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Quantum-Chemical Calculations of Molecular Structure of *trans*-Isomeric Chelate of Ni(II) with Hydrazinomethanethioamide Using Different Versions of DFT Method

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Abstract—The results of quantum-chemical calculations of the molecular structure parameters (bond lengths, bond and torsion angles) of the *trans*-chelate of Ni(II) with hydrazinomethanethioamide obtained by different versions of the density functional theory (DFT) method and GAUSSIAN09 program are summarized. The calculated data were compared with the corresponding experimental data. Although the structural data obtained using different methods of DFT are in good agreement with experiment they give different results in the evaluation of the spin multiplicity of the ground state and the relative energies between ground and excited states. The best agreement with experiment was observed in the calculation by OPBE/TZVP method.

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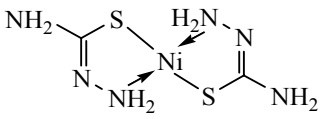
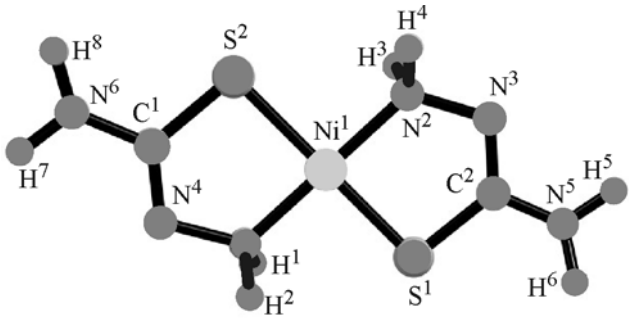
Earlier [1–7] we have performed quantum-chemical calculations of macrocyclic metal complex of ions M (II) of 3*d*-elements with chelate ligands and chelating sites N_2S_2 using B3LYP 6-31G(d) method. Utilizing the *trans*-isomer of the Ni(II) complex with hydrazinomethanethioamide $H_2N–HN–C(=S)–NH_2$ as an example it has been shown [8] that this method of calculation describes well the details of the molecular structure [9] and also correctly predicts the spin multiplicity of its ground state.



However, in some cases this calculation method evaluates incorrectly the ratio between the energy of high- and low-spin states of a number of metal chelates of 3*d*-elements that results in the errors when determining the spin multiplicity of the ground states. The same is true in the case of the *cis*-chelate of Ni(II) with the same ligand, for which the method B3LYP 6-31G(d) forecasts a spin triplet as a ground state, whereas, according to the available experimental data [10], the ground state of the complex is also a spin singlet. In this connection it is important to compare the theoretical data on the molecular structure and the multiplicity of the ground state of *trans*-chelate of Ni(II) with hydrazinomethanethioamide obtained by other versions of DFT method and then select the one which would provide a good agreement between the theoretically calculated and experimentally found key parameters of the molecular structure of metal chelate of 3*d*-elements and allow to reliably determine the spin multiplicity of the ground state. To this purpose, we carried out quantum-chemical calculation of the above chelate complex using such versions of DFT method as B3LYP/6-31G(d), B3LYP/6-31G(d)//LanL2DZ, B3LYP/6-31G(d)//SDDAll, B3LYP/cc-pVTZ, B3PW91/6-31G(d), B3LYP/6-311++G(df,p), wB97XD/6-31G(d), and OPBE/TZVP included in GAUSSIAN09 software [11].



Molecular structure of *trans*-bis(hydrazinomethanethioamido)-nickel(II).

