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Quantum-Chemical Simulation of Structure of Bischelate Ni(II) Complexes Based on Cyclic Analogs of Azomethines

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Abstract—Relative stability of configuration isomers of bischelate Ni(II) complexes based on cyclic analogs of azomethine (pyridine and benzimidazole) has been studied by means of the density functional theory method. The simulation result allowed elucidation and interpretation of the coordination node composition (NiN_2O_2 or NiN_2S_2) effect on formation of *trans* and *cis* configuration of the complexes, and the stereo effect of the planar coordination node distortion and its transformation into the pseudo tetrahedral one upon annelation of five-membered hetero- and carbocycles.

Keywords: quantum chemistry, molecular structure, coordination compound, azomethine, azine, azole

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Molecular structure, spectral, magnetic, and other properties of bischelate complexes of tetracoordinate transition metal ion with the Schiff's bases have been extensively studied [1–4]. The complexes properties are predominantly affected by the configuration [planar (*cis*/*trans*) or pseudo tetrahedral] of the MN_2Y_2 (Y = O, S, Se, or NR) coordination node; the latter in turn depends on the central and the coordinated atoms nature as well as the ligand structural features (the chelate cycle size, the annelated aromatic or heterocyclic rings nature, etc.) [1–4].

The most prominent feature of Ni(II) bischelates with azomethines is the transition from planar to the pseudo tetrahedral configuration of the coordination node, conditioned by annelation of carbo- or heterocycles at the metal cycles; that was experimentally confirmed [1] and theoretically explained [5, 6].

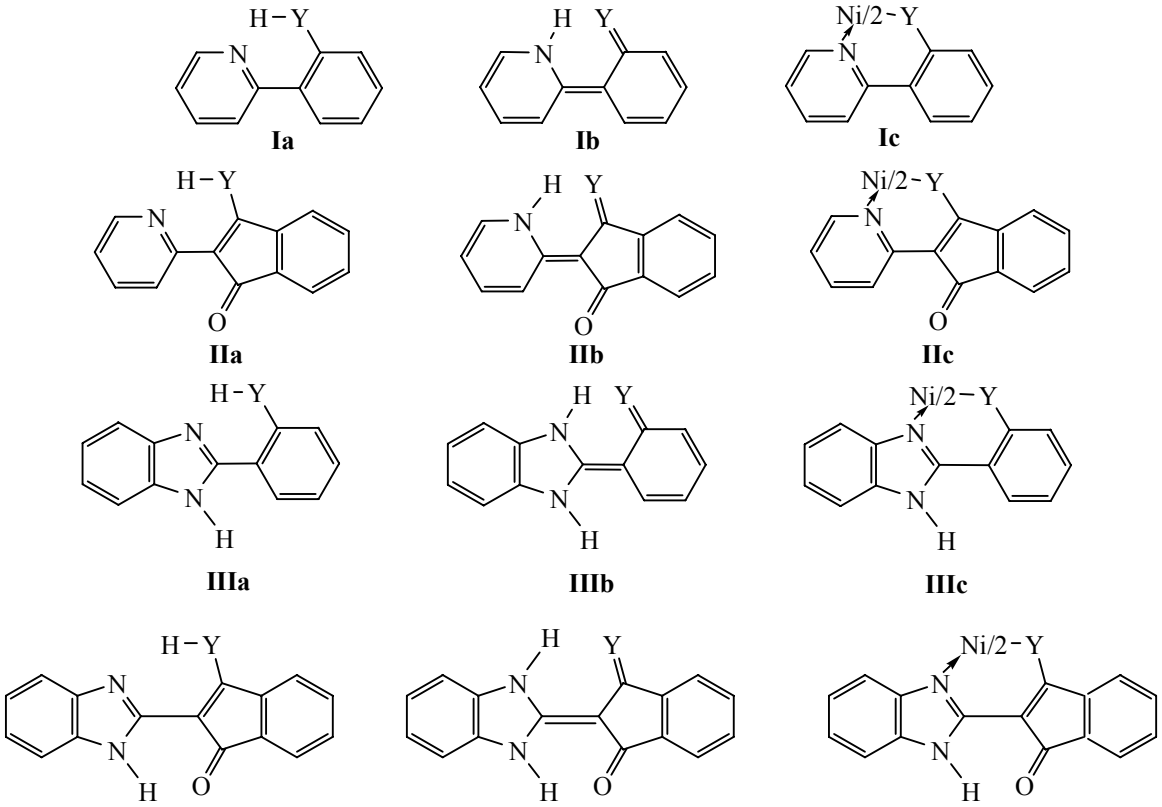
Ni(II) bischelates with several combinations of the annelated cycles (6,6 – **Ic**; 6,5 – **IIc**; 5,6 – **IIIc**; and 5,5 – **IVc**) based on the N,O-chelate donor molecules [hydroxyphenyl and indanedione derivatives of pyridine (**Ia**, **Ib**, **IIa**, **IIb**, Y = O) and benzimidazole (**IIIa**, **IIIb**, **IVa**, **IVb**, Y= O) as well as the N,S-chelate analogs (**I**–**IV**, Y = S)] were simulated to extend the knowledge of the ligands effect on the complexes configuration (Scheme 1).

