.87863	–3129.11796	–2351.46874
$CdN_2O_2X_2$	0	–2600.52542	–1822.87479	–3129.11646	–2351.46585

* *tr-pl* and *ps-tt* are *trans*-planar and *pseudo*-tetrahedral configurations, respectively.

Table 5. Calculated relative energies (ΔE, kcal/mol) and relative zero-point vibration energies (ΔE_{ZPE}, kcal/mol) for stereoisomers **Ic** and **IIc** of the Ni(II), Zn(II), and Cd(II) complexes with the coordination mode MN_2O_2, MN_2O_2X, or $MN_2O_2X_2$ (X = S, Se)

CN	Coordination mode	Spin	**Ic** (X = S)		**Ic** (X = Se)		**IIc** (X = S)		**IIc** (X = Se)	
			ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
4	NiN_2O_2 (*tr-pl*)*	0	0.0	0.0	0.0	0.0	5.6	6.7	5.0	6.2
4	NiN_2O_2 (*ps-tt*)*	1	2.0	1.1	2.3	1.2	0.0	0.0	0.0	0.0
4	NiN_2O_2 (*tr-pl*)	0	0.0	0.7	0.0	0.8	11.9	13.2	11.6	13.1
4	NiN_2O_2 (*ps-tt*)	1	2.0	1.8	2.3	2.0	6.3	6.5	6.6	6.9
5	NiN_2O_2X	1	0.3	0.0	0.4	0.0	0.0	0.0	0.0	0.0
6	$NiN_2O_2X_2$	1	1.6	1.1	2.2	1.6	0.3	0.2	0.6	0.4
4	ZnN_2O_2 (*ps-tt*)	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5
5	ZnN_2O_2X	0	2.2	1.7	1.8	1.5	0.6	0.2	0.1	0.0
6	$ZnN_2O_2X_2$	0	7.1	6.4	7.3	6.8	4.8	4.1	4.9	4.5
4	CdN_2O_2 (*ps-tt*)	0	2.2	2.4	3.0	3.1	3.4	3.7	4.4	4.6
5	CdN_2O_2X	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6	$CdN_2O_2X_2$	0	1.9	1.5	2.4	1.9	0.9	0.7	1.8	1.4

* *tr-pl* and *ps-tt* are *trans*-planar and *pseudo*-tetrahedral configurations, respectively.

$CdN_2O_2X_2$ mode due to the inclusion of two additional coordination bonds X → Cd into the mode is possible for complexes **IIc** (Table 5).

A comparison of the relative stabilities of the stereoisomers of the cadmium and zinc complexes (Table 5), i.e., the complexes differed primarily by the size of the central metal atom, explicitly indicates the corresponding tendency to an increase in the coordination number for the Cd(II) complexes.

Thus, it is shown on the basis of the quantum-chemical calculations of the molecular structures of possible prototropic tautomeric forms of the studied ligands of the (N,O) chelate type that the enol–imine (N–HO) tautomeric form is preferable for the heterocyclic derivatives of *o*-hydroxybenzaldimines, whereas the keto–enimine tautomeric form (NH–O) is preferable for the derivatives of pyrazole enaminoketones. The calculations of the configuration isomers of the tetracoordinated Ni(II) complexes allowed one to establish (in accord with the available experimental data) the reversal of the relative stabilities of the *trans*-planar and *pseudo*-tetrahedral configurations on going from the ligands with the six-membered annelated cycles to the ligands with the five-membered annelated cycles. The molecular DFT simulation of the tetra-, penta-, and hexacoordination modes for the Ni(II), Zn(II), and Cd(II) complexes based on the tridentate azomethine ligands showed that the pentacoordination mode combined with the *trans*-planar (complexes **Ic**) or *pseudo*-octahedral (complexes **IIc**) configurations (depending on the structural features of the ligands) was preferable for the Ni(II) complexes. The pentacoordination mode in combination with the hexacoordination mode (complexes **IIc** (X = S)) is also preferable for the Cd(II) complexes, whereas the Zn(II) complexes prefer the *pseudo*-tetrahedral configuration combined with the pentacoordination mode (complexes **IIc**) of the central metal atom. A tendency to an increase in the coordination number was established by the calculation for the Cd(II) complexes compared to the corresponding Zn(II) complexes.

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