Table 1. Calculated and experimental [9] bond lengths (pm) in the *trans*-complex of Ni(II) with hydrazinomethanethioamide[a]

Bond	Experiment	Calculation							
		B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)// LanL2DZ	B3LYP/ 6-311++ G(df,p)	wB97XD/ 6-31G(d)	B3LYP/ 6-31G(d)// SDDAll	B3LYP/ cc-pVTZ	B3PW91/ 6-31G(d)	OPBE/ TZVP
$Ni^1–N^1$	190.5	189.9 (0.6)	192.8 (2.3)	193.0 (2.5)	189.6 (0.9)	192.5 (2.0)	193.1 (2.6)	188.6 (1.9)	190.9 (0.4)
$Ni^1–N^2$	190.5	189.9 (0.6)	192.8 (2.3)	193.0 (2.5)	189.6 (0.9)	192.5 (2.0)	193.1 (2.6)	188.6 (1.9)	190.9 (0.4)
$Ni^1–S^1$	216.8	219.1 (2.3)	223.8 (7.0)	221.0 (4.2)	217.6 (0.8)	221.5 (4.7)	220.9 (4.1)	217.0 (0.2)	216.5 (0.3)
$Ni^1–S^2$	216.8	219.2 (2.4)	223.8 (7.0)	221.0 (4.2)	217.6 (0.8)	221.5 (4.7)	220.9 (4.1)	217.0 (0.2)	216.5 (0.3)
$N^1–N^4$	144.7	145.5 (0.8)	145.0 (0.3)	144.8 (0.1)	144.3 (0.4)	145.1 (0.4)	144.8 (0.1)	144.3 (0.4)	143.3 (1.4)
$N^2–N^3$	144.7	145.5 (0.8)	145.0 (0.3)	144.8 (0.1)	144.3 (0.4)	145.1 (0.4)	144.8 (0.1)	144.3 (0.4)	143.3 (1.4)
$N^4–C^1$	129.6	129.6 (0.0)	129.7 (0.1)	129.2 (0.4)	129.3 (0.3)	129.7 (0.1)	129.1 (0.5)	129.5 (0.1)	129.8 (0.2)
$N^3–C^2$	129.6	129.6 (0.0)	129.7 (0.1)	129.2 (0.4)	129.3 (0.3)	129.7 (0.1)	129.1 (0.5)	129.5 (0.1)	129.8 (0.2)
$C^1–S^2$	176.1	176.9 (0.8)	177.2 (1.1)	176.6 (0.5)	175.9 (0.2)	177.0 (0.9)	176.3 (0.2)	176.0 (0.1)	175.7 (0.4)
$C^2–S^1$	176.1	176.9 (0.8)	177.1 (1.0)	176.6 (0.5)	175.9 (0.2)	177.0 (0.9)	176.3 (0.2)	176.0 (0.1)	175.7 (0.4)
$C^1–N^6$	134.2	137.2 (3.0)	137.3 (3.1)	136.5 (2.3)	136.6 (2.4)	137.3 (3.1)	136.8 (2.6)	136.7 (2.5)	137.1 (2.9)
$C^2–N^5$	134.2	137.3 (3.1)	137.3 (3.1)	136.5 (2.3)	136.6 (2.4)	137.3 (3.1)	136.8 (2.6)	136.7 (2.5)	137.1 (2.9)
$N^1–H^1$	87.3	102.5 (15.2)	102.4 (15.1)	102.0 (14.7)	102.3 (15.0)	102.4 (15.1)	101.8 (14.5)	102.4 (15.1)	102.3 (15.0)
$N^1–H^2$	89.5	102.3 (12.8)	102.2 (12.7)	102.0 (12.5)	102.1 (12.6)	102.3 (12.8)	101.7 (12.2)	102.3 (12.8)	102.2 (12.7)
$N^6–H^7$	87.5	101.3 (13.8)	101.3 (13.8)	100.8 (13.3)	101.0 (13.5)	101.3 (13.8)	100.7 (13.2)	101.1 (13.6)	101.1 (13.6)
$N^6–H^8$	88.5	101.0 (12.5)	101.0 (12.5)	100.5 (12.0)	100.7 (12.2)	101.0 (12.5)	100.4 (11.9)	100.9 (12.4)	100.8 (12.3)
		max (15.2)	max 15.1)	max (14.7)	max (15.0)	max (15.1)	max (14.5)	max (15.1)	max (15.0)
		min (0.0)	min (0.1)	min (0.1)	min (0.2)	min (0.1)	min (0.1)	min (0.1)	min (0.2)
		average (4.3)	average (5.1)	average (4.5)	average (4.0)	average (4.8)	average (4.5)	average (4.0)	average (4.1)

[a] The absolute values of the deviations from the corresponding experimental values are given in parentheses. The experimental bond lengths N–H in the terminal amino groups have a low reliability.