Comparison of the configuration isomers of S-containing Ni(II) complexes (**Ic**–**IVc**, Y = S) with their O-analogs (Y = O) allows analysis of the stereo effect associated with relative stability of planar *cis* and *trans* configuration isomers of the complexes as affected by the coordination node composition (NiN_2O_2 or NiN_2S_2). That effect was thoroughly studied on the case of Ni(II) complexes with aromatic azomethines [1–6].

The effect of the ligand surrounding on configuration of the studied Ni(II) bischelate complexes was elucidated taking advantage of the density functional theory method DFT/B3LYP/6-311++G(d,p). The choice of the simulation scheme was based on the earlier results of that method application to various structural tasks [7–9] including the coordination compounds study [9].

π-Conjugated N,O-prototropic tautomers. Tautomerism determined by prototropism is known for the hydroxyphenyl and indanedione derivatives of pyri-

Scheme 1.

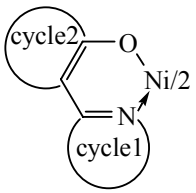


Y = O, S (**I**–**IV**).

dine and benzimidazole **I**–**IV** donor molecules. The following forms are possible: the enol-imine ones (**Ia**–**IVa**) with proton localized at the oxygen atom and the keto-enimine ones (**Ib**–**IVb**) with proton localized at the nitrogen atom. Tautomerism of chelate π-conjugated N,O-donor molecules based on azomethines as well as their cyclic analogs (five- and six-membered rings containing the C=N bond) has been studied in detail [10–12]. According to the available experimental data, the enol-imine tautomer (**Ia** and **IIIa**) is typical of the derivatives of pyridine (**I**) and benzimidazole (**III**) [13–15]. Physico-chemical analysis of the indanedione derivatives of pyridine (**II**) and benzimidazole (**IV**) have revealed that the keto-enimine tautomer form (**IIb** and **IVb**) is favorable for these compounds [16, 17].

The results of computation of relative energy of the **a** and **b** forms of the prototropic tautomers **I**–**IV** (Table 1) were fully in line with the above-stated experimental data.

Ni(II) bischelates based on cyclic analogs of azomethines (Ic–IVc, Y = O). Ni(II) bischelates **Ic**–**IVc** (Y = O) contained a pair of five/six-membered rings (A and B) annelated with the metal cycle in each of the ligands.



Ic (6,6), **IIc** (6,5), **IIIc** (5,6), **IVc** (5,5).

The effect of the annelated cycles size on the configuration of the NiN_2O_2 coordination node of the studied complexes was elucidated via computation of relative energy of their planar (*trans*/*cis*) and pseudo tetrahedral configuration isomers (Table 2).

The obtained results revealed that annelation of the five-membered carbo- or heterocycles at the metal cycle led to distortion of the planar NiN_2O_2 coordina-

Table 1. Relative energy (kcal/mol) of forms a and b of prototropic tautomers of hydroxyphenyl (**I** and **III**) and indanedione (**II** and **IV**) derivatives (Y = O)

Tautomers	**I**		**III**		**II**		**IV**	
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
a	0.0	0.0	0.0	0.0	4.0	3.8	8.0	7.8
b	–[a]	–[a]	9.5	8.3	0.0	0.0	0.0	0.0

[a] Only a form was detected in the simulation of molecule **I**.

Table 2. Relative energy (kcal/mol) of configuration isomers of Ni(II) complexes **Ic**–**IVc**, Y = O

Configuration[a]	**Ic** (6,6)		**IIc** (6,5)		**IIIc** (5,6)		**IVc** (5,5)	
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
cis	10.8	10.5	7.1	8.1	9.0	10.2	10.6	11.7
trans	0.0	0.0	1.2	2.4	1.5	2.9	6.6	7.7
ps-tt	6.6	5.4	0.0	0.0	0.0	0.0	0.0	0.0

[a] Hereafter *ps-tt* stands for the pseudo tetrahedral configuration .

tion node in the Ni(II) complexes with the cyclic analogs of azomethines to form the pseudo tetrahedral conformation (the "tetrahedral distortion") (Table 2), similarly to Ni(II) complexes with aromatic azomethines [1, 5].

Basing on the data collected in Table 2, we determined the most favorable (with respect to the full energy) configuration isomers of the **Ic**–**IVc** complexes (Y = O); their molecular structures are given in Fig. 1 along with the values of the dihedral angle θ between the planes of the metal chelate cycles. The simulated structures demonstrated the "tetrahedral distortion" of the NiN_2O_2 coordination node in the complexes with annelated five-membered carbo- and heterocycles, coinciding with the ideas of the stereochemical model of the ligands effect on configuration of tetracoordinate d^8-metals [6]. The simulated parameters of the NiN_2Y_2 coordination node (Y = O, S) for all the configuration isomers of the studied complexes are collected in Table 3.

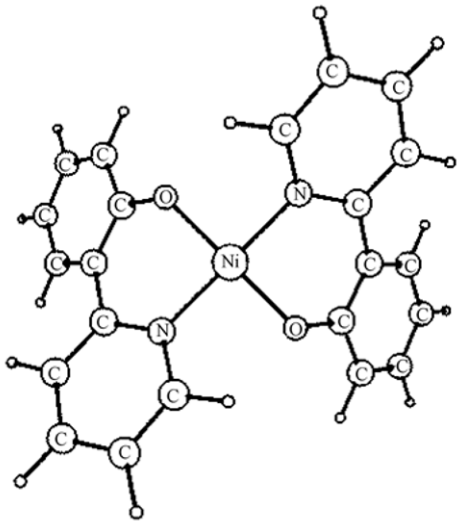
The simulation of the configuration isomers of the discussed Ni(II) complexes was performed taking into account that the singlet electron state determining the low-spin complexes form was the ground one for the planar *trans* and *cis* configurations, whereas the ground state of the pseudo tetrahedral configuration was the triplet one, determining the high-spin complexes form.

Simulation of the Ni(II) bischelates **Ic**–**IVc** (Y = O, coordination node NiN_2O_2) in the singlet electron state demonstrated that the *trans* isomers of the complexes were energetically more favorable than the *cis* ones (Table 2). The conclusion coincided with the relative stability of *trans* and *cis* isomers of Ni(II) complexes with aromatic azomethines (the same coordination node) stated experimentally [1–4] as well as theoretically [5].

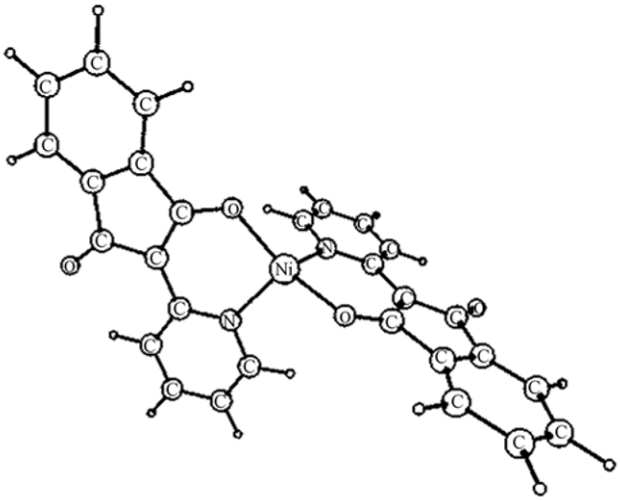
π-Conjugated N,S-prototropic tautomers. Simulation of **a** and **b** forms of the π-conjugated N,S-prototropic tautomers **I**–**IV** (Y = S) (Table 4) revealed that the thione-enimine forms (**IIb** and **IVb**) were favorable in the cases of the thioindanone derivatives of pyridine and benzimidazole, while the thiol-imine forms (**Ia** and **IIIa**) were favorable for the pyridine and benzimidazole derivatives of thiophenol, similarly to the cases of the above-discussed tautomers with Y = O (Table 1).