Table 2. Calculated and experimental [9] bonds angles (deg) in the *trans*-complex of Ni(II) with hydrazinomethanethioamide

Angle	Experiment	Calculation							
		B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)// LanL2DZ	B3LYP/ 6-311++ G(df,p)	wB97XD/ 6-31G(d)	B3LYP/ 6-31G(d)// SDDAll	B3LYP/ cc-pVTZ	B3PW91/ 6-31G(d)	OPBE/ TZVP
$S^2Ni^1N^1$	87.1	87.8 (0.7)	86.8 (0.3)	86.8 (0.3)	87.8 (0.7)	87.1 (0.0)	86.8 (0.3)	87.9 (0.8)	86.7 (0.4)
$S^3Ni^1N^1$	92.9	92.2 (0.7)	93.2 (0.3)	93.2 (0.3)	92.2 (0.7)	92.9 (0.0)	93.2 (0.3)	92.1 (0.8)	93.3 (0.4)
$Ni^1S^2C^1$	96.3	94.8 (1.5)	94.5 (1.8)	95.4 (0.9)	95.0 (1.3)	94.9 (1.4)	95.4 (0.9)	94.9 (1.4)	96.2 (0.1)
$N^4C^1S^2$	123.2	125.1 (1.9)	125.6 (2.4)	124.9 (1.7)	125.0 (1.8)	125.3 (2.1)	125.1 (1.9)	124.8 (1.6)	124.4 (1.2)
$N^1N^4C^1$	112.3	111.3 (1.0)	111.9 (0.4)	112.2 (0.1)	111.4 (0.9)	111.7 (0.6)	112.1 (0.2)	111.1 (1.2)	110.8 (1.5)
$S^2C^1N^6$	116.9	116.5 (0.4)	116.2 (0.7)	116.6 (0.3)	116.6 (0.3)	116.5 (0.4)	116.5 (0.4)	116.6 (0.3)	116.9 (0.0)
$N^4C^1N^6$	119.9	118.3 (1.6)	118.1 (1.8)	118.4 (1.5)	118.3 (1.6)	118.2 (1.7)	118.4 (1.5)	118.5 (1.4)	118.6 (1.3)
$H^1N^1H^2$	102.7	104.4 (1.7)	105.3 (2.6)	105.4 (2.7)	104.4 (1.7)	105.2 (2.5)	105.3 (2.6)	104.4 (1.7)	105.3 (2.6)
$H^7N^6H^8$	122.1	115.3 (6.8)	115.4 (6.7)	117.5 (4.6)	116.2 (5.9)	115.3 (6.8)	116.4 (5.7)	115.6 (6.5)	115.1 (7.0)
$Ni^1N^1H^1$	113.2	110.3 (2.9)	107.7 (5.5)	108.2 (5.0)	109.3 (3.9)	108.1 (5.1)	108.3 (4.9)	108.9 (4.9)	107.2 (6.0)
$Ni^1N^1H^2$	108.9	109.2 (0.3)	108.8 (0.1)	108.8 (0.1)	110.3 (1.4)	109.1 (0.2)	109.0 (0.1)	110.3 (1.4)	108.8 (0.1)
$C^1N^6H^7$	115.8	115.1 (0.7)	115.1 (0.7)	117.2 (1.4)	115.8 (0.0)	115.1 (0.7)	116.1 (0.3)	115.4 (0.4)	115.0 (0.8)
$C^1N^6H^8$	119.5	116.5 (3.0)	116.6 (2.9)	118.4 (1.1)	117.2 (2.3)	116.6 (2.9)	117.1 (2.4)	116.8 (2.7)	116.1 (3.4)
$N^4N^1H^1$	100.7	105.8 (5.1)	106.9 (6.2)	106.6 (5.9)	105.8 (5.1)	106.6 (5.9)	106.5 (5.8)	105.9 (5.2)	106.6 (5.9)
$N^4N^1H^2$	109.5	105.2 (4.3)	106.3 (3.2)	106.3 (3.2)	105.3 (4.2)	106.1 (3.4)	106.1 (3.4)	105.2 (4.3)	106.0 (3.5)
		max (6.8)	max (6.7)	max (5.9)	max (5.9)	max (6.8)	max (5.8)	max (6.5)	max (7.0)
		min (0.3)	min (0.1)	min (0.1)	min (0.0)	min (0.0)	min (0.1)	min (0.3)	min (0.0)
		average (2.2)	average (2.4)	average (1.9)	average (2.1)	average (2.2)	average (2.0)	average (2.3)	average (2.3)