Ni(II) bischelates based on cyclic analogs of azomethines (Ic–IVc, Y = S). Simulation of the relative energy of configuration isomers of S-containing bischelates **Ic**–**IVc** (Table 5) revealed that distortion of the planar NiN_2S_2 coordination node due to the annelation of five-membered cycles was observed only when the two five-membered cycles were annelated at each of the metal cycles of the complex (5,5; **IVc**). The difference between the full energies of planar and pseudo tetrahedral configurations of the **IIc** and **IIIc** complexes with the one annelated five-membered cycle was as low as 1 kcal/mol, whereas in the case of annelation of the two six-membered cycles (**Ic**) the planar configuration was the favorable one.

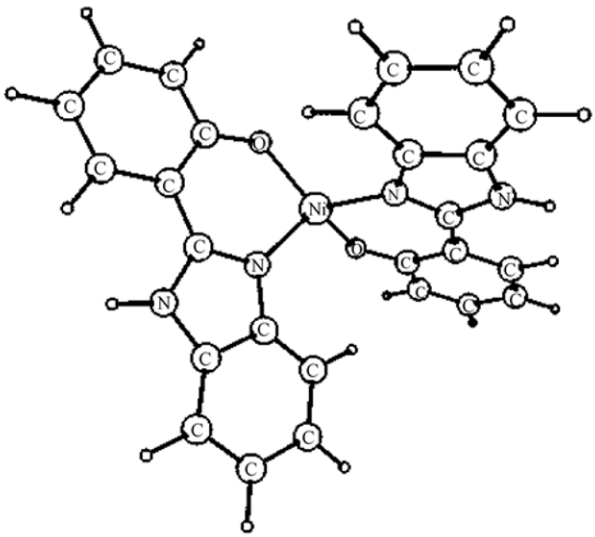
The simulated relative energies of *cis* and *trans* isomers of the S-containing bischelates **Ic**–**IVc** (Y = S,



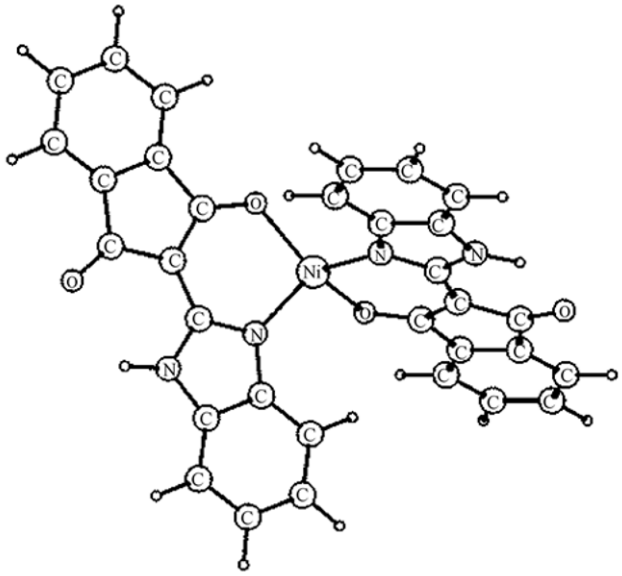
Ic (Y = O, *trans*, θ = 0°)



IIc (Y = O, *ps-tt*, θ = 77°)



IIIc (Y = O, *ps-tt*, θ = 50°)



IVc (Y = O, *ps-tt*, θ = 77°)

Fig. 1. Simulated molecular structures of energetically favorable *trans*- and pseudo tetrahedral configuration isomers of Ni(II) complexes **Ic** (6,6), **IIc** (6,5), **IIIc** (5,6), and **IVc** (5,5). (θ is the dihedral angle between the planes of the metal chelate cycles).

coordination node NiN_2S_2) were comparable (Table 5), in contrast to the above-discussed O-containing bischelates exhibiting the higher stability of the *trans* isomers (Table 2). The obtained result was fully in line with the data on relative stability of Ni(II) complexes with aromatic azomethines [5].

Comparison of the simulation of the ΔE and ΔE_{ZPE} values of relative energy (the latter one being computed accounting for the zero vibrations) of the π-conjugated N,O- and N,S-prototropic tautomers (**Ia**, **Ib**–**IVa**, **IVb**) (Tables 1 and 4) and the configuration isomers of the corresponding Ni(II) bischelates (**Ic**–**IVc**) (Tables 2 and 5) showed that accounting for the zero-point energy had practically no effect on the result in the considered simulation.

The close values of full energy for *cis* and *trans* isomers of the complexes **Ic**–**IVc** (Y = S) (Table 5) were primarily owing to the conformational features of the S-containing metal cycles, exhibiting significant bending along the donor atoms line N–S (Fig. 2). Such

Table 3. Simulated geometry parameters of the NiN_2Y_2 (Y = O, S) coordination node in configuration isomers of Ni(II) complexes **Ic**–**IVc**

Complex	Configuration	Ni–N, Å	Ni–Y, Å	NNiY, deg	NNiN, deg	YNiY, deg	NNiY*[a], deg
Ic (6,6), Y = O	*cis*	1.934	1.855	89.5	95.1	87.0	171.3
	trans	1.945	1.855	90.3	175.5	179.3	89.7
	ps-tt	2.023	1.891	92.7	105.9	148.8	106.1
IIc (6,5), Y = O	*cis*	1.941	1.879	93.1	93.8	83.7	164.8
	trans	1.965	1.868	93.2	172.3	169.2	87.5
	ps-tt	2.013	1.933	95.3	107.6	143.0	106.4
IIIc (5,6), Y = O	*cis*	1.917	1.871	90.3	96.6	85.1	167.3
	trans	1.924	1.863	90.7	176.5	173.9	89.5
	ps-tt	1.995	1.917	91.4	110.8	138.4	112.3
IVc (5,5), Y = O	*cis*	1.920	1.913	93.9	95.1	82.8	161.0
	trans	1.941	1.895	93.9	173.0	165.3	86.9
	ps-tt	1.988	1.984	95.4	114.8	138.7	106.6
Ic (6,6) Y = S	*cis*	1.978	2.202	90.8	92.9	88.0	167.8
	trans	1.937	2.253	89.1	171.4	170.8	91.6
	ps-tt	2.060	2.278	93.8	104.6	156.6	100.5
IIc (6,5), Y = S	*cis*	1.971	2.214	93.4	91.1	85.9	165.0
	trans	1.946	2.244	93.5	167.1	158.5	88.8
	ps-tt	2.032	2.263	98.3	101.3	125.1	116.2
IIIc (5,6), Y = S	*cis*	1.953	2.217	91.1	94.1	85.7	168.4
	trans	1.917	2.259	90.4	171.1	164.3	90.8
	ps-tt	2.018	2.259	95.2	104.7	119.9	121.5
IVc (5,5), Y = S	*cis*	1.947	2.246	95.5	93.2	84.2	157.6
	trans	1.926	2.272	95.8	165.2	147.3	88.4
	ps-tt	1.991	2.323	98.2	106.9	123.5	114.9

[a] The NNiY* angle, in contrast to the NNiY one, is the angle between coordination bonds of the two ligands in the complex.

Table 4. Relative energy (kcal/mol) of the prototropic tautomers forms (**I**–**IV**, Y = S)

Tautomers	**I**		**III**		**II**		**IV**	
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
a	0.0	0.0	0.0	0.0	9.9	7.4	12.3	10.1
b	3.0	3.9	2.2	3.3	0.0	0.0	0.0	0.0

distortion of the cycles noticeably decreased the steric interligand interactions so that they were practically equivalent in the *cis* and *trans* configurations. Fig. 2 displays the simulated molecular structures of *cis* and *trans* isomers of Ni(II) complexes based on thioindanone derivatives of pyridine (**IIc**) and benzimidazole (**IVc**) along with the values φ of the metal cycles bending angle along the N–S donor atoms line. The most favorable conformation of the *cis* isomers was the *step* one, and the most favorable conformation of the *trans* isomers was the *umbrella* one.

Coincidence of the bending angles of the metal cycles in the *cis* and *trans* isomers of the complexes (Fig. 2) pointed out that the metal cycles bending was determined by the metal cycles composition rather

Table 5. Relative energy (kcal/mol) of configuration isomers of Ni(II) complexes (**Ic**–**IVc**, Y = S)

Configuration	**Ic** (6,6)		**IIc** (6,5)		**IIIc** (5,6)		**IVc** (5,5)	
	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}	ΔE	ΔE_{ZPE}
cis	0.5	0.4	0.1	1.0	0.6	1.3	6.7	7.7
trans	0.0	0.0	1.8	2.6	0.3	1.0	6.1	7.1
ps-tt	4.4	3.6	0.0	0.0	0.0	0.0	0.0	0.0

than originated from the interligand steric interactions (the latter being initially different in the *cis* and *trans* isomers); that has been earlier pointed out in [5, 6] as well.