Table 3. Calculated and experimental [9] torsion angles (deg) in the *trans*-complex of Ni(II) with hydrazinomethanethioamide

Angle	Experiment	Calculation							
		B3LYP/ 6-31G(d)	B3LYP/ 6-31G(d)// LanL2DZ	B3LYP/ 6-311++ G(df,p)	wB97XD/ 6-31G(d)	B3LYP/ 6-31G(d)// SDDAll	B3LYP/ cc-pVTZ	B3PW91/ 6-31G(d)	OPBE/ TZVP
$Ni^1N^1N^4C^1$	5.5	6.1 (0.6)	5.5 (0.0)	2.7 (2.8)	4.8 (0.7)	4.9 (0.6)	3.3 (2.2)	6.5 (1.0)	4.9 (0.6)
$N^1N^4C^1S^2$	2.4	2.4 (0.0)	2.9 (0.5)	1.7 (0.7)	2.0 (0.4)	2.7 (0.3)	2.1 (0.3)	2.4 (0.0)	2.6 (0.2)
$N^4C^1S^2Ni^1$	7.4	1.4 (6.0)	0.3 (7.1)	0.1 (7.3)	0.9 (6.5)	0.1 (7.3)	0.2 (7.2)	1.7 (5.7)	0.2 (7.2)
$C^1S^2Ni^1N^1$	7.1	3.4 (3.7)	2.4 (4.7)	1.0 (6.1)	2.6 (4.5)	2.1 (5.0)	1.2 (5.9)	3.8 (3.3)	2.1 (5.0)
$S^2Ni^1N^1N^4$	8.4	5.9 (2.5)	4.7 (3.7)	2.2 (6.2)	4.5 (3.9)	4.2 (4.2)	2.7 (5.7)	6.4 (2.0)	4.3 (4.1)
$Ni^1S^2C^1N^6$	173.2	179.0 (5.8)	178.2 (5.0)	178.3 (5.1)	179.0 (5.8)	178.1 (4.9)	178.1 (4.9)	179.4 (6.2)	177.6 (4.4)
$N^1N^4C^1N^6$	178.2	175.2 (3.0)	175.0 (3.2)	176.8 (1.4)	176.0 (2.2)	175.3 (2.9)	176.2 (2.0)	175.2 (3.0)	174.7 (3.5)
$S^2C^1N^6H^8$	13.0	13.3 (0.3)	26.8 (13.8)	19.1 (6.1)	24.1 (11.1)	26.7 (13.7)	22.9 (9.9)	26.2 (13.2)	27.0 (14.0)
$S^2Ni^1N^1H^2$	127.4	128.8 (1.4)	128.1 (0.7)	125.3 (2.1)	127.5 (0.1)	127.4 (0.0)	125.8 (1.6)	129.5 (2.1)	127.9 (0.5)
$S^2Ni^1N^1H^1$	119.1	117.0 (2.1)	118.3 (0.8)	120.7 (1.6)	118.3 (0.8)	118.8 (0.3)	120.2 (1.1)	116.5 (2.6)	118.7 (0.4)
$C^1N^4N^1H^2$	130.6	131.5 (0.9)	130.0 (0.6)	127.0 (3.6)	130.1 (0.5)	129.5 (1.1)	127.8 (2.8)	132.0 (1.4)	129.8 (0.8)
$C^1N^4N^1H^1$	121.7	118.3 (3.4)	117.9 (3.8)	121.0 (0.7)	119.7 (2.0)	118.8 (2.9)	120.4 (1.3)	117.8 (3.9)	118.3 (3.4)
		max (6.0) min (0.3) average (2.5)	max (13.8) min (0.0) average (3.7)	max (7.3) min (0.7) average (3.6)	max (11.1) min (0.1) average (3.2)	max (13.7) min (0.0) average (3.6)	max (9.9) min (0.3) average (3.7)	max (13.2) min (0.0) average (3.7)	max (14.0) min (0.2) average (3.7)