Since the thioindanone derivatives of pyridine (**II**) and benzimidazole (**IV**) were ambidentate ligands capable of coordination bonding via either the O (O→Ni) or S (S→Ni) atom, the issue of competing coordination upon the complex formation was important in the cases of the complexes **IIc** and **IVc** (Y = S) (Scheme 2).

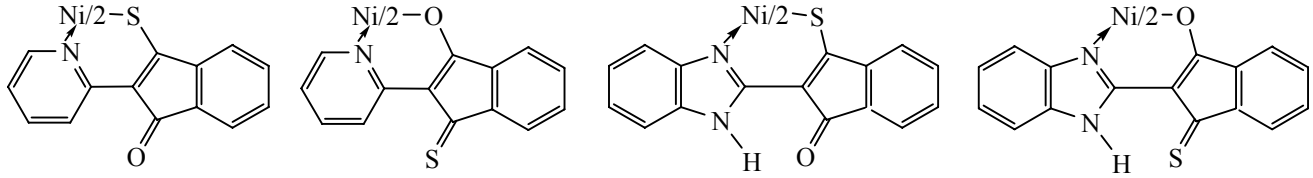
Simulation of the Ni(II) bischelates isomers **IIc** (Y = S, O→Ni) and **IVc** (Y = S, O→Ni) with the NiN_2O_2 coordination node revealed that the full energy of those isomers was noticeably higher than that of the **IIc** (Y = S, S→Ni) and **IVc** (Y = S, S→Ni) isomers with the NiN_2S_2 coordination node (Table 6). Hence, formation of the Ni–S bond was energetically advantageous over formation of the Ni–O bond in those complexes. That conclusion has been experimentally confirmed for Ni(II) complex with the thioindanone derivative of pyridine (**IIc**, Y = S) [18]. Thus, the simulation (Table 6) and the experimental [18] data showed that Ni^{2+} exhibited the properties of soft Lewis acid resulting in the preferential binding at the soft S-donor site rather than at the hard O-donor site, in line with the HSAB Pearson's theory [19].

To summarize, quantum-chemical simulation of π-conjugated N,O-prototropic tautomers revealed that, in accordance with the experiment, the enol-imine form was favorable in the cases of the hydroxyphenyl deriva-tives of pyridine and benzimidazole, whereas the keto-enimine form was favorable in the cases of the indanedione derivatives. DFT simulation of molecular structure of the configuration isomers of the studied Ni(II) bischelates revealed the stereo effect of distortion of the planar coordination node (trans-formation into the pseudo tetrahedral conformation) upon annelation of five-membered carbo- and heterocycles at the metal chelate cycles; furthermore, the influence of the coordination node composition (NiN_2O_2 or NiN_2S_2) on the relative stability of *trans* and *cis* isomers of the complexes was elucidated. Similarity of the discussed effects in the cases of Ni(II) bischelates with aromatic azomethines and cyclic analogs of azomethines was demonstrated.