The molecular structure of the studied complex with the numbering of the atoms is shown in the figure. A comparison of the data obtained by calculations using the above methods is shown in Tables 1–3. As can be seen from the above data, the most reliable methods are B3LYP/6-311++G(df,p) and OPBE/TZVP, but the second requires significantly less time. Table 4 shows the calculation data on the relative energy difference between the *cis*- and *trans*-isomers of nickel(II) chelates with hydrazinomethanethioamide with different spin multiplicity. Considering these data as well as the fact that the experimental data [10] for *cis*-chelate indicate clearly the singlet ground state, it can be concluded that the method OPBE/TZVP is the most promising of the calculation methods for determining the molecular structure of the Ni(II) chelates and those close to it 3*d*-elements ions.

EXPERIMENTAL

Quantum-chemical calculations were performed using GAUSSIAN09 software package [11]. As in [1–8], the correspondence of the found stationary points to energy minima was proved by calculation of the second derivatives of energy with respect to the coordinates of the atoms. All the equilibrium structures that corresponded to the minimum points on the potential energy surfaces had real positive frequencies.

Table 4. Relative energies (kJ mol^{-1}) of the *cis*- and *trans*-isomeric Ni(II) complexes with hydrazinomethanethioamide with various multiplicity (M_S) of the ground state

Calculation method	*cis*-Complex		*trans*-Complex	
B3LYP/6-31G(d)	M_S 1	M_S 3	M_S 1	M_S 3
	17.9	0.0	0.0	14.2
	6.8		0.0	
B3LYP/6-31G(d)//LanL2DZ	M_S 1	M_S 3	M_S 1	M_S 3
	0.0	7.0	0.0	36.2
	23.2		0.0	
B3LYP/6-311++G(df,p)	M_S 1	M_S 3	M_S 1	M_S 3
	0.0	12.7	0.0	43.8
	22.7		0.0	
wB97XD/6-31G(d)	M_S 1	M_S 3	M_S 1	M_S 3
	25.2	0.0	0.0	11.7
	1.4		0.0	
B3LYP/6-31G(d)//SDDAll	M_S 1	M_S 3	M_S 1	M_S 3
	14.5	0.0	0.0	22.3
	12.5		0.0	
B3LYP/cc-pVTZ	M_S 1	M_S 3	M_S 1	M_S 3
	0.0	13.6	0.0	43.8
	22.2		0.0	
B3PW91/6-31G(d)	M_S 1	M_S 3	M_S 1	M_S 3
	17.4	0.0	0.0	16.9
	8.3		0.0	
OPBE/TZVP	M_S 1	M_S 3	M_S 1	M_S 3
	0.0	39.1	0.0	67.3
	21.8		0.0	

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