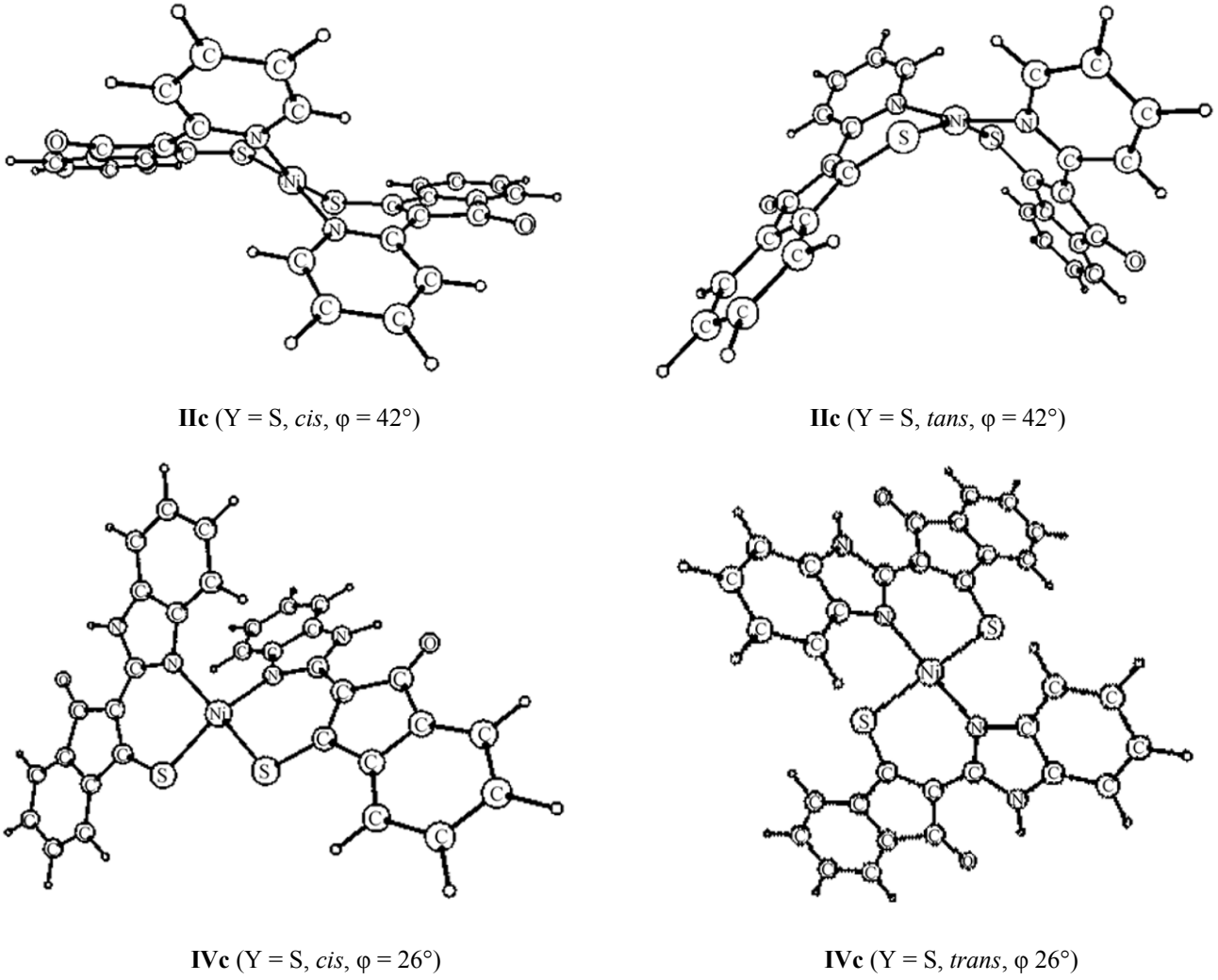
EXPERIMENTAL

Quantum-chemical simulations were performed using GAUSSIAN03 software [20] taking advantage of the density functional theory method [21] utilizing the B3LYP hybrid density functional [22, 23] in combination with the split-valence basis set including the diffuse and polarization functions at light and heavy atoms [DFT/B3LYP/6-311++G(d,p)]. The stationary points at the potential energy surface were located via the full optimization of the molecular geometry. The molecular structures were visualized using ChemCraft software [24] with Cartesian coordinates of the atoms obtained in the quantum-chemical simulation used as the visualization input.

Scheme 2.



IIc, Y = S, S→Ni **IIc**, Y = S, O→Ni **IVc**, Y = S, S→Ni **IVc**, Y = S, O→Ni



IIc (Y = S, *cis*, φ = 42°) **IIc** (Y = S, *tans*, φ = 42°)

IVc (Y = S, *cis*, φ = 26°) **IVc** (Y = S, *trans*, φ 26°)

Fig. 2. Simulated molecular structures of *cis*- and *trans* isomers of Ni(II) complexes **IIc** and **IVc** (φ is the bending angle of the metal chelate cycles along the N–S donor atoms line).

Table 6. Relative energy (kcal/mol) of isomers of complexes **IIc** and **IVc**

Isomers	Δ*E* (*cis*)	Δ*E* (*trans*)	Δ*E* (*ps-tt*)
IIc (Y=S, O→Ni)	10.8	4.0	6.8
IIc (Y=S, S→Ni)	0.0	0.0	0.0
IVc (Y=S, O→Ni)	8.5	5.5	6.2
IVc (Y=S, S→Ni)	0.0	0.0	0.0

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